Boltzmann gain-loss-based non-Hookean spring model and sinh-type nonlinear coupled constitutive relation for viscoelastic fluids

Rho Shin Myong (명노신)[1, a)]

[1]School of Mechanical and Aerospace Engineering and ACTRC, Gyeongsang National University, Jinju, Gyeongnam 52828, Republic of Korea

[a)]Author to whom correspondence should be addressed: *myong@gnu.ac.kr*

ABSTRACT

This study proposes a theoretical non-Hookean spring force model based on Boltzmann's 1872 gain-and-loss concept for the molecular-level description of polymer stresses in viscoelastic fluids. The resulting thermodynamically consistent second-order constitutive model, which is obtained from the Fokker-Planck kinetic equation of elastic dumbbells with a Boltzmann interaction term using the cumulant expansion-based balanced closure, takes the form of a hyperbolic sine function. The mean cumulant inside the hyperbolic sine factor represents a combination of the Rayleigh-Onsager dissipation function and a macromolecular property-dependent softening parameter. In parallel, the study presents a non-negative non-equilibrium distribution function in the exponential form, unlike conventional non-equilibrium distribution functions in polynomial-based perturbation form. The study also revealed similarities and differences between the present Boltzmann model of gain and loss of dumbbells and the Yamamoto model of reformation and breakage of network junctions. Further, two phenomenological sinh-type models, the Ree-Eyring model for non-Newtonian flow and the Johnson-Tevaarwerk model for elastohydrodynamic lubrication, were found to be a subset of the new theoretical model. To validate the new model, it was applied to two benchmark problems of extensional and shear flows, and good agreement with experimental data was found for a wide range of Weissenberg numbers. The computational stability of the new model was also demonstrated based on the planar stability theory of autonomous dynamical systems. Finally, preliminary results using OpenFOAM-RheoTool solvers indicate that the new model is free of the high-Weissenberg-number problem for two-dimensional viscoelastic flow over a confined cylinder up to the maximum Weissenberg number considered, 1,000.

KEYWORDS: Boltzmann theory; Spring model; Viscoelastic fluids; Constitutive equations; finite volume method; OpenFOAM RheoTool

I.INTRODUCTION

The macroscopic description of fluids is based on the physical laws of conservation of conserved variables (mass, momentum, and energy) and associated constitutive equations of non-conserved variables (viscous shear stress and heat flux). For Newtonian fluids, the two-century-old Navier-Stokes-Fourier (NSF) equation [1]—the conservation laws in conjunction with linear Newtonian constitutive relations—is considered to be the de facto mathematical equation for every possible flow problem. However, the linear Navier and Fourier laws are not valid when the molecular nature of fluids, such as the constituent molecule type and interaction among molecules, becomes important [2-5]. These occur in soft matter and complex fluids such as polymer melts and polymeric liquids [6-10] and rarefied or micro- and nano-scale gases [11-16].

On the other hand, as the elastic properties of fluids become important, the interplay between viscous and elastic forces must be considered. To describe soft matter and complex media in high nonequilibrium states, including viscoelastic fluids, intramolecular interaction spring models are essential. The Hookean spring model is based on the empirical Hooke's law, named after 17th-century British physicist Robert Hooke, who first stated the law in 1676 as a Latin anagram and published the solution of his anagram in 1678 [17]. It describes the behavior of an ideal spring where the force exerted by the spring is directly proportional to its displacement from its equilibrium position.

Hooke's law and the Hookean spring model are fundamental in physics and engineering. They describe the behavior of elastic materials and provide the basis for more complex models, and are used to analyze the behavior of springs, understand the elasticity of materials, and design various mechanical systems. However, many real-world materials and systems exhibit nonlinear behavior beyond linear Hooke's laws, especially when subjected to larger forces or stresses, and require non-Hookean spring models.

The relation between the microscopic (molecular) and macroscopic (continuum) physics of a specific fluid of interest is represented by a constitutive equation. As the only ingredient able to bridge the two distinctive worlds, it plays a critical role in describing the motion of fluids. For example, the type of molecules constituting a polymer solution will determine what kind of solution it will become.

The constitutive equations can take various forms, differential or integral, and explicit or implicit, depending on the different types of fluids. However, all of them are remarkably similar, probably because all fluidic

molecules, despite their diversity, follow two simple actions at a molecular level: *movement* and *interaction* with other molecules (or *intramolecular interaction*). This insight may help us understand the properties of the constitutive equations already in use or develop new constitutive equations that are free from the limitations that existing constitutive equations might suffer from.

A variety of constitutive equations—numbering in the hundreds—already exist, including elastic, generalized viscous Newtonian, linear, and nonlinear viscoelastic models [6-10]. Among them, the upper convected Maxwell model (UCM) and the Oldroyd-B model introduced in 1950 [6], which will hereafter be called the Maxwell-Oldroyd model for convenience, occupy a special place in the study of viscoelastic fluids. This is because the model is the simplest *nonlinear viscoelastic* model, while still retaining the essential physics of fluids at a molecular level: kinematic (moving or streaming) and interacting (colliding or deforming).

However, despite its fundamental importance, the Maxwell-Oldroyd model was found to break down at relatively low values of the Weissenberg (Wi) number (around the order of one), casting a shadow over theoretical modelling of viscoelastic fluids in high nonequilibrium states. This is known as the "high Weissenberg number (HWN) problem" in the literature [18-31] and has been extensively addressed in the rheology and non-Newtonian fluids communities, such as in the International Workshop on Numerical Methods in Viscoelastic Flows.

