Nonlinear Rheology of FENE Dumbbell with Friction-Reduction: Analysis of Brownian Force Intensity through Comparison of Extensional and Shear Viscosities

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Normalized extensional and shear viscosities, \( \eta_E/\eta_0 \) and \( \eta_s/\eta_0 \), with the subscript “0” standing for quantities in the linear viscoelastic (LVE) regime, are theoretically analyzed for the FENE-dumbbell in the presence of isotropic friction-reduction under flow. The basic parameters in the analysis are the friction reduction factor \( r_s = \zeta_s/\zeta_{eq} \), FENE factor \( r_s = \kappa_s/\kappa_{eq} \) and the Brownian force intensity factor \( r_B = B/B_{eq} \) with \( \zeta \) and \( \kappa \) being the bead friction coefficient and spring strength of the dumbbell, \( B \) denoting the intensity of the Brownian force acting on the bead, and the subscripts “sf” and “eq” standing for the quantities under steady flow and at equilibrium, respectively: \( B_{eq} = 2\zeta_{eq}\kappa_{eq}T \) being the thermal energy, according to the fluctuation-dissipation theorem valid at equilibrium. The normalized viscosities were found to be analytically expressed as

\[
\frac{\eta_E}{\eta_0} = \left( \frac{r_s}{r_s^p} \right) \left[ 1 - 2\left( \frac{r_s}{r_s^p} \right) W_i^{-\gamma} \right] \left[ 1 + \left( \frac{r_s}{r_s^p} \right) W_i^{-\gamma} \right]
\]

and \( \frac{\eta_s}{\eta_0} = \frac{B}{B_{eq}} \), with \( W_i \) being the Weissenberg number defined with respect to the LVE relaxation time. Both \( \eta_E/\eta_0 \) and \( \eta_s/\eta_0 \) are proportional to the \( r_B \) factor, so that comparison of these quantities allows us to characterize the intensity of the Brownian force \( B \) under flow. For example, for a test case of power-law decay of \( r_s \) with \( W_i \), the above expressions of \( \eta_E/\eta_0 \) and \( \eta_s/\eta_0 \) suggested a relationship

\[
2\zeta_{eq}\kappa_{eq}T < B < 2\zeta_{eq}\kappa_{eq}T (i.e., \text{failure of the fluctuation-dissipation theorem}) \text{ under fast flow given that } \eta_E/\eta_0 \text{ and } \eta_s/\eta_0 \text{ at high } W_i \text{ are proportional to each other and exhibit the same power-law thinning behavior, } \eta_E/\eta_0 \propto \eta_s/\eta_0 \propto W_i^{-0.5}.
\]

Thus, the analysis presented in this work offers an experimental route for specifying the Brownian force intensity under flow through direct comparison of the \( \eta_E/\eta_0 \) and \( \eta_s/\eta_0 \) data.

Key Words: FENE-dumbbell / Friction reduction / Extensional viscosity / Shear viscosity / Brownian force intensity

1. INTRODUCTION

Extensional flow behavior of linear polymers is a “traditional” subject of rheological research1-3, but recent studies4-25 revealed unexpected differences in the nonlinearities under extensional and shear flow thereby demonstrating a “novel” aspect in the extensional rheology, as explained below.

Entangled melts and solutions exhibit nonlinear thinning of their shear viscosity \( \eta \), and a magnitude of this thinning is insensitive to the chemical structure and concentration of the polymer, given that the number of entanglements per chain, \( Z \), is the same for the melts and solutions and their \( \eta \) data are compared at the same Weissenberg number \( W_i \) (strain rate normalized by the linear viscoelastic relaxation time)1-3, 12, 25. In this sense, the nonlinear shear behavior of entangled melts and solutions has a universal character. In contrast, this universality vanishes in the nonlinear extensional behavior: Extensional viscosity \( \eta_E \) of entangled melts typically exhibits thinning4, 7, 11-13, 15 occasionally followed by thickening4 on an increase of \( W_i \), but the magnitude of thickening changes with the chemical structure of polymers even if \( Z \) is common for those melts4, 11, 12, 15, 25. Furthermore, for a given \( Z \), the thickening is much more significant for polymer solutions than for melts having the same chemical structure4, 5, 9-14, 16, 25.

The above non-universality of the extensional flow behavior is related to the finite extensible nonlinear elasticity20 (FENE) as well as the reduction of segmental friction17 (ζ-reduction) for polymer chains in a highly oriented and stretched environment. The magnitude of local orientation/stretch in the segmental length scale changes considerably with the chemical structure of polymers and also with the polymer concentration (because solvent molecules relax instantaneously to serve as an isotropic component in the environment), which may result in the non-universality in the extensional rheology. In fact, this non-universality has been found also for unentangled melts having different chemical
structures\textsuperscript{22}), which demonstrates that the local segmental friction is an essential factor governing the non-universality irrespective of the entanglement.

In principle, the shear viscosity $\eta$ is also affected by the FENE and $\zeta$-reduction. However, the shear anisotropy of polymer chains governing $\eta$ is equivalent to a correlation of the chain conformations in the flow velocity and velocity gradient directions (cf. eq 18c shown later). This correlation is rather insensitive to the FENE and $\zeta$-reduction effects, which contributes to the universality of $\eta$ explained above. In contrast, $\eta_e$ detects a difference of the chain conformation in the extensional and radial directions (cf. eq 6 shown later) so that those effects result in the non-universality of $\eta_e$.

