QUEEN'S UNIVERSITY

POLYMER RESEARCH GROUP

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

POLYMER BRANCHING AND FIRST NORMAL STRESS DIFFERENCES IN SMALL-AMPLITUDE OSCILLATORY SHEAR FLOW

M.A. Kanso¹ and A.J. Giacomin^{1,2,*}

¹Chemical Engineering Department, Polymers Research Group

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

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*Corresponding author (giacomin@queensu.ca)

QU-CHEE-PRG-TR--2019-61

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¹ Chemical Engineering Department, Polymers Research Group

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

ABSTRACT

General rigid bead-rod theory [Hassager, *J Chem Phys*, 60, 4001 (1974)] explains polymer viscoelasticity from macromolecular orientation. By means of general rigid bead-rod theory, we relate the normal stress differences of polymeric liquids to the branch position on a backbone branched macromolecule. In this work, we explore the first normal stress differences coefficients of different axisymmetric polymer configurations. When non-dimensionalized with the zero-shear first normal stress difference coefficient, the normal stress differences depend solely on the dimensionless frequency. In this work, in this way, we compare and contrast the normal stress differences of macromolecular chains that are branched. We explore the effects of branch position, length, functionality, spacing, and multiplicity, along a straight chain, in addition to rings and star-shaped macromolecules in small-amplitude oscillatory shear flow.

Keywords: general rigid bead-rod theory, polymer orientation, first normal stress differences coefficients, zero-shear first normal stress difference coefficient, branched polymers, star-branched polymers, and ringed polymers.

* Corresponding author (giacomin@queensu.ca).

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I. INTRODUCTION

We explore the role of macromolecular architecture on the linear viscoelastic properties of polymeric liquids, and specifically, we use general rigid bead-rod theory to examine the first normal stress difference responses to small-amplitude oscillatory shear flow. The physics of complex fluids is normally explored experimentally by means of this time-honored experiment ([1], [2] and Chapter 11 of [3]). Such experiments yield the complex viscosity, but can also yield the first normal stress difference responses [6,20]. The first normal stress difference responses in oscillatory shear flow deepen our insight into the physics of complex fluids. Moreover, these are known to affect directly the free boundary flows in rheometers. For instance, the edge distortions of a right rectangular sample in oscillatory sliding-plate flow are caused by the normal stress differences ([4], Figure 3.10. of [5] and subsection I.B.7.b of [6]). Also, the end distortions at the free boundary of an annular sample in oscillatory torsional flow are also caused by the normal stress differences [7].

General rigid bead-rod theory relies exclusively on macromolecular orientation to explain the rheological properties. This distinguishes general rigid bead-rod theory from its competing approaches, which include, reptation or disentanglement. We refer the reader to [8] for the detailed derivation of the general rigid bead-rod theory, and specifically, to Section III. of [8]. We are attracted to general rigid bead-rod theory for the broad diversity of macromolecular architectures that it can accommodate. We design each macromolecular structure by rigidly connecting nearest bead centers with massless dimensionless rods. We use 2 different subgroups of macromolecular structures, a shish-kebab, and a quadra-functional branch. Continuum theory has been bridged to general rigid bead-rod theory [17]. Thus, we use the relations between normal stress difference coefficients and architectural constants. We then, thus explore how branching affects the normal stress difference responses.

We locate each bead of mass m_i with the position vector of the i th bead $\mathbf{r}_i$, where the macromolecular center of mass $\mathbf{R}$ satisfies:

$$\sum_{i=1}^N m_i (\mathbf{r}_i - \mathbf{R}) = 0 \quad (1)$$

so that:

$$\mathbf{R} = \frac{1}{M} \sum_{i=1}^N m_i \mathbf{r}_i \quad (2)$$

where, N is the total number of beads and $M \equiv \sum_{i=1}^N m_i$, the total mass. Since we construct our macromolecules with identical beads of diameter d and mass m , then $M \equiv mN$, and thus the center of mass is:

$$\mathbf{R} = \frac{1}{N} \sum_{i=1}^N \mathbf{r}_i \quad (3)$$

which we will use below.

We next install *molecular coordinates*, at the macromolecular center of mass, and we orient these Cartesian coordinates such that $\hat{\delta}_3$ is along the polar axis of the *moment of inertia ellipsoid* (MIE).