Many suggestions have been put forward as possible causes [21, pp. 173-199], based on observations of symptoms (for example, the bifurcation and the failure of the iterative numerical schemes [18]) and physical considerations (for example, the unsuitability of the models due to infinitely extensible interconnecting springs [32]). Although some researchers have argued that the HWN problem has already been solved and therefore does not exist, it is safe to say that its ultimate origins remain elusive today [31, pp. 21-22], especially in multidimensional numerical simulations, as evidenced by many ongoing efforts, such as the introduction of a log conformation representation for the Giesekus model [23].

To explain the diverse phenomena observed in experiments and to overcome the limitations of the Maxwell-Oldroyd model, Giesekus [7], in 1966, proposed a nonlinear viscoelastic model of a quadratic nature that captures phenomena like shear-thinning and non-zero second normal stress differences, which are commonly observed in viscoelastic fluids, particularly those found in polymer solutions. This model is based on the concept

of anisotropic drag, which arises from the modification of the relaxation of an elastic dumbbell when surrounded by other dumbbells with different orientations.

Drastically different nonlinear viscoelastic models were also developed, based on the network concept of polymeric (macromolecular) fluids. Yamamoto in 1956 [33], Lodge in 1960 [34], and Wiegel in 1969 [35] proposed network-type viscoelastic models based on the probability of chain-reformation and chain-breakage, segment-creation and segment-loss, and bond-creation and bond-destruction, respectively. Starting from the Yamamoto-Lodge-Wiegel-type concept of reformation-creation-creation and breakage-loss-destruction of network junctions in macromolecules, in 1977, Phan-Thien and Tanner [8] developed a popular viscoelastic model, known as the Phan-Thien-Tanner (PTT) model, by introducing a slip velocity that accounts for the inability of the junctions to follow the imposed velocity field exactly.

Meanwhile, the popular finitely extensible nonlinear elastic (FENE) dumbbell models were developed by Bird et al. [36] and others [32, 37], based on a kinetic theory of the nonlinear elastic dumbbell model to represent polymer molecules in dilute solutions and the Peterlin closure, of which about 16 models are listed in Kroger [38, Table 1]. Interestingly, as discussed in a recent study by Davoodi et al. [39], there are some similarities between the FENE dumbbell (Peterlin closure) model and the simplified PTT model in simple and complex flows. It was shown that for steady homogeneous flows, such as steady simple shear flow or pure extension, the response of both models is identical under some conditions.

This study presents a unique approach that combines the kinetic theory of nonlinear elastic dumbbell models pioneered by the rheological community with the kinetic theory developed by Ludwig Boltzmann in 1872 [3] to derive a theoretical non-Hookean spring force model. Based on this non-Hookean model, it further presents a novel nonlinear coupled constitutive relation (NCCR) for viscoelastic fluids.

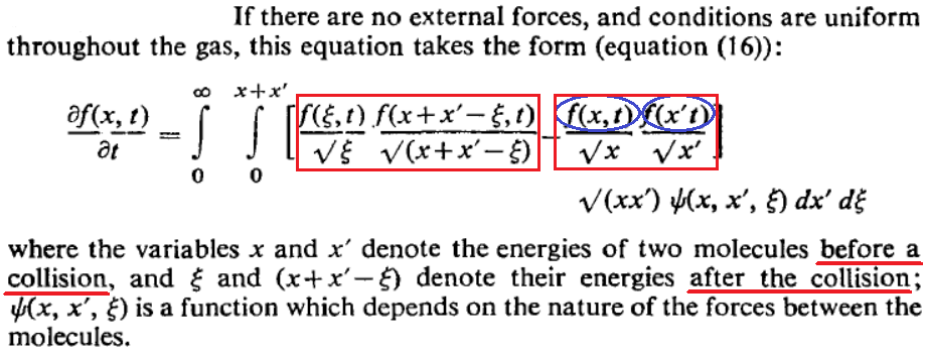
The core idea of the new theory is to introduce Boltzmann's concept of *gain (after) minus loss (before)*, '$f^* - f$', for handling intramolecular interaction in spring models, along with a cumulant-expansion-based balanced closure from the master kinetic equation, which is compatible with the second law of thermodynamics. The essence of the new theory can be summarized as follows:

$$\frac{1}{\lambda}\left\langle h^{(1)}\left(f^* - f\right)\right\rangle \underset{2nd}{=} -\frac{1}{\lambda}\boldsymbol{\tau}\, q_{2nd}(\kappa_1), \text{ where } h^{(1)} = S_0\mathbf{rr} - k_B T\mathbf{I},\ \ q_{2nd}(\kappa_1) = \frac{\sinh\kappa_1}{\kappa_1},\ \ \kappa_1 = \alpha\frac{\sqrt{\boldsymbol{\tau}:\boldsymbol{\tau}}}{\mu/\lambda}. \qquad (1.1)$$

Here, $f(\mathbf{r},t)$, $\boldsymbol{\tau}$ represent the probability density function of finding a dumbbell in the configuration vector space $\mathbf{r}$ connecting two beads for a given time, and the viscoelastic stress tensor, respectively. The symbol $\langle\ \rangle$ represents the volume integral in configuration space. The quantities S_0, λ, μ, α represent a spring constant, the relaxation of the dumbbell configuration, the polymeric viscosity, and a macromolecular property-dependent softening parameter, respectively. The subscript '2nd' represents the second-order approximation.

To the best of the author's knowledge, kinetic modeling of viscoelastic fluids based on the Boltzmann concept of gain and loss applied to the intramolecular interaction of the spring in the dumbbell, along with a cumulant-expansion-based balanced closure, has not been reported in the past.

The heart of the Boltzmann's 1872 theory is his treatment of the collision (or interaction) term based on the concept of gain ('after' in his term, f^* in his symbol) and loss ('before' in his term, f in his symbol); that is, a replenishing (inverse or post) interaction and a depleting (forward or pre) interaction. For convenience, the original form of Boltzmann's collisional integral is reproduced in Fig. 1 from his 1872 paper [3].