Following the experiments\textsuperscript{18-20} that established the above non-universal character of $\eta_e$, theoretical analyses of $\eta_e$ were conducted on the basis of the tube model\textsuperscript{20,21,24} and the primitive chain network simulation\textsuperscript{18,19} (for entangled chains) and of the FENE-Rouse (FENE-PM)\textsuperscript{22} and Fraenkel chain\textsuperscript{23,24} models (for unentangled chains), with a focus being placed on the roles of the FENE and $\zeta$-reduction in the thickening and thinning behavior of $\eta_e$. The analyses successfully described $\eta_e$ data of entangled melts/solutions and unentangled melts, demonstrating the importance of $\zeta$-reduction in the thinning behavior of $\eta_e$ at high $Wi$. Nevertheless, the analyses were still incomplete in description of transient changes of the tensile stress growth and decay coefficients on start-up and cessation of extensional flow\textsuperscript{18,21,22}, possibly because the memory of the segmental friction (a delay in adjustment of the segmental motion to the environment) was not properly considered in the analyses and also because the fluctuation-dissipation theorem, relating the thermal Brownian force and segmental friction at equilibrium\textsuperscript{11}, was assumed in the analysis of the fast extensional flow behavior. The first problem of the memory effect is not important in the steady flow state (wherein $\zeta$ stays constant) and does not influence the analysis of $\eta_e$ in that state. However, the second problem is crucial because $\eta_e$ is directly related the Brownian force under flow.

Thus, we have attempted to examine the second problem by analyzing a contribution of the Brownian force to the extensional and shear viscosities, $\eta_e$ and $\eta$. For this purpose, we focused on unentangled polymers because the $\zeta$-reduction is irrelevant to the entanglement, and analyzed the viscosity deduced from the simplest model, the FENE-dumbbell model\textsuperscript{26} incorporating the $\zeta$-reduction. This model is a single-mode model and not rigorously applicable to unentangled polymers having the relaxation mode distribution. However, in both linear and nonlinear regimes, the viscosity of unentangled polymers is dominated by their lowest relaxation mode, and the dumbbell model is still useful for semi-quantitative analysis of the viscosity of those polymers.

The analysis revealed that both $\eta_e$ and $\eta$ are proportional to the intensity $B$ of the Brownian force under flow and thus decrease with increasing $Wi$ given that the fluctuation-dissipation theorem fails and $B$ decreases at high $Wi$. The analysis also showed that $Wi$ dependence of $\eta_e$ and $\eta$ is differently affected by the magnitude of $\zeta$-reduction (coupled with $B$), thereby offering a route for an experimental test of $B$ under flow through direct comparison of the $\eta_e$ and $\eta$ data. Details of these results are presented in this article.

2. MODEL

Figure 1 illustrates the FENE-dumbbell model focused in this work. In general, the spring strength $k$ increases on the dumbbell stretch, and is a function of the dumbbell conformation represented by its end-to-end vector $R(t)$ at a given time $t$. The bead friction coefficient $\zeta$ decreases on the dumbbell stretch and orientation and is also a function of $R(t)$ at $t$. In this study, we assume this $\zeta$-reduction to occur isotropically. In general, polymer chains are expected to exhibit anisotropic $\zeta$-reduction\textsuperscript{27}. However, in a previous study\textsuperscript{22} based on the FENE-Rouse model, $\eta_e$’s calculated for the cases of isotropic and anisotropic $\zeta$-reduction were found to be numerically indistinguishable and agreed with the data for unentangled melts, given that $\zeta$ in the flow direction were chosen to be (almost) identical in those cases. Thus, the assumption of isotropic $\zeta$-reduction adopted in this study should be still acceptable for our discussion of the intensity of the Brownian force under flow. In relation to this point, a brief comment for the case of anisotropic $\zeta$-reduction is given in the Conclusion section.

The FENE-dumbbell model has been analyzed on the basis of the Smoluchowski equation for the conformation distribution of the dumbbell\textsuperscript{27}. However, in this study, we focus on the Brownian force intensity under flow that is more
straightforwardly expressed in the Langevin equation (stochastic equation of motion). Thus, we start our analysis with the Langevin equation describing time evolution of the position of the two beads, \( \mathbf{r}_j(t) \) with \( j = 1 \) and 2 (cf. Fig. 1), as

\[
\dot{\mathbf{r}}_j(t) = -\kappa_\parallel \mathbf{r}_j(t) + \mathbf{F}_\parallel(t) + \mathbf{F}_\perp(t) + \mathbf{F}_B(t) + \mathbf{F}_V(t) + \mathbf{F}_W(t) + \mathbf{F}_E(t) \quad (\omega(t) = (1,2) or (2,1) \quad (1)
\]

Here, \( \mathbf{F}_B(t) \) is the thermal Brownian force. A medium velocity at the position of that bead. Under extensional and shear flow with constant strain rates of \( \dot{\varepsilon} \) and \( \dot{\gamma} \), respectively, \( \mathbf{v}(t) \) is expressed as

\[
\text{extensional flow: } \mathbf{v}(t) = \begin{bmatrix} -\dot{r}_\parallel(t) \\ -\dot{r}_\perp(t) \\ 2\dot{r}_z(t) \end{bmatrix} \quad (2a)
\]

The extensional flow direction is chosen to be the \( z \)-direction in eq 2a, and the flow velocity and velocity gradient direction under shear, \( x \) - and \( y \)-directions in eq 2b.

Comments need to be made for the bead friction \( \zeta \) and the spring strength \( \kappa \) appearing in eq 1. \( \zeta \) and \( \kappa \) are determined by \( R = \mathbf{r}_j - \mathbf{r}_t \) at respective \( t \), as explained above. Nevertheless, \( \zeta \) and \( \kappa \) can be formally regarded as functions of \( t \), because eq 1 is supposed to give \( \mathbf{R}(t) \) as a function of \( t \) and we can utilize this \( \mathbf{R}(t) \), if given, to express \( \zeta \) and \( \kappa \) as functions of \( t \) (through eq 21 shown later for \( \kappa \), for example). In this formal sense, the bead friction and the spring strength in eq 1 have been expressed as \( \zeta(t) \) and \( \kappa(t) \). Actually, eq 1 does not allow us to calculate \( \mathbf{R}(t) \), \( \zeta(t) \), and \( \kappa(t) \) explicitly and analytically as functions of \( t \), but the use of formally \( t \)-dependent \( \zeta(t) \) and \( \kappa(t) \) still enables us to deduce analytical expressions of the steady state viscosity in terms of \( \zeta \) and \( \kappa \) in that state, as explained in later sections.