The position vector of the i th bead with respect to the center of mass is given by (Eq. (16.7-16) of [9]):

$$\mathbf{R}_i \equiv [R_{i1}, R_{i2}, R_{i3}] \quad (4)$$

Table IV. of [17] lists such bead positions for each of the macromolecular architectures studied herein. We can define the principal moments of inertia I_1 , I_2 and I_3 by (Eqs. (16.7-17) and (16.7-18) of [9], or (13.6-17) and (13.6-18) of [10]):

$$I_1 \equiv m \sum_{i=1}^N (R_{i2}^2 + R_{i3}^2) \quad (5)$$

$$I_2 \equiv m \sum_{i=1}^N (R_{i1}^2 + R_{i3}^2) \quad (6)$$

$$I_3 \equiv 2m \sum_{i=1}^N R_{i1}^2 \quad (7)$$

where the subscript i is the bead number. We design each macromolecular structure by first rigidly connecting nearest bead centers with massless dimensionless rods. Throughout our work L is thus this center to center distance between nearest bead centers. We then complete the general rigid bead-rod construction by rigidly connecting the remaining bead centers to their nearest neighbours.

Hassager derives the expression for the shear relaxation function for general rigid bead-rod theory:

$$G(s) \equiv (2\eta_s + n\zeta L^2 a) \delta(s) + nkTbe^{-s/\lambda} \quad (8)$$

which nondimensionalizes as:

$$\frac{G(s)}{nkT} = \frac{\delta(s)}{kT} \left(\frac{2\eta_s}{n} + \zeta L^2 a \right) + be^{-s/\lambda} \quad (9)$$

and in which (Eqs. (16.7-38) of [9] or Eqs. (13.6-44), (13.6-45), and (13.6-46) of [10]):

$$a \equiv \frac{2I_1 + I_3}{6mL^2} - \frac{(I_1 - I_3)^2}{5mL^2 I_1} \quad (10)$$

$$b \equiv \frac{3(I_1 - I_3)^2}{5I_1^2} \quad (11)$$

$$\nu \equiv \frac{6mL^2}{I_1} \quad (12)$$

The three quantities a , b and ν thus define completely the differences in linear viscoelastic behaviors arising between different axisymmetric macromolecular structures. Whereas we associate a with the Dirac delta function contribution to the relaxation function, we associate b with the dying exponential.

The relaxation time can be expressed as follows:

$$\lambda \equiv \frac{\zeta I_1}{6mkT} \equiv \frac{\zeta L^2}{\nu kT} \quad (13)$$

where:

$$\zeta \equiv 3\pi d\eta_s \quad (14)$$

and, for the rigid dumbbell:

$$\lambda_0 \equiv \frac{\zeta L^2}{12kT} = \frac{\pi d \eta_s L^2}{4kT} \quad (15)$$

Dividing Eq. (13) by Eq. (15) normalizes the relaxation time of the general macromolecule to that of the simplest:

$$\frac{\lambda}{\lambda_0} \equiv \frac{12}{\nu} \quad (16)$$

In this paper, we study 4 macromolecules, a shishkebab (Macromolecule 1), and 3 quadra-functional branched macromolecules with the branch position alternating between the center and the end of the molecule (Macromolecules 2,3, and 4). Using Eqs. (5) through (7), we determine the moments of inertia of the macromolecules, and we use them to calculate the macromolecular lopsidedness. Table 1 gives the values of the moments of inertia and lopsidedness for each of our 4 macromolecules.

II. OSCILLATORY SHEAR FLOW

Since its conception in 1935 [11,12,13], the complex viscosity has become by far the most commonly measured viscoelastic property for exploring the physics of polymeric liquids. We measure this in oscillatory shear flow, generated by confining the fluid to a simple shear apparatus and then by subjecting one solid-liquid boundary to a coplanar sinusoidal displacement generating a corresponding cosinusoidal shear rate:

$$\dot{\gamma}(t) = \dot{\gamma}^0 \cos \omega t \quad (17)$$

such that, the rate of deformation tensor is given by:

$$\dot{\gamma}(t) = \begin{bmatrix} 0 & \dot{\gamma}^0 \cos \omega t & 0 \\ \dot{\gamma}^0 \cos \omega t & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (18)$$

Using the characteristic relaxation time of the viscoelastic fluid, λ , we can nondimensionalize Eq. (17) as:

$$\lambda \dot{\gamma}(t) = \lambda \dot{\gamma}^0 \cos \lambda \omega (t/\lambda) \quad (19)$$

where, $\lambda \omega$ and $\lambda \dot{\gamma}^0$ are the Deborah and Weissenberg numbers. We devote this paper to connecting the complex viscosity to macromolecular architecture. We thus focus on small-amplitude oscillatory shear flow (SAOS). By *small-amplitude*, we normally mean:

$$\lambda \dot{\gamma}^0 < 1 \quad (20)$$

which yields the molecular definition of small amplitude:

$$\frac{\zeta L^2}{kT} \dot{\gamma}^0 \ll \frac{1}{\sqrt{2}} \quad (21)$$

whose left side is the molecular Weissenberg number.