If there are no external forces, and conditions are uniform throughout the gas, this equation takes the form (equation (16)):

$$\frac{\partial f(x,t)}{\partial t} = \int_0^{\infty}\int_0^{x+x'} \left[\frac{f(\xi,t)}{\sqrt{\xi}}\frac{f(x+x'-\xi,t)}{\sqrt{(x+x'-\xi)}} - \frac{f(x,t)}{\sqrt{x}}\frac{f(x',t)}{\sqrt{x'}}\right] \sqrt{(xx')}\,\psi(x,x',\xi)\,dx'\,d\xi$$

where the variables x and x' denote the energies of two molecules before a collision, and ξ and $(x+x'-\xi)$ denote their energies after the collision; $\psi(x, x', \xi)$ is a function which depends on the nature of the forces between the molecules.

Fig. 1. The original form of the Boltzmann collisional integral for the binary collision of particles (reproduced in the public domain from its publication in 1872 [3]). Note that there are two probability functions because two molecules are involved in the collision process.

Another key observation is that while f^* and f may be linear individually (definitely, f is linear because it has only one f^1 for the dependent variable f, not like nonlinear function such as $\ln f$ or f^2), their difference ($f^* - f$) is nonlinear in general, which distinguishes the Boltzmann's 1872 theory from other popular and yet still linear models, such as the Bhatnagar-Gross-Krook (BGK) approximation ($f^{(eq)} - f$) proposed in 1954 based on the small amplitude assumption [40] ($f^{(eq)}$ being the equilibrium distribution function).

The present Boltzmann-type modeling based on ($f^* - f$) has a unique advantage: it can provide precise information about the accuracy of the nonlinear factor of the new model, since the nonlinear feature of the spring force model beyond the linear Hookean spring law can be systematically derived in a thermodynamically consistent manner. In the present NCCR model, it is second-order, as indicated by a subscript '2nd' like $q_{2\mathrm{nd}}$ of the dissipative origin in (1.1), meaning that only the leading cumulant (mean) among the higher cumulants (variance, skewness, and kurtosis) is retained in the cumulant expansion to balance the other terms of the kinematic origin, which are also second-order.

The elastic dumbbell model, which serves as the basis for the kinetic description used in this study, is a very crude representation of polymer molecules [38]. It lacks the detailed internal structure of macromolecules that may be necessary to account for the extremely rapid motions that contribute to the complex viscosity at high frequencies, making it of little interest to polymer chemists. However, the elastic dumbbell model possesses orientation and stretchability, two properties essential for qualitatively describing steady-state rheological properties and properties that involve slow time-varying behavior.

This universal behavior, revealed through experimental studies, suggests that the macroscopic properties of polymers are determined by a few large-scale properties of the polymer molecules. Because different polymer molecules behave in the same manner at nanometer length scales, structural details can be neglected even in microscopic (beyond-atomistic) models. This observation justifies the introduction of simple mechanical models, such as the bead-spring dumbbell model, to represent real polymer molecules.

In natural science and engineering, the merits and performance of new models must ultimately be tested through comparison with experimental data and competing models. In this study, an experimental comparison will be conducted using experimental data of the viscosities of extensional and shear flows, which are the two most important benchmark problems for viscoelastic fluids. In parallel, performance verification is achieved by applying the new model to a state-of-the-art computational code and analyzing the viscoelastic flow in a two-dimensional benchmark problem.

In the field of computational rheology, significant progress has been made over the past decades in the areas of discontinuous Galerkin methods [41] and finite volume methods [42-44]. In particular, RheoTool [45], an

open-source toolbox based on OpenFOAM®, has recently become readily available to researchers interested in simulating generalized Newtonian and viscoelastic fluids in pressure- and/or electrically driven flows.

This study implements the newly proposed non-Hookean term ($\boldsymbol{\tau}\, q_{2\mathrm{nd}}(\kappa_1)/\lambda$ in (1.1)) in OpenFOAM®, in place of the Hookean term ($\boldsymbol{\tau}/\lambda$) in the Maxwell-Oldroyd model. It then analyzes viscoelastic flows around a confined cylinder up to Wi = 1000, and verifies its performance by comparing it with other models. [46-53].

The rest of the paper is organized as follows. Section II presents a new non-Hookean spring force model based on the Boltzmann concept of gain and loss for the microscopic Fokker-Planck equation. Using the second law of thermodynamics as a guiding principle, this model yields a sinh-type nonlinear coupling constitutive relation for viscoelastic fluids. The essential difference between the new cumulant expansion and the conventional polynomial expansion, and the mathematical procedure used in deriving the nonlinear sinh factor via the second law of thermodynamics, are explained in detail in the Appendices.

Section III validates the new constitutive model by comparing it with experimental data for extensional and shear flows over a wide range of Weissenberg numbers. In addition, the new model is compared with the phenomenological models, Ree-Eyring for non-Newtonian flow [54, 55], Johnson-Tevaarwerk for elastohydrodynamic lubrication [56, 57], and other popular viscoelastic fluid models, Giesekus [7, 58], Phan-Thien-Tanner (PTT) [8], and FENE-P (Peterlin) [36]. Finally, concluding remarks on the limitations of the present model and future topics are given.