Comments need to be made also for the Brownian force \( \mathbf{F}_B \) acting on the bead \( j \). This \( \mathbf{F}_B \), representing a force due to stochastic collision of particles (molecules) in the medium against the bead \( j \), can be characterized by the averages as

\[
\langle \mathbf{F}_B(t) \rangle = 0 \quad (3a)
\]

\[
\langle \mathbf{F}_B(t) \mathbf{F}_B(t') \rangle = B(t)\delta(t-t')I \quad (3b)
\]

3. ANALYSIS OF STEADY STATE VISCOSITY

3.1 Extensional Viscosity

From eqs 1 and 2a, the time evolution equations for components of the end-to-end vector \( \mathbf{R}(t) = \mathbf{r}_j(t) - \mathbf{r}_t(t) \) under extensional flow are straightforwardly obtained as

\[
\frac{d\mathbf{R}_{\parallel}(t)}{dt} = -\frac{1}{2\tau(t)} \mathbf{R}_{\parallel}(t) + \frac{\mathbf{F}_{\parallel}(t)}{\zeta(t)} \quad (x,y) \quad (4a)
\]

\[
\frac{d\mathbf{R}_{\perp}(t)}{dt} = -\frac{1}{2\tau(t)} \mathbf{R}_{\perp}(t) + \frac{\mathbf{F}_{\perp}(t)}{\zeta(t)} \quad (4b)
\]

Here, \( \tau(t) \) is a viscoelastic characteristic time defined by

\[
\tau(t) = \frac{\zeta(t)}{4\kappa(t)} \quad (5)
\]

From the standard Kramers formula1-3 of the stress tensor, the steady state extensional viscosity \( \eta_e \) is expressed in terms of solutions of eqs 4a and 4b as

\[
\eta_e = \frac{1}{\dot{\varepsilon}} \nu \kappa \langle (R^2_{\parallel}/\dot{\varepsilon}^2 - R^2_{\perp}/\dot{\varepsilon}^2) \rangle \quad (6)
\]

Here, \( \nu \) is the number density of the dumbbell, and the
The subscript “sf” stands for the quantities in the steady flow state. Note that eq 6 has adopted a pre-averaging approximation for the spring strength $\kappa$. (Without this approximation, $\kappa$ should be included in the average $\langle \cdots \rangle_{st}$ in eq 6.)

Equations 4a and 4b are formally solved to give

\[ \langle R_{\alpha}^2 \rangle = \text{const.} \times \left( \frac{1}{2} \kappa_{st} + \frac{\tau_{st}}{\kappa_{st}} \right) \langle \tau \rangle \langle \tau \rangle \quad (\alpha = x, y) \]

\[ \langle R_{\alpha}^2 \rangle = \text{const.} \times \left( \frac{1}{2} \kappa_{st} - \frac{\tau_{st}}{\kappa_{st}} \right) \langle \tau \rangle \langle \tau \rangle \quad (\alpha = x, y) \]

From eqs 7a and 7b combined with eq 3, the averages $\langle R_{\beta}^2 \rangle (\beta = x, y, z)$ necessary for calculation of $\eta_E$ (cf. eq 6) are obtained as

\[ \langle R_{\beta}(t')^2 \rangle = \exp \left( -\frac{B(t')}{\zeta(t')} t' \right) \left[ \langle R_{\beta}(0)^2 \rangle + \frac{2B(t')}{\zeta(t')} \int \langle \tau(t') \rangle dt' \right] \quad (\alpha = x, y) \]

\[ \langle R_{\beta}(t')^2 \rangle = \exp \left( -\frac{B(t')}{\zeta(t')} t' \right) \left[ \langle R_{\beta}(0)^2 \rangle + \frac{2B(t')}{\zeta(t')} \int \langle \tau(t') \rangle dt' \right] \quad (\alpha = x, y) \]

In derivation of eqs 8a and 8b, we have made a pre-averaging approximation to separately average $\tau$ in the first exponential term in the right-hand side of eqs 7a and 7b and the other terms containing $F_{i\beta}(t) (i = x, y, z)$, and also utilized a relationship $\langle R(0)F_{i\beta}(t') \rangle = 0$ representing lack of correlation between the Brownian force at time $t'$ and the dumbbell conformation at time 0.

From eqs 8a and 8b, we find time evolution equations for $\langle R_{\beta}(t')^2 \rangle$:

\[ \frac{d}{dt} \langle R_{\beta}(t')^2 \rangle = -\left( \frac{1}{\tau(t')} + \epsilon \right) \langle R_{\beta}(t')^2 \rangle + \frac{2B(t')}{\zeta(t')} \quad (\alpha = x, y) \]

\[ \frac{d}{dt} \langle R_{\beta}(t')^2 \rangle = -\left( \frac{1}{\tau(t')} - 2\epsilon \right) \langle R_{\beta}(t')^2 \rangle + \frac{2B(t')}{\zeta(t')} \]

Obviously, $\langle R_{\beta}(t')^2 \rangle / dt = 0$ in the steady flow state. Thus, irrespective of details of the transient $t$ dependence of $\zeta(t)$, $\tau(t)$, and $B(t)$, $\langle R_{\beta}^2 \rangle_{st}$ in that state is simply obtained from eqs 9a and 9b as

\[ \langle R_{\beta}^2 \rangle_{st} = \frac{1}{1 - \delta t_{st} \langle R_{\beta}^2 \rangle_{st} \zeta_{st}} \langle R_{\beta}^2 \rangle_{st} \]

\[ \langle R_{\beta}^2 \rangle_{st} = \frac{1}{1 - \delta t_{st} \langle R_{\beta}^2 \rangle_{st} \zeta_{st}} \langle R_{\beta}^2 \rangle_{st} \]