III. FIRST NORMAL STRESS DIFFERENCE COEFFICIENTS

By substituting Eqs. (64)–(66) of [17] into Eqs. (68)–(70) of [17], Kanso and Giacomini bridged continuum theory to macromolecular, yielding expressions for the normal stress difference responses from general rigid bead-rod theory. By *continuum*

theory, we mean any cases of the Oldroyd 8-constant framework (see Table III of [14] and Table I of [15]; [16]), including the corotational Jeffreys model. The coefficients of the displacement term of the normal stress differences in SAOS is (Eq. (71) of [17,18]):

$$\frac{\Psi_1^d}{nkT\lambda^2} = \frac{b}{1+(\lambda\omega)^2} \quad (22)$$

and of the parts that are in-phase with $\cos 2\omega t$ (Eq. (72) of [17]):

$$\frac{\Psi_1'}{nkT\lambda^2} = b \frac{(1-2(\lambda\omega)^2)}{(1+(\lambda\omega)^2)(1+4(\lambda\omega)^2)} \quad (23)$$

and, out-of-phase with $\cos 2\omega t$ (Eq. (73) of [17]):

$$\frac{\Psi_1''}{nkT\lambda^2} = 3b \frac{\lambda\omega}{(1+(\lambda\omega)^2)(1+4(\lambda\omega)^2)} \quad (24)$$

Thus, using Eqs. (22) through (24) we can study the effect of our macromolecules in Table 1, on the frequency dependence of the normal stress differences. Eqs. (21) through (23) obey the well-known *two omega relations* (Eqs. (40) through (42) of Section **Error! Reference source not found.**).

As $\omega \rightarrow 0$, we get zero-shear first normal stress difference coefficient:

$$\frac{\Psi_{1,0}}{nkT\lambda^2} = b \quad (25)$$

Normalizing Eqs. (22), (23), and (24) with respect to the zero-shear first normal stress difference in Eq. (25) we get:

$$\frac{\Psi_1^d}{\Psi_{1,0}} = \frac{1}{1+(\lambda\omega)^2} \quad (26)$$

$$\frac{\Psi_1'}{\Psi_{1,0}} = \frac{1-2(\lambda\omega)^2}{(1+(\lambda\omega)^2)(1+4(\lambda\omega)^2)} \quad (27)$$

$$\frac{\Psi_1''}{\Psi_{1,0}} = \frac{3\lambda\omega}{(1+(\lambda\omega)^2)(1+4(\lambda\omega)^2)} \quad (28)$$

which we plot in Figure 1 through Figure 3. Eqs. (26) through (28) are the main results of this paper.

The dimensionless complex viscosity counterparts to Eqs. (27) and (28) are Eqs. (40) and (41) of [17]. Whereas, the right sides of Eqs. (26) through (28) depend upon $\lambda\omega$ alone, the right sides of the dimensionless complex viscosity counterparts are functions of both $\lambda\omega$, and the macromolecular architecture ($2b/av$). In other words, we find that, from general rigid bead-rod theory, for the oscillatory responses to small-amplitude oscillatory shear flow, only the value of $\Psi_{1,0}$ depends upon the macromolecular architecture [see Eq. (25)].

From Eq. (26), we get the inflection frequency:

$$(\lambda\omega_i)^d = \frac{\sqrt{3}}{3} \quad (29)$$

with the inflection value:

$$\frac{(\Psi_1^d)_i}{\Psi_{1,0}} = \frac{3}{4} \quad (30)$$

From Eq. (27), we get the inflection frequencies:

$$(\lambda\omega_i)' = \frac{5}{19}, \frac{176}{100} \quad (31)$$

with the respective inflection values:

$$\frac{(\Psi_1')_i}{\Psi_{1,0}} = \frac{631}{1000}, -\frac{19}{200} \quad (32)$$

and abscissa intercept:

$$(\lambda\omega_0)' = \frac{\sqrt{2}}{2} \quad (33)$$

and high frequency asymptote zero. From Figure 2, we see that $\Psi_1'(\omega)$ descends, inflects, changes sign, and rises asymptotically to zero. These behaviours are observed experimentally for pure linear polymer melts (compare pure melt curves in Fig. 6a. of [20] with Figure 2).