II. NON-HOOKEAN SPRING MODEL AND NONLINEAR COUPLED CONSTITUTIVE RELATIONS FOR VISCOELASTIC FLUIDS

A. Boltzmann gain-loss concept and comparison with network models

The original form of the Boltzmann collision integral for a binary interaction, $C[f]$, is

$$C[f] = \int_{-\infty}^{\infty}\int_{0}^{2\pi}\int_{0}^{\infty} b\left|\mathbf{v}-\mathbf{v}_2\right|\left(f^{*}f_2^{*} - ff_2\right)dbd\phi d\mathbf{v}_2\,, \tag{2.1}$$

where $\mathbf{v}$, b, ϕ represent the molecular velocity of the particle, the impact parameter of a two-body collision, and the azimuthal angle of scattering, respectively. Note that the gain-and-loss concept is expressed as $\left(ff_2\right)^{*} - \left(ff_2\right)$. The reason there are two probability functions f, f_2 in this expression is that two molecules are involved in the collision process. Note also that if the binary collision assumption is removed, the integrals

$\int_0^\infty(\cdots)db$, $\int_0^{2\pi}(\cdots)d\phi$, and $\int_{-\infty}^{\infty}(\cdots)d\mathbf{v}_2$ will disappear, and the gain-loss term $\left(ff_2\right)^*-\left(ff_2\right)$ will reduce to f^*-f .

Now, one can extend the Boltzmann gain-loss concept for binary collisions of particles to the intramolecular interaction of the spring in the dumbbell. In the model of an elastic dumbbell immersed in a Newtonian solvent, the Fokker-Planck equation of the dumbbell probability density function, $F(\mathbf{v};\mathbf{r},t)$, may be written as [21]

$$\frac{\partial F}{\partial t}+\nabla\cdot\left[\left(\mathbf{v}+(\nabla\mathbf{u})^T\mathbf{r}\right)F\right]-\frac{1}{m}\nabla_{\mathbf{v}}\cdot\left(\varsigma\mathbf{v}F\right)-\frac{2k_BT\varsigma}{m^2}\nabla_{\mathbf{v}}^2F=\frac{1}{m}\nabla_{\mathbf{v}}\cdot\left(2\mathbf{s}F\right). \tag{2.2}$$

Here, $\mathbf{s}$ is the spring force, the constant ς is the so-called friction coefficient given as $6\pi\mu_s a$, where a is the radius of a bead and μ_s is the solvent viscosity. The m, k_B, T represent the mass of the bead, the Boltzmann constant, and the temperature, respectively. Note that the term $\nabla_{\mathbf{v}}\cdot\left(2\mathbf{s}F\right)/m$ on the right-hand side arising from the interaction of the spring force with a bead of the dumbbell is expressed as the gradient of the spring force field in the conventional method.

Now, a different way of modeling the interaction term may be developed by extending the Boltzmann method of the collision integral for the binary collision of gas particles based on the gain-loss concept to the intramolecular interaction of the spring in the dumbbell immersed in solvent fluid;

$$\frac{S_0}{m}\left(F^*-F\right), \tag{2.3}$$

where the asterisk denotes the post-interaction (gain) value of the quantity. Note that instead of the nonlinearity $fn(r)$, which is present in a relation $\mathbf{s}F=S(r)\mathbf{r}F=S_0fn(r)\mathbf{r}F$ of $\nabla\cdot\left(\mathbf{r}fn(r)F/2\lambda\right)$ of a conventional gradient-based non-Hookean spring (2.2), a different nonlinearity in an integral form, $rfn(r)F=2\int(F^*-F)dr$, of an implicit type—the dependent variable F itself appearing in the integral—is used. The relaxation of the dumbbell configuration λ is related to a spring constant S_0 and the friction coefficient ς via $\lambda=\varsigma/4S_0$. Thus, the nonlinearity in the new spring model is derivable in a purely theoretical manner if one works directly on the term F^*-F , which is unlike some existing models in which the nonlinear factor $fn(r)$ is determined by empirical consideration.

After introducing the marginal probability density function $f(\mathbf{r},t)=\int F(\mathbf{v};\mathbf{r},t)d\mathbf{v}$, the resulting kinetic equation of (2.2) with (2.3) for finding a dumbbell in the configuration vector space **r** connecting two beads for a given time is reduced to

$$\frac{\partial f}{\partial t}+\nabla\cdot\left((\nabla\mathbf{u})^T\mathbf{r}-\frac{2k_BT}{\varsigma}\nabla\right)f=C[f] \text{ where } C[f]=\frac{1}{\lambda}\left(f^*-f\right) \text{ for a Boltzmann-type model.} \quad (2.4)$$

This can be regarded as *a Fokker-Planck equation with a non-gradient Boltzmann-type interaction term*, called FP-*m*Boltzmann in short (*m* meaning 'modified'), because the Boltzmann concept based on gain (f^*) and loss (f) in (2.1) was presented in 1872, much earlier than Yamamoto's 1956 network concept [33]. Note that the relaxation time parameter in the present Boltzmann treatment is independent of the configuration space, which distinguishes it from the Yamamoto treatment, where the chain-breakage coefficient depends on the configuration space. Compare also the new interaction form $(f^*-f)/\lambda$ with the conventional gradient-based form $\nabla\cdot(\mathbf{r}f/2\lambda)$, which can be derived from the term $\nabla_{\mathbf{v}}\cdot(2\mathbf{s}F)/m$ on the right-hand side of (2.2).