These expressions of $\langle R_{\beta}^2 \rangle_{st}$ can be also obtained directly from Ito formula(26), as pointed out by an anonymous reviewer.) Finally, from eqs 6, 10a, and 10b, we find an expression of the normalized steady state extensional viscosity,

\[ \eta_\beta = \left\{ \frac{1}{1 - 2\epsilon \tau_{eq}} \right\}_{\beta} \eta_{eq} \]

with

\[ \eta_{eq} = \frac{1}{1 - \frac{B_{eq}}{2\zeta_{eq}\kappa_{eq}}} \]

\[ \frac{B_{eq}}{2\zeta_{eq}\kappa_{eq}} \]

The subscript “eq” stands for the quantities at equilibrium (in the LVE regime). $Wi_{eq}$ (eq 12) is the Weissenberg number for the extensional flow defined with respect to $\tau_{eq} = \zeta_{eq}/4\kappa_{eq}$. In general, the factors representing deviations of the friction coefficient $\zeta$ and spring stiffness $\kappa$ from those at equilibrium, $r_\zeta$ ($\leq 1$) and $r_\kappa$ ($\geq 1$), change with $Wi_{eq}$. The factor $r_\zeta$ representing a deviation of the Brownian force intensity also changes $Wi_{ext}$. For $r_\zeta = r_\kappa = r_B = 1$ (in the absence of the FENE and $\zeta$-reduction effects and with a negligible disturbance of the Brownian force), eq 11 reduces to the well known expression,

\[ \eta_\beta = \frac{1}{1 - 2Wi_{ext}} \eta_{eq} \]

(14)

From eqs 10a and 10b, the squared stretch ratio of the dumbbell, $\lambda^2 = \langle R_{\beta}^2 \rangle_{st}$, is also obtained straightforwardly as

\[ \lambda^2 = \left\{ \frac{1}{1 - 2\epsilon \tau_{eq}} \right\}_{\beta} \eta_{eq} \]

(15)

From eqs 11 and 15, we note a simple relationship between $\lambda^2$ and the $\eta_\beta/\eta_{eq}$ ratio,

\[ \lambda^2 = \left\{ \frac{1}{1 - 2\epsilon \tau_{eq}} \right\}_{\beta} \eta_{eq} \]

(16)

The $r_B$ factor does not explicitly appear in eq 16. Thus, eq 16
is useful for experimental analysis of the $\zeta$-reduction factor $r_e$ on the basis of data of $\lambda^2$ and the $\eta_s/\eta_{10}$ ratio, even without the information for the Brownian force intensity under flow, $B_d$ appearing in eq 3b. Then, this $r_e$ can be utilized in eq 11 to deduce $r_0 = B_d/B_{s0}$ from the $\eta_s/\eta_{10}$ data. Details of this analysis are discussed later in relation to the FENE factor, $r_v$.

### 3-2 Shear viscosity and normal stress difference coefficient

From eqs 1 and 2b, the time evolution equations for components of $\mathbf{R}(t)$ under shear flow are written as

\[
\frac{dR_x(t)}{dt} = -1 \frac{1}{2\tau(t)} R_x(t) + \frac{F_{R_x}(t) - F_{R_{10}}(t)}{\zeta(t)} \tag{17a}
\]

\[
\frac{dR_y(t)}{dt} = -1 \frac{1}{2\tau(t)} R_y(t) + \frac{F_{R_y}(t) - F_{R_{10}}(t)}{\zeta(t)} \tag{17b}
\]

where $\tau(t)$ is the viscoelastic characteristic time defined by eq 5 under shear. Utilizing eqs 17a and 17b, we can calculate $\langle R_x^2(t) \rangle$ and $\langle R_y^2(t) \rangle$ in the steady flow state by setting this derivative to be 0, as we did in the calculation under extensional flow. The results can be summarized as

\[
\langle R_x^2 \rangle_{s0} = \langle R_y^2 \rangle_{s0} = \frac{2B_d \tau_{s0}}{\zeta_{s0}} \tag{18a}
\]

\[
\langle R_x^2 \rangle_{s0} = \langle R_y^2 \rangle_{s0} = \frac{2B_d \tau_{s0} \{1 + 2\gamma^2 \tau_{s0}\}}{\zeta_{s0}} \tag{18b}
\]

\[
\langle R_x R_y \rangle_{s0} = \gamma \tau_{s0} \langle R_z^2 \rangle_{s0} \tag{18c}
\]

with $\tau_{s0} = \zeta_{s0}/4\kappa_{s0} = \{r_e/r_s\} \tau_{s0}$ (cf. eq 13). From these results, the normalized shear viscosity $\eta/\eta_0 = \kappa_{s0}/\langle R_x^2 \rangle_{s0}/\langle R_y^2 \rangle_{s0}$, the normalized first normal stress difference coefficient $\Psi_1/\Psi_{10} = \kappa_{s0}/\langle R_x^2 \rangle_{s0} - \langle R_y^2 \rangle_{s0}/\Psi_{10}$, and $\lambda^2 = \langle R_x^2 \rangle_{s0}/\langle R_y^2 \rangle_{s0}$ are expressed as

\[
\frac{\eta}{\eta_0} = \frac{r_s}{r_e} \tag{19a}
\]

\[
\frac{\Psi_1}{\Psi_{10}} = \frac{r_s}{r_e} \tag{19b}
\]

\[
\lambda^2 = \frac{r_s}{r_e} \left[1 + \frac{2}{3} \left(\frac{r_e}{r_s}\right)^2 \frac{W_{s0}^2}{\Psi_{10}}\right] \tag{19c}
\]

where $W_{s0} = \gamma \tau_{s0}$ is the Weissenberg number defined under shear flow. From eqs 19a-19c, we find relationships valid under the steady shear flow,

\[
\lambda^2 = \left[1 + \frac{2}{3} \left(\frac{r_e}{r_s}\right)^2 \frac{W_{s0}^2}{\Psi_{10}}\right] \eta \tag{20a}
\]

\[
\frac{\eta}{\eta_0} = \left(\frac{r_s}{r_e}\right)^2 \Psi_{10} \tag{20b}
\]

The factor $r_0$ is not explicitly included in eqs 20a and 20b. Thus, eqs 20a and 20b are useful for an experimental analysis of the $\zeta$-reduction factor $r_e$ even without knowledge of the Brownian force intensity under flow, as discussed below in some detail.