From Eq. (28), we get the peak frequency:

$$(\lambda\omega_p)'' = \frac{381}{1000} \quad (34)$$

with the peak value:

$$\frac{(\Psi_1'')_p}{\Psi_{1,0}} = \frac{1263}{2000} \quad (35)$$

and then the inflection frequency:

$$(\lambda\omega_i)'' = \frac{677}{1000} \quad (36)$$

with the inflection value:

$$\frac{(\Psi_1'')_i}{\Psi_{1,0}} = \frac{123}{250} \quad (37)$$

with a vanishing high-frequency asymptote. From Figure 3, we see that $\Psi_1''(\omega)$ rises, peaks, falls, and inflects asymptotically to zero. These behaviours are observed experimentally for pure linear polymer melts (compare pure melt curves in Fig. 6b. of [20] with Figure 3).

IV. BACKBONE-BRANCHED POLYMERS

In the following subsections we use general rigid bead-rod theory to explore the roles of branch position along a straight chain, branched-chain backbone length, branched-chain branch-functionality, branch spacing along a straight chain

(including pom-poms), and the number of branches along a straight chain on the normal stress difference coefficients. Using Eq. (25), we construct Column 6 in Table 3 through Table 10. Table 3 shows the $\Psi_{1,0}/nkT\lambda^2$ for four linear chains. We learn that the rigid dumbbell (Macromolecule 1) and all shish-kebabs (Macromolecules 2 through 4) give the same first normal stress response, $\Psi_{1,0}/nkT\lambda^2$.

a. BRANCH POSITION

By comparing the value of λ/λ_0 for Macromolecule 4 with any of Macromolecules 5 through 7 in Table 4, we learn that adding branching to a straight chain always increases the relaxation time.

From Table 4, comparing the values of $\Psi_{1,0}/nkT\lambda^2$, we first learn that branching decreases $\Psi_{1,0}/nkT\lambda^2$. In addition we learn that the macromolecule with the quadra-functional branch at the centre of the backbone (Macromolecule 5), gives the lowest value for $\Psi_{1,0}/nkT\lambda^2$, and as the quadra-functional branch moves to the end bead (Macromolecule 7) $\Psi_{1,0}/nkT\lambda^2$ increases.

b. BACKBONE LENGTH

By comparing the value of λ/λ_0 for Macromolecules 6 and 8 through 10 in Table 5, we learn that the longer the backbone of the branched macromolecule, the longer the relaxation time.

From Table 5, comparing the values of $\Psi_{1,0}/nkT\lambda^2$, we learn that increasing the backbone length increases $\Psi_{1,0}/nkT\lambda^2$. In addition we notice that Macromolecule 8, gives no $\Psi_{1,0}/nkT\lambda^2$, since it is spherically symmetrical [17].

c. BRANCH FUNCTIONALITY

By comparing the value of λ/λ_0 for Macromolecules 4, 6 and 11 in Table 6, we learn that increasing the number of branches to a straight backbone chain always increases the relaxation time.

From Table 6, comparing the values of $\Psi_{1,0}/nkT\lambda^2$, we learn that increasing the number of branches decreases $\Psi_{1,0}/nkT\lambda^2$.

d. BRANCH SPACING

By comparing the value of λ/λ_0 for Macromolecules 2, 12 and 13 in Table 7, we learn that increasing the number of quadra-functional branches to a straight backbone chain always increases the relaxation time. By examining the values of λ/λ_0 for Macromolecules 12 and 13 we learn that placing two quadra-functional branches of a branched macromolecule apart (Macromolecule 13 or pom-pom), increases relaxation time.

From Table 7, comparing the values of $\Psi_{1,0}/nkT\lambda^2$, we learn that placing the quadra-functional branches apart (Macromolecule 13) increases $\Psi_{1,0}/nkT\lambda^2$.

e. BRANCH MULTIPLICITY

By comparing the value of λ/λ_0 for Macromolecules 2, 12, 14 and 15 in Table 8, we learn that increasing the number of quadra-functional branches from 1 (Macromolecule 13) to 3 (Macromolecule 16) on a straight backbone chain always increases the relaxation time.

From Table 8, comparing the values of $\Psi_{1,0}/nkT\lambda^2$, we learn that increasing the number of quadra-functional branches decreases $\Psi_{1,0}/nkT\lambda^2$.

V. RIGID RINGS

By comparing the value of λ/λ_0 for Macromolecules 16 through 19 in Table 9, we learn that increasing the chain length of the rigid ring always increases the relaxation time.