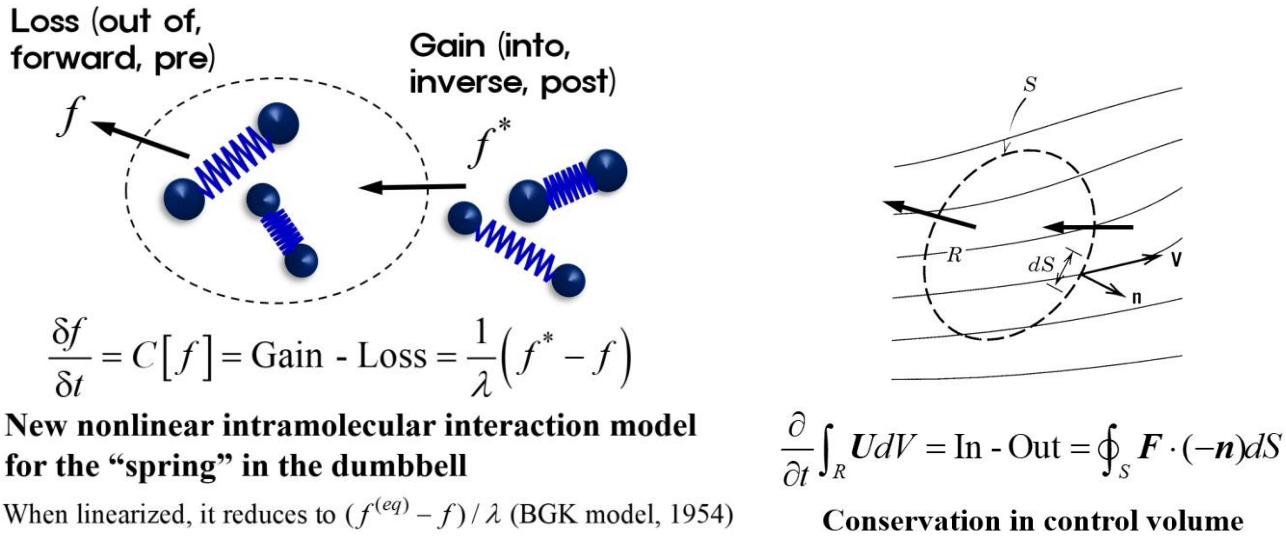


Fig. 2. The gain-and-loss concept in microscopic phase space (Boltzmann-type) (left) versus the control volume concept in macroscopic thermodynamic space (right).

The new interaction term $(f^*-f)/\lambda$ represents the net change (gain and loss) in the number of dumbbells in time and is a result of two competing processes: replenishing (inverse or post) interaction f^* through scattering into the range, and depleting (forward or pre) interaction f through scattering out of the range, as

shown in Fig. 2 (left). Note that in contrast to the two probability functions f, f_2 in the original Boltzmann equation (2.1), in the present dumbbell case, there is only one probability function f of a bead of the dumbbell. For the dumbbell models where the interaction occurs through the "spring" in the dumbbell, the forces on the two beads are equal and opposite, leading to a connector force and only one probability function [59, p. 60]. Nonetheless, the probability function f can describe the *orientation and stretchability* of the dumbbell via the direction and magnitude of the configuration vector **r**.

In some respects, the Boltzmann concept of gain and loss is not new. In elementary fluid dynamics, the Eulerian description of fluid motion is based on the so-called control volume approach to ensure the conservation laws. One can easily notice the analogy between the present gain-loss concept in phase (configuration) space and the well-known influx-outflux concept in macroscopic (thermodynamic) space, as illustrated in Fig. 2 (right).

In the Introduction, it was noted that the new interaction term, $(f^* - f)/\lambda$, is nonlinear in general, and this distinguishes it from the 1954 linear BGK approximation, $(f^{(eq)} - f)/\lambda(|\mathbf{r}|)$ [40]. In the BGK approximation, dumbbells obeying the actual distribution function f are removed exponentially (due to interactions), and the 'removed' dumbbells are 'replaced' by another population of dumbbells following the equilibrium distribution function $f^{(eq)}$. The BGK method is mathematically simple, since the approximation does not make any specific assumption about the nature of the intramolecular forces, thus avoiding any detailed evaluation of the very complicated form ($f^* - f$) [60, pp. 167-174].

However, the BGK method is known to suffer several shortcomings: 1) the approximation cannot be considered to be a rigorous theory; 2) the relaxation time is treated as a given parameter $\lambda(|\mathbf{r}|)$, and its value is determined empirically (and sometimes very inaccurately); 3) and while replacing f^* by $f^{(eq)}$ makes the interaction term mathematically tractable, its validation range is limited to the small amplitude (or not-far-from equilibrium, or not HWN) problem.

Based on the network concept of polymeric (macromolecular) fluids, a class of nonlinear viscoelastic models was developed by Yamamoto [33], Lodge [34], and Wiegel [35]. Further, Phan-Thien and Tanner [8] developed a popular viscoelastic model, known as the Phan-Thien-Tanner (PTT) model, starting from the Yamamoto-

Lodge-Wiegel-type concept of the creation and destruction of network junctions in macromolecules. It would be interesting to compare the new model and the network-based models.

If one takes Yamamoto's 1956 theory, which is the starting point of network theory, on the number of the network chains of segments with end-to-end distance $\mathbf{r}$, which actually construct the network at time t, the interaction term in the kinetic equation of the chain-distribution function $f(\mathbf{r},t)$ reads as follows:

$$C[f] = g(\mathbf{r},t) - h(\mathbf{r}) f(\mathbf{r},t) . \tag{2.5}$$

The first and second terms on the right-hand side represent the chain-reformation (chain-gain in Boltzmann term) and the chain-breakage (chain-loss in Boltzmann term), respectively, and are responsible for the dissipative processes in the network system [33, p. 417].

One can observe a similarity between (2.4) and (2.5) in that they subtract loss/breakage from gain/reformation. However, there are two important differences. First, the relaxation time parameter λ in the present Boltzmann treatment is independent of the configuration space $\mathbf{r}$, whereas the chain-breakage coefficient $h(\mathbf{r})$ in the Yamamoto treatment depends on the configuration space $\mathbf{r}$. Second, the present method directly solves the Boltzmann interaction term, $(f^* - f)/\lambda$, using the second law of thermodynamics and cumulant expansion-based balanced closure up to the second order. In contrast, the Yamamoto-Lodge-Wiegel method introduces a small deformation (or amplitude) approximation and solves the interaction term only up to the first order based on a polynomial-based perturbation method.