### 4. DISCUSSION

#### 4-1 Experimental method for characterizing $\zeta$-reduction and Brownian force intensity

Under steady extensional flow, we can measure the stretch ratio $\lambda$ (with small angle neutron scattering, for example) and the $\eta_s/\eta_{10}$ ratio. Furthermore, we may adopt a reasonable expression for the FENE spring strength $\kappa_{s0}$, for example, the pre-averaged FENE-P expression given by

\[
\kappa_{s0} = \frac{1}{1 - \left[\left(\frac{\langle R^2 \rangle_{s0}}{\langle R^2 \rangle_{eq}}\right) \left(\frac{\langle R^2 \rangle_{eq}}{\langle R^2 \rangle_{max}}\right)^2\right]} \tag{21}
\]

with $\lambda^2 = \langle R^2 \rangle_{s0}/\langle R^2 \rangle_{eq}$. The number of Kuhn segments per dumbbell, $n_{s0}$, is equivalent to the squared maximum stretch ratio $\lambda_{max}^2 = \langle R^2 \rangle_{max}/\langle R^2 \rangle_{eq}$.

From eq 21, the factor $r_e = \kappa_{s0}/\kappa_{s0}$ (cf. eq 13) can be expressed in terms of $\lambda$ and $n_{s0}$. Substituting this expression in eq 16, we find

\[
r_e = \left(\frac{n_{s0} - 1}{n_{s0} - \lambda_{max}^2}\right) \kappa_{s0} \tag{22}
\]

where the subscript “ext” has been added to $r_e$ and $\lambda$ so as to avoid confusion with the shear flow case explained below. Equation 22 suggests that the $\zeta$-reduction factor $r_{ext} = \zeta_{ext}/\zeta_{eq}$ can be simply evaluated from the $\lambda_{ext}$ and $\eta_s/\eta_{10}$ data and the known values of $n_s$ and $W_{ext}$. For given $W_{ext}$, we can utilize this $r_{ext}$ factor, the known $r_e$ factor (obtained from eq 21), and the $\eta_s/\eta_{10}$ data in eq 11 to experimentally estimate the Brownian intensity factor $r_{eq}$ under extensional flow.

Under shear flow, eqs 20b and 21 give

\[
r_{eq} = \left(\frac{n_{s0} - 1}{n_{s0} - \lambda_{eq}^2}\right) \kappa_{s0} \tag{23}
\]

Equation 23 allows us to estimate the $\zeta$-reduction factor under shear, $r_{eq}$, from the data of $\lambda_{eq}$, $\eta_s/\eta_{10}$ and $\Psi_1/\Psi_{10}$. This $r_{eq}$ may differ from $r_{ext}$ even under a flow condition of...
Specifically, we assume the simplest λ dependence of $r_{cs}$, $r_{cs}$, and $r_0$ as

$$r_{cs} = \frac{\eta_0 - 1}{\eta_0 - \lambda^*}$$  \hspace{1cm} (25)

$$r_{cs} = \left( \frac{2}{1 + \lambda^2} \right)^{\beta_2} \text{ with } \beta_2 > 0$$  \hspace{1cm} (26)

$$r_0 = \left( \frac{2}{1 + \lambda^2} \right)^{\beta_3}$$  \hspace{1cm} (27)

Equation 25, equivalent to eq 21, shows that the FENE spring always stiffens on the dumbbell stretch. For unentangled polymer melts, experiments suggest that the segmental friction always decreases on the stretch. This $\beta$-reduction behavior is mimicked in eq 26 by setting the exponent $\beta_2$ to be positive. In contrast, it is not known whether the Brownian force intensity $B_d$ increases or decreases with increasing $\lambda$ (namely, with increasing flow rate). Thus, we may consider several different types of the behavior of $B_d$ depending on the value of the exponent $\beta_3$, as deduced from eqs 13, 26, and 27. The results are summarized in Table I. For example, for $\beta_3 = 0$, $B_d$ coincides with the equilibrium Brownian force intensity $B_\text{eq} = 2\zeta_{\text{eff}} k_0 T$ even in the presence of $\zeta$-friction (for $\beta_2 > 0$). In contrast, for $\beta_3 = \beta_2 > 0$, $B_d$ is smaller than $B_\text{eq}$ but fully correlated with the friction $\zeta_d$ under flow as $B_d = 2\zeta_{\text{eff}} k_0 T$. (In relation to this point, $B_\text{eq}$ may be expressed, in general, as $B_d = 2\zeta_{\text{eff}} k_0 T_{\text{eq}}$ with $T_{\text{eq}}$ being an effective temperature utilized in non-equilibrium statistical physics, as suggested by an anonymous reviewer.)

Substituting eqs 25-27 in eq 15, we can calculate $\lambda_{\text{ext}}$ under the steady extensional flow as a function of $W_i$. This $\lambda_{\text{ext}}$ gives the $r_{cs}$, $r_{cs}$, and $r_0$ factors as functions of $W_i$, through eqs 25-27, which enables us to calculate the $\eta_i/\eta_0$ ratio through eq 11. Similarly, eqs 25-27 combined with eq 19c give the $\lambda_{\text{shear}}$ under steady shear flow as a function of $W_i$. This $\lambda_{\text{shear}}$ gives the $r_{cs}$, $r_{cs}$, and $r_0$ factors (eqs 25-27) thereby specifying the $W_i$ dependence of the $\eta_i/\eta_0$ ratio (eqs 19a).

