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MOLECULAR CONTINUA FOR POLYMERIC LIQUIDS IN LARGE-AMPLITUDE OSCILLATORY SHEAR FLOW

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Abstract

In this paper, we connect a molecular description of the rheology of a polymeric liquid to a continuum description, and then test this connection for large-amplitude oscillatory shear flow (LAOS). Specifically, for the continuum description we use the 6-constant Oldroyd framework, and for the molecular, we use the simplest relevant molecular model, the suspension of rigid dumbbells. By *relevant*, we mean predicting at least higher harmonics in the shear stress response in LAOS. We call this connection a *molecular continuum*, and we examine two ways of arriving at this connection. The first goes through the retarded motion expansion, and the second, expands each of a set of specific material functions (complex, steady shear, and steady uniaxial extensional viscosities). Both ways involve comparing the coefficients of expansions to then solve for the six constants of the continuum framework in terms of the two constants of the rigid dumbbell suspension. The purpose of a molecular continuum is that many well-known results for rigid dumbbell suspensions in other flow fields can then also be easily obtained, without having to first find the orientation distribution function. In this paper, we focus on the recent result for the rigid dumbbell suspension in LAOS. We compare the accuracies of the *retarded motion molecular continuum* (RMMC) with the *material function molecular continuum* (MFMC). We find the RMMC to be the most accurate for LAOS.

Keywords: Molecular continua; large-amplitude oscillatory shear flow; LAOS; Oldroyd 6-constant fluid; rigid dumbbell suspension; retarded motion expansion.

1. Introduction

Section 6.2 of Ref. 1 teaches a three step method for arriving at molecular continua. Firstly, the 6 constants of the retarded motion expansion (to third order) are compared to the coefficients of the expansions of the material functions of the Oldroyd 6-constant model for steady shear flow and uniaxial extensional flow (see column 3 of Table 6.2-2 of Ref. 1). Secondly, the 6 constants of third order fluid are compared to the coefficients of the expansions for the material functions of the 2-constant rigid dumbbell model for steady shear flow and uniaxial extensional flow (see column 4 of Table 6.2-1 of Ref. 1).

Thirdly, by comparing the entries in column 3 of Table 6.2-2 with column 4 of Table 6.2-1 of Ref. 1, six equations are obtained. Solving simultaneously yields:

$$\eta_0 - \eta_s = nkT\lambda, \quad \lambda_1 = \lambda, \quad \lambda_2 = \frac{2}{5}\lambda, \quad \mu_1 = -\frac{1}{7}\lambda, \quad \mu_2 = -\frac{26}{35}\lambda, \quad \mu_0 = -\frac{2}{7}\lambda. \quad (1)$$

1.1. The Oldroyd 6-Constant Framework

The Oldroyd 6-constant framework is defined by:

$$\boldsymbol{\tau} + \lambda_1 \frac{\mathcal{D}\boldsymbol{\tau}}{\mathcal{D}t} + \frac{1}{2}\mu_0 (\text{tr } \boldsymbol{\tau}) \dot{\boldsymbol{\gamma}} - \frac{1}{2}\mu_1 \{ \boldsymbol{\tau} \cdot \dot{\boldsymbol{\gamma}} + \dot{\boldsymbol{\gamma}} \cdot \boldsymbol{\tau} \} = -\eta_0 \left(\dot{\boldsymbol{\gamma}} + \lambda_2 \frac{\mathcal{D}\dot{\boldsymbol{\gamma}}}{\mathcal{D}t} - \mu_2 \{ \dot{\boldsymbol{\gamma}} \cdot \dot{\boldsymbol{\gamma}} \} \right), \quad (2)$$

where η_0 is zero-shear viscosity; the λ 's and μ 's are the Oldroyd fluid constants; $\boldsymbol{\tau}$, $\dot{\boldsymbol{\gamma}}$ are the extra stress and rate-of-strain tensors. Having many constitutive equations as special cases makes Eq. (2) a versatile continuum framework (see Table IV of Ref. 2). Eq. (2) has been closely connected to molecular models, and specifically, to suspensions of rigid or finitely extensible nonlinear elastic dumbbells (see §5 of Ref. 3).