Yamamoto introduced the small deformation assumption and derived a BGK-like simplified model [33, p. 418],

$$\frac{1}{1/h(\mathbf{r})}\left(f^{(eq)}(\mathbf{r},t) - f(\mathbf{r},t)\right), \tag{2.6}$$

which is the same as the linear BGK approximate model for the Boltzmann collision integral, $(f^{(eq)} - f)/\lambda(|\mathbf{r}|)$, except for a minor difference in the dependence on $\mathbf{r}$: $1/h(\mathbf{r})$ versus $\lambda(|\mathbf{r}|)$.

B. Closing the Fokker-Planck equation of the elastic dumbbell model with the Boltzmann gain-loss-based non-Hookean spring model based on the closing-last balancing

Elastic dumbbell models are very crude representations of polymer molecules. They clearly do not have enough internal degrees of freedom to describe the very rapid motions that may contribute, for instance, to

complex viscosity at high frequencies. Nonetheless, the elastic dumbbell models have proven to be very helpful in developing a broad understanding of the relation between macromolecular motions and rheological phenomena [59, 61]. The Fokker-Planck kinetic equation has often been criticized for not satisfying the conservation of momentum. However, for viscoelastic fluids, this criticism is misplaced because polymer stresses of viscoelastic fluids do not need to satisfy the law of conservation of momentum.

Though it looks complicated, the Fokker-Planck kinetic equation with the Boltzmann gain-loss-based non-Hookean spring model (2.4) basically consists of the time derivative term, a higher-order term, the hydrodynamic force, the Brownian force, and the interacting force (which acts through the spring in the dumbbell). Using integrating by parts and remembering that f vanishes at infinity [6, 21, 62], multiplying (2.4) by **rr** and then integrating yields

$$\frac{\partial\langle \mathbf{r}\mathbf{r}f\rangle}{\partial t}+\mathrm{H.O.}(\mathbf{rrr})-\left[(\nabla\mathbf{u})^{T}\langle \mathbf{r}\mathbf{r}f\rangle+\langle \mathbf{r}\mathbf{r}f\rangle\nabla\mathbf{u}\right]-\frac{4nk_{B}T}{\varsigma}\mathbf{I}=\left\langle \mathbf{r}\mathbf{r}C[f]\right\rangle . \tag{2.7}$$

Here, n represents the number of dumbbells per unit volume. Note that there is always a higher-order term, $\mathrm{H.O.}(\mathbf{rrr})$, on the left-hand side, which leads to the well-known closure problem. Therefore, *the closure problem exists in two places*, along with the closure on the right-hand side of the interaction $\left\langle \mathbf{r}\mathbf{r}C[f]\right\rangle$. This point seems obvious with no particular significance, but the condition that requires the two closures to be balanced may provide a theoretical clue regarding the ultimate cause of the HWN problem in some viscoelastic fluid problems.

Further derivation can be made once the interacting term $C[f]$, describing the force on the bead exerted by the spring, is specified; for example, the conventional spring model,

$$C[f]=\nabla\cdot\left(\frac{2\mathbf{s}}{\varsigma}f\right),\ \left\langle \mathbf{r}\mathbf{r}C[f]\right\rangle=-\frac{4}{\varsigma}\langle \mathbf{r}\mathbf{s}f\rangle . \tag{2.8}$$

By ignoring the higher-order terms, $\mathrm{H.O.}(\mathbf{rrr})$, on the left-hand side of (2.7) and further assuming that the spring force in (2.8) has the same direction as $\mathbf{r}$ and follows a *linear* Hookean, expressed as

$$\mathbf{s}=S_{0}\mathbf{r}, \tag{2.9}$$

we are led to

$$\frac{\partial \langle \mathbf{rr}f \rangle}{\partial t} - \left[(\nabla \mathbf{u})^T \langle \mathbf{rr}f \rangle + \langle \mathbf{rr}f \rangle \nabla \mathbf{u} \right] - \frac{4nk_BT}{\varsigma} \mathbf{I} = -\frac{1}{\lambda} \langle \mathbf{rr}f \rangle . \tag{2.10}$$

Then, after applying the upper-convected derivative and a relation $\overset{\nabla}{\mathbf{I}} = -(\nabla \mathbf{u}^T + \nabla \mathbf{u})$, the preceding equation can be written as

$$\frac{D\boldsymbol{\tau}}{Dt} - \left[(\nabla \mathbf{u})^T \boldsymbol{\tau} + \boldsymbol{\tau} \nabla \mathbf{u} \right] - \frac{\mu}{\lambda} (\nabla \mathbf{u}^T + \nabla \mathbf{u}) = -\frac{1}{\lambda} \boldsymbol{\tau} . \tag{2.11}$$

where the viscoelastic stress tensor is defined as

$$\boldsymbol{\tau} \equiv S_0 \langle \mathbf{rr}f \rangle - nk_BT\mathbf{I} . \tag{2.12}$$

Here, D/Dt represents the material derivative. The polymeric viscosity is given as $\mu = nk_BT\lambda$. This is the well-known Maxwell-Oldroyd viscoelastic model.