In this way, we calculated the $\eta_i/\eta_0$ and $\eta_i/\eta_0$ ratios for some values of the exponents $\beta_3$ and $\beta_2$ (cf. eqs 26 and 27) and the number of Kuhn segments per dumbbell $n_K$. It turned out that $\lambda > 1$ never satisfies eq 27 with $\beta_3 < 0$ combined with eq 11 or eq 19 with $W_i > 0$. Thus, within the current analysis of

| $\beta_3$ | $B_d$ |
|----------|-------|
| $\beta_3 < 0$ | $B_d < 2\zeta_{\text{eff}} k_0 T$ |
| $\beta_3 = 0$ | $B_d = 2\zeta_{\text{eff}} k_0 T$ |
| $\beta_3 > 0$ | $B_d > 2\zeta_{\text{eff}} k_0 T$ |

| $\beta_2$ | $B_d$ |
|----------|-------|
| $\beta_2 < 0$ | $B_d < 2\zeta_{\text{eff}} k_0 T$ |
| $\beta_2 = 0$ | $B_d = 2\zeta_{\text{eff}} k_0 T$ |
| $\beta_2 > 0$ | $B_d > 2\zeta_{\text{eff}} k_0 T$ |

Table I. Brownian force intensity $B_d$ under steady flow.
the FENE-dumbbell model, the Brownian force intensity under flow cannot exceed that at equilibrium (cf. Table I). In contrast, a particular value of \( \lambda > 1 \) can satisfy eq 27 with \( \beta_{n} \geq 0 \) and eq 11 or eq 19a simultaneously. Examples of \( \lambda_{ext} \) and \( \lambda_{shear} \) thus obtained for \( n_{k} = 100 \) are shown in Figs. 2 and 3 together with the corresponding \( \eta_{l}/\eta_{0} \) and \( \eta/\eta_{0} \) ratios (eqs 11 and 19a) and the \( r_{c} \) and \( r_{n} \) factors (eqs 25 and 26).

As well known, the Hookean dumbbell exhibits divergence of \( \eta_{l} \) at \( Wi = 1/2 \) (cf. eq 14) and has a constant \( \eta \) in the entire range of \( Wi \); see thick gray curves in Figs. 2a and 3a. The divergence of \( \eta_{l} \) results from an infinite stretch of the Hookean dumbbell in the \( z \) direction at \( Wi = 1/2 \), as noted from an expression \( \langle R_{z} \rangle = \langle k_{B} T/k_{w} \rangle / \{ 1 - 2 Wi \} \) deduced from eqs 10b and 13 with \( r_{c} = r_{w} = 1 \). The infinite stretch occurs also under shear (in the \( x \) direction) at \( \dot{\gamma} \to \infty \); cf. eq 18b. Nevertheless, \( \eta \) reflects the normalized shear anisotropy \( \langle R_{z} R_{z} \rangle_{eq}/\dot{\gamma}^{2} \). For the Hookean dumbbell, this anisotropy remains constant (= \( \varepsilon_{eq} \), cf. eq 18c) to give constant \( \eta \). Consequently, in the presence of the FENE effect, the stretch is limited \( \lambda < \lambda_{max} = n_{k}^{2} \); see blue curves in Figs. 2b and 3b) so that \( \eta_{l} \) remains finite whereas \( \eta \) exhibits thinning at high \( Wi \), as noted for the filled blue circles in Figs. 2a and 3a.

The effects of \( \zeta \)-reduction on \( \eta_{l} \) and \( \eta \) can be understood as modification of the above FENE dumbbell behavior. The \( \zeta \)-reduction weakens a driving force for the flow-induced stretch, thereby giving a retarded increase of \( \lambda \) with \( Wi \) commonly under the extensional and shear flow; cf. red curves in Figs. 2b and 3b calculated for \( \beta_{c} = 1 \) \( (r_{c} < 1) \) and \( \beta_{n} = 0 \) \( (r_{n} = 1) \). Consequently, the FENE stiffening of the dumbbell is also retarded, as shown with the red circles in Figs. 2c and 3c. The maximum attainable stretch is not affected by the \( \zeta \)-reduction, but the retarded increase of \( r_{c} \) shifts the thinning of the shear viscosity \( \eta \) to a higher-\( Wi \) side, as noted from eq 19a and confirmed for the red circles in Fig. 3a. For \( \beta_{c} = 1 \), the retarded increase of \( r_{c} \) combined with the decrease of \( r_{c} \) still gives the thickening of the extensional \( \eta_{l} \) but significantly reduces its high-\( Wi \) asymptote; compare red and blue circles in Fig. 2a.

For the given value of \( \beta_{c} = 1 \), an increase of \( \beta_{n} \) from 0 to

![Fig. 2 Results of FENE-dumbbell analysis under extensional flow for \( n_{k} = 100 \) and \( (\beta_{c}, \beta_{n}) = (1,0), (1,1), \) and (2,1). The sense of the symbols and curves is the same in the panels (a)-(c).](image)

![Fig. 3 Results of FENE-dumbbell analysis under shear flow for \( n_{k} = 100 \) and \( (\beta_{c}, \beta_{n}) = (1,0), (1,1), \) and (2,1). The sense of the symbols and curves is the same in the panels (a)-(c).](image)
1 (a decrease of the Brownian force intensity from $B_{eq} = 2\zeta_0 k_\beta T$ to $B_{eq} = 2\zeta_0 k_B T$) hardly affects the stretch ratio $\lambda_{ext}$ under extensional flow; see black and red curves in Fig. 2b. Consequently, the $r_\zeta$ and $r_\kappa$ factors and the $n/\eta_0$ ratio hardly change on this increase of $\beta_h$, as noted for the red and black circles in Fig. 2. In contrast, under shear flow, the increase of $\lambda_{shear}$ with $W_{shear}$ is considerably retarded on the increase of $\beta_h$, which results in delayed decrease and increase of $r_\zeta$ and $r_\kappa$, respectively, and enhanced thinning of the $n/\eta_0$ ratio; cf. black and red curves/circles in Fig. 3.