For the MFMC, for the Oldroyd 6-constant framework, we use both axes of the Pipkin map. For the Pipkin map abscissa, we use the well-known result for the complex viscosity (see Eqs. (8.1-10) and (8.1-11) of Ref. 4):

$$\eta'/\eta_0 = (1 + \lambda_1 \lambda_2 \omega^2) / (1 + \lambda_1^2 \omega^2), \quad \eta''/\eta_0 = (\lambda_1 - \lambda_2) \omega / (1 + \lambda_1^2 \omega^2). \quad (3), (4)$$

For the Pipkin map ordinate, we expand the well-known result for the steady shear viscosity (Eq. (14) of Ref. 5) about $\dot{\gamma} = 0$:

$$\eta/\eta_0 = 1 - (\sigma_1 - \sigma_2) \dot{\gamma}^2 + (\sigma_1 - \sigma_2) \sigma_1 \dot{\gamma}^4 - O(\dot{\gamma}^6), \quad (5)$$

where (Eqs. (15) and (16) of Ref. 5):

$$\sigma_1 \equiv \lambda_1^2 + (\mu_0 - \mu_1) \mu_1, \quad \sigma_2 \equiv \lambda_1 \lambda_2 + (\mu_0 - \mu_1) \mu_2. \quad (6), (7)$$

We then expand the well-known result for the steady uniaxial extensional viscosity (Eq. (8B.1-3) of Ref. 4) about $\epsilon = 0$ to get:

$$\bar{\eta}/\eta_0 = 1 + (\mu_1 - \mu_2) \epsilon - 3(\mu_0 - \mu_1)(\mu_1 - \mu_2) \epsilon^2 + O(\epsilon^3). \quad (8)$$

1.2. Rigid Dumbbell Molecule

We next consider the rigid dumbbell suspended in a sea of Newtonian solvent. The SAOS responses are given by (see Eqs. (84) and (85) of Ref. 6):

$$\eta'/(nkT\lambda + \eta_s) = (1 + \frac{2}{5}\lambda^2 \omega^2) / (1 + \lambda^2 \omega^2), \quad \eta''/(nkT\lambda + \eta_s) = \frac{3}{5}\lambda \omega / (1 + \lambda^2 \omega^2), \quad (9), (10)$$

where $\lambda \equiv \pi \eta_s b L^2 / 4kT$ is the characteristic time for the suspension, and $\eta_0 - \eta_s = nkT\lambda$. The steady shear viscosity expands as (Eq. 6.7 of Ref. 7):

$$(\eta - \eta_s)/nkT\lambda = 1 - \frac{18}{35}(\lambda\dot{\gamma})^2 + \frac{1326}{1925}(\lambda\dot{\gamma})^4 - O((\lambda\dot{\gamma})^6), \quad (11)$$

and the steady uniaxial elongational viscosity, as (Eq. 16.5 of Ref. 7):

$$(\bar{\eta} - 3\eta_s)/3nkT\lambda = 1 + \frac{3}{5}(\lambda\dot{\epsilon}) + \frac{9}{35}(\lambda\dot{\epsilon})^2 - \frac{27}{175}(\lambda\dot{\epsilon})^3 + O((\lambda\dot{\epsilon})^4). \quad (12)$$

2. Material Function Molecular Continuum

For the complex viscosity, we compare Eqs. (3) and (4) with (9) and (10) to get:

$$\eta_0 - \eta_s = nkT\lambda, \quad \lambda_1 = \lambda, \quad \lambda_2 = \frac{2}{5}\lambda, \quad (13), (14), (15)$$

which match the entries in rows 1–3 of column 2 of Table 1 of Ref. 3, as they should. For the steady shear viscosity, we compare Eqs. (5) with (11) to get:

$$\sigma_1 - \sigma_2 = \frac{18}{35}\lambda^2, \quad (\sigma_1 - \sigma_2)\sigma_1 = \frac{1326}{1925}\lambda^4, \quad (16), (17)$$

or:

$$\sigma_1 = \frac{221}{165}\lambda^2, \quad \sigma_2 = \frac{953}{1155}\lambda^2. \quad (18), (19)$$

Substituting Eqs. (6) and (7) [with Eqs. (14) and (15)] into Eq. (18) and (19) gives:

$$\mu_0\mu_1 - \mu_1^2 = \frac{56}{165}\lambda^2, \quad \mu_0\mu_2 - \mu_1\mu_2 = \frac{491}{1155}\lambda^2. \quad (20), (21)$$

For the steady uniaxial elongational viscosity, we compare the coefficients in Eqs. (8) and (12) to get:

$$\mu_1 - \mu_2 = \frac{3}{5}\lambda. \quad (22)$$

and then solving Eqs. (20), (21) and (22) simultaneously gives:

$$\mu_0 = -\frac{2909}{1155}\lambda, \quad \mu_1 = -\frac{392}{165}\lambda, \quad \mu_2 = -\frac{491}{165}\lambda. \quad (23), (24), (25)$$