From Table 9, comparing the values of $\Psi_{1,0}/nkT\lambda^2$, we learn that rigid rings (Macromolecules 16 through 19) give the same $\Psi_{1,0}/nkT\lambda^2$ for any number of beads. We also learn that the rigid rings and linear chains (Macromolecules 1 through 4) give the same $\Psi_{1,0}/nkT\lambda^2$.

VI. STAR-BRANCHED POLYMERS

By comparing the value of λ/λ_0 for Macromolecules 20 through 23 in Table 10, we learn that functionality of the planar star-branched macromolecule always increases the relaxation time.

From Table 10, comparing the values of $\Psi_{1,0}/nkT\lambda^2$, we learn that star-branched macromolecules give the same $\Psi_{1,0}/nkT\lambda^2$ for any functionality, and have the same $\Psi_{1,0}/nkT\lambda^2$ value as rigid rings and linear chains.

VII. CONCLUSION

This paper focused specifically on the linear viscoelastic property, the first normal stress difference responses. Using general rigid bead-rod theory, we have explored the effects of branch position along a straight chain, branched-chain backbone length, branched-chain branch-functionality, branch spacing along a straight chain, the number of branches along a straight chain, ringed polymer perimeter, and branch-functionality in planar stars (Sections IV through VI). From general rigid bead-rod theory we learn that the orientability of the macromolecules is governed by the bead positions, and specifically, on the corresponding macromolecular moments of inertia. For axisymmetric molecules, general rigid bead-rod theory yields a relaxation function whose three and only three parameters, a , b and ν are computed from the macromolecular moments of inertia [Eqs. (10) through (12)]. We learn that the first

normal stress difference responses are independent of the macromolecular architecture. We show their behaviour in Figure 1 through Figure 3. In addition, we cast results for the zero-shear first normal stress difference coefficient, $\Psi_{1,0}/nkT\lambda^2$, which is dependent on the architectural constant b .

After examining 23 macromolecules, we find that the closer the branch is to the end of the backbone, the longer the λ/λ_0 . We also find that the longer the branched-chain backbone, the longer the λ/λ_0 . We next discover that the higher the branch-functionality, the longer the λ/λ_0 .

We also find that the closer the branch is to the end of the backbone, the higher the $\Psi_{1,0}/nkT\lambda^2$. We also find that the longer the branched-chain backbone, the higher the $\Psi_{1,0}/nkT\lambda^2$. We next discover that the higher the branch-functionality, the lower the $\Psi_{1,0}/nkT\lambda^2$.

In this paper we have addressed questions on first normal stress difference responses for branch position, backbone length, branch functionality, branch spacing, number of branches, ringed polymer perimeter, planar star core functionality, and branch dimensionality (Sections IV through VI). We know of no macromolecular theory flexible enough to address this range of questions (*cf.* Chapter 9 of [19]).

In this paper, our work is strictly delimited to axisymmetric macromolecular architectures, that is, where the moments of inertia about the transverse molecular axes equate. However, for macromolecular architectures where these same moments of inertia nearly equate, we can still use general rigid bead-rod theory to arrive at approximate results by replacing I_1 with the average value of the moments of inertia about the transverse molecular axes, $\frac{1}{2}(I_1 + I_2)$. We have yet to explore this possibility.

One might prefer to add other comparisons with experiment, and specifically with relevant zero-shear first normal stress difference coefficient *versus* macromolecular architecture observations. However, we know of no experimental measurements on backbone branched polymers wherein the branch position, or backbone length, or branch functionality is varied or controlled. In other words, to our knowledge, the structural details explored in this paper have yet to be explored in the laboratory.

We find general rigid bead-rod theory to be remarkably flexible for exploring our various questions about polymer viscoelasticity. Although we have restricted our questions to macromolecular structures that we know exist, architects of macromolecular structure can use general rigid bead-rod theory to explore structures that have yet to be synthesized.

VIII. ACKNOWLEDGMENT

Giacomin is indebted to the Faculty of Applied Science and Engineering of Queen's University at Kingston, for its support through a Research Initiation Grant (RIG). This research was undertaken, in part, thanks to support from the Canada Research Chairs program of the Government of Canada for the Natural Sciences and Engineering Research Council of Canada (NSERC) Tier 1 Canada Research Chair in Rheology. This research was also undertaken, in part, thanks to support from the Discovery Grant.