For the given value of $\beta_h = 1$, an increase of $\beta_c$ from 1 to 2 leads to a significant change in the extensional behavior only if a moderate change in the shear behavior; compare green circles/curves with black ones in Figs. 2 and 3. Under extensional flow, the increases of $\lambda$ and $r_\kappa$ with $Wi$ are strongly retarded on this increase of $\beta_c$, which allows $\eta_0$ to exhibit the thickening followed by thinning. In contrast, under shear flow, $\lambda$ and $r_\kappa$ exhibit moderate changes on the increase of $\beta_c$ thereby giving rise to just a moderate change in the thinning behavior of $n/\eta_0$.

The above results suggest that a change of the Brownian force intensity $B_{eq}$ (combined with a change of the $\zeta$-reduction factor) gives rise to different changes in the $Wi$ dependence of $\eta_b$ and $\eta$. These differences in turn offer an interesting route of specifying $B_{eq}$ through direct comparison of the $n/\eta_0$ and $n/\eta_0$ ratios. Figure 4 presents an example of this comparison made for the parameters $n_k$, $\beta_c$, and $\beta_h$ as indicated. The corresponding stretch $\lambda$, the $\zeta$-reduction factor $r_\zeta$, and the FENE factor $r_\kappa$ are shown in Fig. 5.

As noted in Figs. 4a and 4b, the thinning of the $n/\eta_0$ ratio (green circles) is significantly enhanced on an increase of $\beta_h$ from 1 to 2 for a given set of $n_k$ and $\beta_c$ values (100 and 2) whereas the $n/\eta_0$ ratio (red circles) hardly changes its $Wi$ dependence (thickening followed by thinning) on this increase of $\beta_h$. The $n/\eta_0$ ratio coincides with the $r_\kappa/r_\zeta$ ratio (cf. eq 19a), and $r_\kappa$ hardly increases from unity in the range of $Wi$ examined; cf. green curves in Figs. 5a and 5b. Thus, the thinning of the $n/\eta_0$ ratio almost entirely reflects the decrease of $r_\kappa$ with $Wi$ and is enhanced on the increase of $\beta_h$ (cf. eq 27). In contrast, the $n/\eta_0$ ratio is related to the parameters $r_\zeta$, $r_\kappa$, and $\lambda$ through eq 16. These parameters hardly change on the
increase of \( \beta_0 \) (compare red circles/curves in Figs. 5a and 5b), which results in lack of a significant change of the \( \eta_{\text{B}}/\eta_0 \) ratio on this increase.

This difference between the \( \eta_{\text{B}}/\eta_0 \) and \( \eta/\eta_0 \) ratios may provide us with a clue for specifying \( B_\alpha \) through direct comparison of the \( \Wi \) dependence of these ratios. In particular, both ratios are roughly proportional to \( \Wi^{-0.5} \) at high \( \Wi \) for the case of \( \beta_\alpha = 2 \) and \( \beta_\alpha = 1 \) (\( < \beta_\alpha \)) as seen in Fig. 4a, namely, for the case of \( 2\kappa_0/\eta_0T < B_\alpha < 2\kappa_0/\eta_0T \) shown in Table I. (From eqs 26 and 27, \( B_\alpha = 2\kappa_0/\eta_0T \) for \( \beta_\alpha = 2 \) and \( \beta_\alpha = 1 \).) This \( \Wi^{-0.5} \) dependence, being common for the \( \eta_{\text{B}}/\eta_0 \) and \( \eta/\eta_0 \) ratios, is found also for larger \( n_\kappa \) (= 10000) that allows \( r_x \) to stay very close to unity in the entire range of \( \Wi \) examined in Fig. 5c. For such large \( n_\kappa \), the power-law thinning behavior, \( \eta_{\text{B}}/\eta_0 \propto \eta/\eta_0 \propto \Wi^{-0.5} \), is indeed deduced analytically, as shown in Appendix. This thinning behavior, noted for large \( n_\kappa \), is not related to the FENE effect at all (because \( r_x = 1 \)) but reflects coupled effects of the decreases of the friction and the Brownian force intensity under flow.

Concerning this result, we remember that the relationships \( n_{\text{B}}/n_0 \propto \Wi^{-0.5} \) and \( \eta_{\text{B}}/\eta_0 \propto \Wi^{-0.5} \) have been experimentally observed separately for unentangled polystyrene melts having different molecular weights of \( M = 10.5 \times 10^4, 19.8 \times 10^3, \) and \( 27.1 \times 10^3 \). This experimental observation might lend support to the above argument for \( B_\alpha \). At the same time, we should emphasize lack of the set of \( n_{\text{B}} \) and \( \eta \) data measured for the same melt sample. Furthermore, the above argument was made for the simplest dumbbell model with an assumption of the functional forms of \( r_x, r_\kappa, \) and \( r_\theta \) (eqs 25-27). Despite these problems, the analysis of the dumbbell model suggests that a correlation between the power-law thinning behavior of \( n_{\text{B}} \) and \( \eta \) at high \( \Wi \) reflects decreases of the friction and the Brownian force intensity being coupled with each other under flow. This correlation deserves further attention.

5. CONCLUDING REMARKS

We have analyzed the dynamics of the FENE-dumbbell model in the presence of isotropic \( \zeta \)-reduction to obtain analytical expressions of the normalized extensional and shear viscosities, \( \eta_{\text{B}}/\eta_0 \) and \( \eta/\eta_0 \), in terms of the Weissenberg number \( \Wi \) and the factors \( r_\kappa, r_x, \) and \( r_\theta \) representing changes of the bead friction, spring stiffness, and the Brownian force intensity from those at equilibrium (eqs 11 and 19a combined with eq 13). The expression was obtained also for the normalized first normal stress difference coefficient under steady shear flow, \( \Psi_{\text{B}}/\Psi_0 \) (eq 19b).