This study will take a different route to close the reduced form (2.7) of the Fokker-Planck equation with a Boltzmann gain-loss-based non-Hookean spring model, $\left\langle \mathbf{rr}\left(f^* - f\right) \right\rangle \big/ \lambda$. The term $\langle \mathbf{rr}C[f] \rangle$ on the right-hand side of (2.7) represents the dissipation, which is attributed to the interaction operator in the kinetic equation. At this point, it should be mentioned that the constitutive equations (2.7) are an exact consequence of the Boltzmann-type Fokker-Planck equation (FP-*m*Boltzmann) (2.4) and are thus capable of capturing the entire physics if they are provided with accurate closure on the open higher-order terms, H.O.(**rrr**) and $\langle \mathbf{rr}C[f] \rangle$.

Among closure theories, in the present study the so-called "closing-last balanced closure" is employed, which was proposed by Myong in 2014 [63] from a keen observation of the essence of the closure problem in a complex system: when closing open terms, the number of places to be closed is two (movement and interaction) and thus the order of approximations in handling the two terms—kinematic (movement) and dissipation (interaction) terms—must be the same to satisfy balancing. For instance, the second-order closure for both terms is $\text{H.O.}(\mathbf{rrr}) \underset{\text{2nd}}{=} 0$ and $\langle \mathbf{rr}C[f] \rangle_{\text{2nd}}$, respectively.

The term on the right-hand side of (2.7), $\langle \mathbf{rr}C[f] \rangle$, which becomes $\left\langle \mathbf{rr}\left(f^* - f\right) \right\rangle \big/ \lambda$ for a Boltzmann gain-loss-based non-Hookean spring model, represents the open high-order term of the dissipative motion in the system. Closing this dissipation term requires special care because it is directly related to the energy dissipation accompanying the irreversible processes, the non-equilibrium entropy production in the system, and the second

law of thermodynamics. A closure on this nonlinear term may be achieved by expanding the distribution function f in the traditional Taylor (polynomial) series.

However, a different route pioneered by Eu [64-68] will be taken in the present study, for two reasons. First, via the non-polynomial cumulant expansion, it assures the *non-negativity of the distribution function* f, regardless of the level of approximations (see Appendix A for the details). Second, via the explicit treatment of the positivity of the non-equilibrium entropy production, *it satisfies the second law of thermodynamics.* The difference between the new cumulant expansion and the conventional polynomial expansion is explained in detail in Appendix B.

C. Theoretical derivation of the dissipation term of the intramolecular interaction of the spring in the dumbbell via the second law of thermodynamics and the cumulant-expansion-based balanced closure

The starting point to take the second law of thermodynamics into account in the process is the equation for non-equilibrium entropy Ψ [63, 65],

$$\Psi(t) = -k_B \left\langle \left[\ln f^c(\mathbf{r},t) - 1 \right] f(\mathbf{r},t) \right\rangle . \tag{2.13}$$

where the non-equilibrium canonical distribution function f^c represents the thermodynamic branch of the solution of the kinetic equation (2.4) f. By differentiating the non-equilibrium entropy Ψ with time and combining it with equation (2.4), the following equation can be obtained;

$$\begin{aligned} \frac{d\Psi}{dt} &= -k_B \left\langle \left[\frac{\partial f}{\partial t} \left(\ln f^c - 1 \right) + \frac{f}{f^c} \frac{\partial f^c}{\partial t} \right] \right\rangle \underset{f=f^c}{=} -k_B \left\langle \frac{\partial f^c}{\partial t} \ln f^c \right\rangle = \\ & k_B \left\langle \ln f^c \nabla_{\mathbf{r}} \cdot \left((\nabla \mathbf{u})^T \mathbf{r} - \frac{2k_B T}{\varsigma} \nabla_{\mathbf{r}} \right) f^c \right\rangle - k_B \left\langle \ln f^c \; C[f^c] \right\rangle, \end{aligned} \tag{2.14}$$

where fluctuations of the distribution functions f from the thermodynamic branch, $\Delta f \equiv f - f^c$, are neglected. Since the first integral on the right-hand side integrates to zero identically by the boundary conditions, which set $f^c(\mathbf{r},t)$ to vanish at the boundaries in the configuration space, (2.14) reduces to the non-equilibrium entropy production σ_{ne},

$$\frac{d\Psi}{dt} = \sigma_{ne} \left(\equiv -k_B \left\langle \ln f^c \; C[f^c] \right\rangle \right). \tag{2.15}$$

At this stage, a useful relation valid in the Boltzmann-type interaction term can be derived. An integral of a function $\psi(\mathbf{r})$ can be defined as follows:

$$I[\psi] \equiv \langle \psi C[f] \rangle = \frac{1}{\lambda} \left\langle \psi \left(f^* - f \right) \right\rangle . \tag{2.16}$$

where the superscripts *c* in the distribution function f^c are dropped for simplicity. On reversal of the interaction process and by noting $d\mathbf{r} = d\mathbf{r}^*$, the following form can be obtained:

$$I[\psi] = -\frac{1}{4\lambda} \left\langle \left(\psi^* - \psi \right) \left(f^* - f \right) \right\rangle . \tag{2.17}$$

Similar to the case of the Boltzmann collision integral for a binary interaction (2.1), there are three interaction invariants to satisfy $I[\psi] = 0$: S_0, $S_0\mathbf{r}$, and $S_0 r^2/2$.

The non-equilibrium entropy production is now expressed as

$$\sigma_{ne} = -k_B \langle \ln f \; C[f] \rangle = \frac{1}{4\lambda} k_B \left\langle \ln \left(f^*/f \right) \left(f^* - f \right) \right\rangle, \tag{2.18}$$

which is always positive since

$$\ln(x/y)(x-y) \; \geq \; 0 \, ,$$

and thereby satisfies the second law of thermodynamics.