IX. APPENDIX: TWO OMEGA RELATIONS

In small-amplitude oscillatory shear flow, first normal stress difference responds with an average value upon which an oscillatory component is superposed (Eq. (4.4-14) of [21]):

$$\frac{\tau_{xx} - \tau_{yy}}{(\dot{\gamma}^0)^2} = -\Psi_1^d(\omega) - \Psi_1'(\omega)\cos 2\omega t - \Psi_1''(\omega)\sin 2\omega t \quad (38)$$

such that, by convention (Eq. (4.4-12) of [21]):

$$\Psi_1^*(\omega) \equiv \Psi_1'(\omega) - i\Psi_1''(\omega) \quad (39)$$

For many constitutive theories (Eqs. (5.1) through (5.3) of [20]; Eqs. (H) through (J) of [21]):

$$\omega\Psi_1^d(\omega) = \eta''(\omega) \quad (40)$$

$$\omega\Psi_1'(\omega) = -\eta''(\omega) + \eta''(2\omega) \quad (41)$$

$$\omega\Psi_1''(\omega) = \eta'(\omega) - \eta'(2\omega) \quad (42)$$

which we call the *two-omega relations*, and which we will use twice below.

a. Oldroyd 8-Constant Fluid

For any Oldroyd 8-constant fluid (Eqs. (32) through (34), (36) and (37) of [15]):

$$\eta' = \eta_0 \left(\frac{\lambda_2 \lambda_1 \omega^2 + 1}{1 + (\lambda_1 \omega)^2} \right) \quad (43)$$

$$\eta'' = \eta_0 \frac{(\lambda_1 - \lambda_2) \omega}{1 + (\lambda_1 \omega)^2} \quad (44)$$

$$\Psi_1^d(\omega) = \lambda_1 \eta_0 \left(1 - \frac{\lambda_2}{\lambda_1} \right) \left(\frac{1}{1 + (\lambda_1 \omega)^2} \right) \quad (45)$$

$$\Psi_1'(\omega) = \lambda_1 \eta_0 \left(1 - \frac{\lambda_2}{\lambda_1} \right) \left[\frac{(1 - 2(\lambda_1 \omega)^2)}{(1 + (\lambda_1 \omega)^2)(1 + 4(\lambda_1 \omega)^2)} \right] \quad (46)$$

$$\Psi_1''(\omega) = 3\lambda_1 \eta_0 \left(1 - \frac{\lambda_2}{\lambda_1} \right) \left[\frac{\lambda_1 \omega}{(1 + (\lambda_1 \omega)^2)(1 + 4(\lambda_1 \omega)^2)} \right] \quad (47)$$

By substituting Eqs. (44) and (45) into Eq. (40), we learn that Eqs. (44) and (45) satisfy Eq. (40). Similarly, by substituting Eqs. (46) and (44) into Eq. (41), we learn that Eqs. (46) and (44) satisfy Eq. (41) too. Finally, substituting Eqs. (47) and (43) into Eq. (42), we learn that Eqs. (47) and (43) satisfy Eq. (42). Thus, every Oldroyd 8-constant fluid satisfies the *two omega relations* [Eqs. (40) through (42)]. To our knowledge, this is new.

b. General Rigid Bead-Rod Theory

For general rigid bead-rod theory, the parts of the complex viscosity are given by Eqs. (38) and (39) of [17]:

$$\frac{\eta'(2\omega) - \eta_s}{nkT\lambda} = \frac{av}{2} + \frac{b}{1 + (2\lambda\omega)^2} \quad (48)$$

$$\frac{\eta''(2\omega)}{nkT\lambda} = b \frac{2\lambda\omega}{1 + (2\lambda\omega)^2} \quad (49)$$

Substituting Eqs. (48) and (49) into Eqs. (40) through (42), with some effort, gives Eqs. (22) through (24). Thus, the main equations upon which this paper relies [Eqs. (22) through (24)] obey the *two omega relations* [Eqs. (40) through (42)].

Table 1: Dimensional Variables.

Name	Unit	Symbol
Angular frequency	t^{-1}	ω
Bead diameter	L	d
Bead friction coefficient	M/t	ζ
Cartesian coordinates	L	x, y, z
Cartesian coordinates with respect to the center of mass	L	$\hat{\delta}_1, \hat{\delta}_2, \hat{\delta}_3$
Complex normal stress coefficient, for small amplitude oscillatory shear response, [Eq. (39)]	M/L	Ψ_1^*
Kronecker delta, [Eq. (8)]	t^{-1}	$\delta(s)$
Energy values in molecular-scale systems	ML^2/t^2	kT
Extra stress tensor	M/Lt^2	τ
Extra stress, xx component	M/Lt^2	τ_{xx}
Extra stress, yy component	M/Lt^2	τ_{yy}
First normal stress coefficient, in-phase with $\cos 2\omega t$, for small amplitude oscillatory shear response [Eq. (23)]	M/L	Ψ_1'
First normal stress coefficient, out-of-phase with $\cos 2\omega t$, for small amplitude oscillatory shear response [Eq. (24)]	M/L	Ψ_1''
First normal stress coefficient, small amplitude oscillatory shear response, displacement term [Eq. (22)]	M/L	Ψ_1^d
Inflection value for the first normal stress coefficient displacement term	M/L	$(\Psi_1^d)_i$
Inflection value for the first normal stress coefficient, in-phase with $\cos 2\omega t$	M/L	$(\Psi_1')_i$
Inflection value for the first normal stress coefficient, out-of-phase with $\cos 2\omega t$	M/L	$(\Psi_1'')_i$