These expressions offer a method(s) of estimating the \( r_\kappa \) and \( r_\theta \) factors from experimental data of those normalized viscoelastic quantities and the stretch ratio \( \lambda \). Furthermore, the expressions allow us to specify the Brownian force intensity and examine validity/failure of the fluctuation-dissipation theorem under steady flow through direct comparison of the \( \Wi \) dependence of the \( \eta_{\text{B}}/\eta_0 \) and \( \eta/\eta_0 \) ratios. Specifically, failure of this theorem can be concluded if the \( \eta_{\text{B}}/\eta_0 \) and \( \eta/\eta_0 \) ratios exhibit the same power-law thinning behavior \( \eta_{\text{B}}/\eta_0 \propto \eta/\eta_0 \propto \Wi^{-0.5} \) at high \( \Wi \). An experimental test of these consequences of the current analysis is considered to be an interesting and important subject of future studies.

For this experimental test, it may be desired to refine the analysis in this study by considering the anisotropy of the \( \zeta \)-reduction and Brownian force and extending the analysis to a bead-spring (Rouse) chain composed of many springs and beads. For the dumbbell, the analysis remains essentially the same even in the presence of the anisotropy, except that the parameters \( B, \zeta, \) and \( r \) become dependent on the spatial directions: For example, in the presence of anisotropy, eq 19a becomes \( \eta/\eta_0 = \{r_\alpha r_x\}^2 \left[ r_\kappa (r_\gamma + r_\kappa) \right] \) with the second subscript \( x \) and \( y \) specifying the directions. Thus, the discussion presented in this study would not be qualitatively affected by the anisotropy. Furthermore, the extension of the analysis to the Rouse chain requires us to conduct eigenmode calculations but the results would be qualitatively similar to those presented in this study. The experimental test with these refinements is an interesting subject of future studies.

APPENDIX. POWER-LAW BEHAVIOR OF \( \eta_{\text{B}}/\eta_0 \) AND \( \eta/\eta_0 \) FOR \( n_\kappa \gg 1 \)

For \( n_\kappa \gg 1 \), we can consider a wide range of \( \lambda \) wherein \( \lambda^2 \ll n_\kappa \) and eq 25 gives \( r_x = 1 \) but \( \lambda^2 \) is still much larger than unity at a given \( \Wi \). In this range of \( \lambda \), eqs 26 and 27 are satisfactorily approximated as

\[
\lambda^2 = \left( \frac{2}{\lambda^2} \right)^{\beta_\gamma} \quad \text{with} \quad \beta_\gamma > 0
\]  
(A1)

\[
r_\kappa = \left( \frac{1}{\lambda^2} \right)^{\beta_\kappa}
\]  
(A2)

In that range of high \( \Wi \) where \( r_x = 1 \), eq 19c can be approximated with the aid of eqs A1 and A2 as

\[
\lambda^2 = \frac{2}{3} \left( \frac{r_\kappa \lambda^2}{\lambda_{\text{shear}}^2} \right) \Wi_{\text{shear}}^2 \quad \text{under shear flow}
\]  
(A3)

which results in a power-law relationship between \( \lambda_{\text{shear}} \) and
\[ W_{\text{shear}} \]

\[ \lambda_{\text{shear}} \propto W_{\text{shear}}^{\beta_{\text{shear}} + 1} \]  

Equation A4 is valid in a range of \( W_{\text{shear}} \) wherein \( \eta_0 \gg \lambda^2 >> 1 \). From eqs A1 and A4 combined with eq 19a in the main text, we find an expression of \( \eta_0/\eta_B \) in this range of \( W_{\text{shear}} \) :

\[ \frac{\eta_0}{\eta_B} \propto W_{\text{shear}}^{\lambda_{\text{shear}}} \]  

(26)

(Consequently, eq 19b gives a relationship, \( \Psi/\Psi_{1,\beta} = r/r_B \propto W_{\text{shear}}^{\lambda_{\text{shear}} + 1} \).

Under extensional flow, a factor \( (r_e/r_e)W_{\text{ext}} \) appearing in eq 15 should approach a constant smaller than 1/2 on an increase of \( W_{\text{ext}} \) so as to prevent divergence of \( \eta_{\text{ext}} \). Then, in the range of large \( W_{\text{ext}} \) wherein \( r_e \) still remains indistinguishable from unity, \( r_e \) should be proportional to \( W_{\text{ext}}^{1/2} \) and \( \lambda_{\text{ext}} \) (related to \( r_e \) through eq A1) should satisfy a power-law relationship,

\[ \lambda_{\text{ext}} \propto r_e^{1/2} \propto W_{\text{ext}}^{1/2} \]  

(A6)

Consequently, eq 11 combined with eqs A2 and A6 allow the \( \eta_{\text{ext}}/\eta_B \) ratio to exhibit power-law dependence on \( W_{\text{ext}} \) :

\[ \frac{\eta_0}{\eta_B} \propto W_{\text{ext}}^{1/2} \]  

(A7)

In general, the power-law exponents with respect to \( W_i \) are different for the quantities under extensional and shear flow, as can be noted from eqs A4-A7. Nevertheless, coincidence of those exponents is noted for a special case of \( \beta_e = \beta_{\text{shear}} + 1 \). For this case, \( \lambda \propto W_i^{1/2(\lambda - 1)} \), \( \zeta \propto W_i^{\lambda/2(\lambda - 1)} \propto W_i^{1} \), \( B_0 \propto W_i^{\lambda/2} \propto W_i^{1} \propto W_i^{1} \) under both extensional and shear flow, and \( \eta_{\text{ext}}/\eta_B \propto \eta/\eta_0 \propto W_i^{\lambda(1-1/\lambda)} \). In fact, the exponents \( \beta_i = 2 \) and \( \beta_{\text{shear}} = 1 \) adopted in Figs. 4c and 5c belong to this special case and give the power-law relationships \( \lambda_{\text{ext}} \propto \lambda_{\text{shear}} \propto W_i^{1/2} \), \( \zeta_{\text{ext}} \propto \zeta_{\text{shear}} \propto W_i^{1} \), and \( \eta_{\text{ext}}/\eta_B \propto \eta/\eta_0 \propto W_i^{-1/2} \), see slopes of the double-logarithmic plots shown therein. These results suggest that the power-law exponents under shear and extensional flow, if observed experimentally, provide us with very useful information for the friction reduction and the Brownian force intensity under flow.

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