Eqs. (13)–(15) and (23)–(25) are the main results of this paper. Inserting these results into Eq. (2) yields, for the MFMC:

$$\boldsymbol{\tau} + \lambda \frac{\mathcal{D}\boldsymbol{\tau}}{\mathcal{D}t} - \frac{2909}{2310}\lambda (\text{tr } \boldsymbol{\tau})\dot{\boldsymbol{\gamma}} + \frac{392}{330}\lambda \{\boldsymbol{\tau} \cdot \dot{\boldsymbol{\gamma}} + \dot{\boldsymbol{\gamma}} \cdot \boldsymbol{\tau}\} = -nkT\lambda \left(\dot{\boldsymbol{\gamma}} + \frac{2}{5}\lambda \frac{\mathcal{D}\dot{\boldsymbol{\gamma}}}{\mathcal{D}t} + \frac{491}{165}\lambda \{\dot{\boldsymbol{\gamma}} \cdot \dot{\boldsymbol{\gamma}}\} \right), \quad (26)$$

and inserting Eq. (1) into Eq. (2) yields, for the RMMC:

$$\boldsymbol{\tau} + \lambda \frac{\mathcal{D}\boldsymbol{\tau}}{\mathcal{D}t} - \frac{1}{7}\lambda (\text{tr } \boldsymbol{\tau})\dot{\boldsymbol{\gamma}} + \frac{1}{14}\lambda \{\boldsymbol{\tau} \cdot \dot{\boldsymbol{\gamma}} + \dot{\boldsymbol{\gamma}} \cdot \boldsymbol{\tau}\} = -nkT\lambda \left(\dot{\boldsymbol{\gamma}} + \frac{2}{5}\lambda \frac{\mathcal{D}\dot{\boldsymbol{\gamma}}}{\mathcal{D}t} + \frac{26}{35}\lambda \{\dot{\boldsymbol{\gamma}} \cdot \dot{\boldsymbol{\gamma}}\} \right). \quad (27)$$

3. Discussion and Conclusion

To compare the accuracies of MFMC (Eq. (26)) with RMMC (Eq. (27)), we plot each against the recent analytical result for the rigid dumbbell model in LAOS (Eq. (20) of Ref. 8, **black** loops in Figs. 1(a) and 1(b)) using Ewoldt fingerprints⁹. For the MFMC, we substitute our main results, Eqs. (13)–(15) and (23)–(25), into Eq. (65) of Ref. 2 and plot the **red** loops of Fig. 1(a). For the RMMC, we substitute Eq. (1) into Eq. (65) of Ref. 2 and plot the **red** loops of Fig. 1(b). In Figs. 1(a) and 1(b), $\mathbb{S} \equiv \tau_{yx}/\eta_0 \dot{\gamma}^0$ and $\mathbb{S}_{\max}$ is the peak value of $\mathbb{S}$ for each loop from Eq. (20) of Ref. 8. Fig. 1 shows MFMC to be accurate where $Wi \leq 1$ or $Wi/De \leq 3/8$, and RMMC, where $Wi \leq 1$ or $Wi/De \leq 3/7$.

Fig. 1. Ewoldt fingerprints of $\mathbb{S}/\mathbb{S}_{\max}$ versus $\cos \omega t$ counterclockwise loops. (a) **red** loops are MFMC (Eq. (26)) and (b), RMMC (Eq. (27)). $De \equiv \lambda \omega$ and $Wi \equiv \lambda \dot{\gamma}^0$. RMMC is slightly more accurate than MFMC.

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References

1. R. B. Bird, O. Hassager, R. C. Armstrong and C. F. Curtiss, *Dynamics of Polymeric Liquids*, vol. 1, 2nd ed. (John Wiley & Sons, Inc., New York, 1987).
2. C. Saengow, A. J. Giacomin and C. Kolitawong, *Phys. Fluids* **29** (2017) 043101.
3. R. B. Bird and A. J. Giacomin, *Annu. Rev. Chem. Biomol. Eng.* **7** (2016) 479.
4. R. B. Bird, O. Hassager, R. C. Armstrong and C. F. Curtiss, *Dynamics of Polymeric Liquids*, vol. 1, 1st ed. (John Wiley & Sons, Inc., New York, 1977).
5. C. Saengow, A. J. Giacomin, P. H. Gilbert and C. Kolitawong, *Korea-Aust. Rheol. J.*, **27** (2015) 267.
6. R. B. Bird, A. J. Giacomin, A. M. Schmalzer and C. Aumnate, *J. Chem. Phys.* **140** (2014) 074904.
7. R. B. Bird, H. Warner and D. Evans, *Fortschritte der Hochpolymeren-Forschung*, **8** (1971) 1.
8. L. M. Jbara, A. J. Giacomin and P. H. Gilbert, *Nihon Reoroji Gakk.* **44** (2016) 289.
9. R. H. Ewoldt, A. E. Hosoi and G. H. McKinley, *Ann. T. Nord. Rheol. Soc.* **15** (2007) 3.