Interval of past time	t	$s \equiv t - t'$
Macromolecular center of mass, [Eq. (3)]	L	$\mathbf{R}$
Mass of each bead	M	m_i
Minus imaginary part of non-linear complex viscosity in Continuum theory	M/Lt	η_2''
Minus imaginary part of non-linear complex viscosity, [Eq. (44)]	M/Lt	η''
Moments of inertia, [Eqs. (5) through (7)]	ML^2	I_1, I_2, I_3
Number of dumbbells per unit volume	$1/L^3$	n
Oldroyd constant, relaxation time	t	λ_1
Oldroyd constant, retardation time	t	λ_2
Peak value for the first normal stress coefficient, out-of-phase with $\cos 2\omega t$	M/L	$(\Psi_1'')_p$
Position vector of the i th bead and j th element with respect to the center of mass, [Eq. (4)]	L	R_{ij}
Position vector of the i th bead with respect to the center of mass, [Eq. (4)]	L	$\mathbf{R}_i$
Position vector of the i th bead, [Eq. (3)]	L	$\mathbf{r}_i$
Rate-of-strain tensor,	t^{-1}	$\dot{\gamma}$
Real part of non-linear complex viscosity	M/Lt	η'
Real part of non-linear complex viscosity in Continuum theory	M/Lt	η_1'
Relaxation time of rigid dumbbell, [Eq. (15)]	t	λ_0
Relaxation time of solution	t	λ
Shear rate amplitude, [Eq. (17)]	t^{-1}	$\dot{\gamma}^0$
Shear rate at specific time t'	t^{-1}	$\dot{\gamma}(t')$
Shear rate tensor, [Eq.(18)]	t^{-1}	$\dot{\boldsymbol{\gamma}}(t)$

Shear rate, [Eq. (17)]	t^{-1}	$\dot{\gamma}(t)$
Shear relaxation function, [Eq. (8)]	M/Lt^2	$G(s)$
Solvent viscosity	M/Lt	η_s
Specific time	t	t'
Time	t	t
Total mass	M	M
Velocity vector	L/t	$\mathbf{v}$
Viscosity, zero shear	M/Lt	η_0
Zero-shear first normal stress difference. [Eq. (25)]	M/L	$\Psi_{1,0}$

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

Table 2: Dimensionless Variables and Groups.

Name	Symbol	Range
Abscissa intercept frequency for the first normal stress coefficient, in-phase with $\cos 2\omega t$	$(\lambda\omega_0)'$	≥ 0
Coefficient in [Eq. (10)]	a	≥ 0
Coefficient in [Eq. (11)]	b	≥ 0
Coefficient in [Eq. (12)]	ν	≥ 0
Deborah number in Continuum theory	$De \equiv \lambda_1\omega$	≥ 0
Deborah number, oscillatory shear	$De \equiv \lambda\omega$	≥ 0
Inflection frequency for the first normal stress coefficient displacement term	$(\lambda\omega_i)^d$	≥ 0
Inflection frequency for the first normal stress coefficient, in-phase with $\cos 2\omega t$	$(\lambda\omega_i)'$	≥ 0
Inflection frequency for the first normal stress coefficient, out-of-phase with $\cos 2\omega t$	$(\lambda\omega_i)''$	≥ 0
Peak value for the first normal stress coefficient, out-of-phase with $\cos 2\omega t$	$(\lambda\omega_p)''$	≥ 0
Total number of beads	N	≥ 0
Weissenberg number	$Wi \equiv \lambda\dot{\gamma}^0$	≥ 0

Table 3: Effect of shish-kebab length.

	Macromolecule	b	ν	$\frac{\lambda}{\lambda_0}$	$\frac{\Psi_{1,0}}{nkT\lambda^2}$
1		$\frac{3}{5}$	12	1	$\frac{3}{5}$
2		$\frac{3}{5}$	3	4	$\frac{3}{5}$
3		$\frac{3}{5}$	$\frac{6}{5}$	10	$\frac{3}{5}$
4		$\frac{3}{5}$	$\frac{3}{5}$	20	$\frac{3}{5}$

Table 4: Effect of branch position.

	Macromolecule	b	ν	$\frac{\lambda}{\lambda_0}$	$\frac{\Psi_{1,0}}{nkT\lambda^2}$
4		$\frac{3}{5}$	$\frac{3}{5}$	20	$\frac{3}{5}$
5		$\frac{4}{15}$	$\frac{1}{2}$	24	$\frac{4}{15}$
6		$\frac{1587}{5120}$	$\frac{27}{64}$	$\frac{256}{9}$	$\frac{1587}{5120}$
7		$\frac{4332}{11045}$	$\frac{27}{94}$	$\frac{376}{9}$	$\frac{4332}{11045}$

Table 5: Effect of backbone length on branched chain.

	Macromolecule	b	ν	$\frac{\lambda}{\lambda_0}$	$\frac{\Psi_{1,0}}{nkT\lambda^2}$
8		0	$\frac{3}{2}$	8	0
6		$\frac{4}{15}$	$\frac{1}{2}$	24	$\frac{4}{15}$
9		$\frac{169}{375}$	$\frac{1}{5}$	60	$\frac{169}{375}$
10		$\frac{2523}{4805}$	$\frac{3}{31}$	124	$\frac{2523}{4805}$

Table 6: Effect of branch functionality.

	Macromolecule	b	ν	$\frac{\lambda}{\lambda_0}$	$\frac{\Psi_{1,0}}{nkT\lambda^2}$
4		$\frac{3}{5}$	$\frac{3}{5}$	20	$\frac{3}{5}$
11		$\frac{867}{2645}$	$\frac{12}{23}$	23	$\frac{867}{2645}$
6		$\frac{4}{15}$	$\frac{1}{2}$	24	$\frac{4}{15}$

Table 7: Effect of branch spacing.

	Macromolecule	b	ν	$\frac{\lambda}{\lambda_0}$	$\frac{\Psi_{1,0}}{nkT\lambda^2}$
2		$\frac{3}{5}$	3	4	$\frac{3}{5}$
12		$\frac{27}{11045}$	$\frac{33}{47}$	$\frac{188}{11}$	$\frac{27}{11045}$
13		$\frac{27}{245}$	$\frac{3}{7}$	28	$\frac{27}{245}$

Table 8: Effect of branch multiplicity.

	Macromolecule	b	ν	$\frac{\lambda}{\lambda_0}$	$\frac{\Psi_{1,0}}{nkT\lambda^2}$
2		$\frac{3}{5}$	3	4	$\frac{3}{5}$
14		$\frac{27}{500}$	$\frac{21}{20}$	$\frac{80}{7}$	$\frac{27}{500}$
12		$\frac{27}{11045}$	$\frac{33}{47}$	$\frac{188}{11}$	$\frac{27}{11045}$
15		$\frac{3}{80}$	$\frac{3}{8}$	32	$\frac{3}{80}$

Table 9: Effect of rigid ring chain length.

	Macromolecule	b	ν	$\frac{\lambda}{\lambda_0}$	$\frac{\Psi_{1,0}}{nkT\lambda^2}$
16		$\frac{3}{5}$	12	1	$\frac{3}{5}$
17		$\frac{3}{5}$	6	2	$\frac{3}{5}$
18		$\frac{3}{5}$	$6 - \frac{6\sqrt{5}}{5}$	$\frac{5+\sqrt{5}}{2}$	$\frac{3}{5}$
19		$\frac{3}{5}$	2	6	$\frac{3}{5}$

Table 10: Effect of planar star-branched functionality.

	Macromolecule	b	ν	$\frac{\lambda}{\lambda_0}$	$\frac{\Psi_{1,0}}{nkT\lambda^2}$
20		$\frac{3}{5}$	4	3	$\frac{3}{5}$
21		$\frac{3}{5}$	3	4	$\frac{3}{5}$
21		$\frac{3}{5}$	$\frac{12}{5}$	5	$\frac{3}{5}$
23		$\frac{3}{5}$	2	6	$\frac{3}{5}$

Figure 1: Effect of branching on the displacement term of the normal stress difference coefficient from Eq. (26).

Figure 2: Effect of branching on the in-phase with $\cos 2\omega t$ of the normal stress difference coefficient from Eq. (27).

Figure 3: Effect of branching on the out-of-phase with $\cos 2\omega t$ term of the normal stress difference coefficient from Eq. (28).

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