Then, if the non-equilibrium entropy production, $\sigma_{ne} \sim \left\langle \ln \left(f^*/f \right) C[f] \right\rangle$, is worked out first, instead of directly working out the complicated interacting term $\mathbf{\Lambda}^{(n)} \equiv \left\langle h^{(n)} C[f] \right\rangle$ where $h^{(n)}$ denotes the molecular expressions for moment (for example, $h^{(1)} = S_0 \mathbf{rr} - k_B T \mathbf{I}$), and if there is a direct relation between σ_{ne} and $\mathbf{\Lambda}^{(n)}$, a thermodynamically consistent form of $\mathbf{\Lambda}^{(n)} = \left\langle h^{(n)} \left(f^* - f \right) \right\rangle / \lambda$ can be obtained.

From *the logarithmic form of the non-equilibrium entropy production* in (2.15), it will be convenient to write the distribution function f in the *exponential form*, instead of a polynomial form;

$$\begin{aligned} & f = f^{(eq)} \exp(-x) \;\; \text{where} \;\; x = \beta \left(\sum_{n=1}^{\infty} X^{(n)} h^{(n)} - N \right), \;\; \beta = \frac{1}{k_B T}, \\ & f^{(eq)} = n \left(\frac{\beta S_0}{2\pi} \right)^{3/2} \exp\left[-\frac{\beta}{2} S_0 r^2 \right]. \end{aligned} \tag{2.19}$$

In this expression, N is the normalization factor, and $X^{(n)}$, unknown macroscopic quantities, are the conjugate variables to the molecular expressions for moment, $h^{(n)}$.

After the lengthy derivation summarized in Appendix C, the resulting equation of $\mathbf{\Lambda}^{(1)} = \left\langle h^{(1)}\left(f^* - f\right)\right\rangle \big/ \lambda$ can be expressed in the following form with the *nonlinear hyperbolic sine function factor, after applying a second-order closure*:

$$\mathbf{\Lambda}^{(1)} \equiv \frac{1}{\lambda}\left\langle h^{(1)}\left(f^* - f\right)\right\rangle \underset{\text{2nd}}{=} -\frac{1}{\lambda}\boldsymbol{\tau} q_{\text{2nd}}(\kappa_1), \text{ where } h^{(1)} = S_0\mathbf{rr} - k_B T\mathbf{I}. \tag{2.20}$$

In summary, after applying the second law of thermodynamics via the positivity of the non-equilibrium entropy production and the second-order balanced closure in the cumulant expansion, the following thermodynamically-consistent *second-order constitutive equations of the viscoelastic stress* can be derived

$$\frac{D\boldsymbol{\tau}}{Dt} - \left[(\nabla\mathbf{u})^T\boldsymbol{\tau} + \boldsymbol{\tau}\nabla\mathbf{u}\right] - \frac{\mu}{\lambda}(\nabla\mathbf{u}^T + \nabla\mathbf{u}) = -\frac{1}{\lambda}\boldsymbol{\tau} q_{\text{2nd}}(\kappa_1), \tag{2.21}$$

where

$$q_{\text{2nd}}(\kappa_1) = \frac{\sinh\kappa_1}{\kappa_1},\ \kappa_1 = \alpha\frac{\sqrt{\boldsymbol{\tau}:\boldsymbol{\tau}}}{\mu/\lambda},\ \alpha = \frac{t_p}{\lambda},\ t_p = \frac{1}{2\lambda}\beta g\mu.$$

Here, the parameter α may be called a molecular property-dependent *softening parameter*, because it has a physical meaning at a molecular level, as follows (l being a characteristic macromolecular length)

$$\alpha = \frac{\beta g\mu}{2\lambda^2} = \frac{2^{1/2}}{l^3}\left(\frac{k_B T}{S_0}\right)^{3/2}. \tag{2.22}$$

The new non-Hookean dumbbell model on the right-hand side of (2.21) recovers the Hookean dumbbell model on the right-hand side of (2.11) in the zero-α limit, since $\lim_{\alpha\to 0}\left[-\frac{1}{\lambda}\boldsymbol{\tau} q_{\text{2nd}}\left(\alpha\frac{\sqrt{\boldsymbol{\tau}:\boldsymbol{\tau}}}{\mu/\lambda}\right)\right] = -\frac{1}{\lambda}\boldsymbol{\tau}$.

The mean cumulant inside the sinh factor, $\kappa_1 = \alpha\sqrt{\boldsymbol{\tau}:\boldsymbol{\tau}}\big/(\mu/\lambda)$, is given as a combination of a macromolecular property-dependent parameter α and the Rayleigh-Onsager dissipation function $\sqrt{\boldsymbol{\tau}:\boldsymbol{\tau}}\big/(\mu/\lambda)$, which is expressed as the double scalar product between polymer viscoelastic stress tensors [69]. This dissipation function indicates a direct measure of departure from thermal equilibrium and is proportional to the Wi number. Note that if the viscoelastic stress tensor is traceless (or deviatoric), $\boldsymbol{\tau}:\boldsymbol{\tau}$ will depend only on the second (frame-independent) invariant, $\text{Tr}(\boldsymbol{\tau}^2)$. Note also that the dissipation term is isotropic due to the

Rayleigh-Onsager dissipation functional form, so it does not contain any anisotropic effects. Such effects should be taken into account by considering additional terms.

The softening parameter α, which we believe is new, is basically the ratio of the elastic force by thermal fluctuation $k_B T$ to the polymeric stiffness S_0, and depends primarily on the characteristic macromolecular length and the stiffness. Thus, the relation (2.22) of the molecular properties of macromolecules can be used to evaluate their stiffness, if the parameter α is determined by comparing theoretical or numerical solutions of the second-order constitutive equations (2.21) with experimental data on macroscopic properties obtained from viscoelastic flows for simple geometries [70]. In the case of entangled macromolecules, the definition of the characteristic length l becomes ambiguous, but according to the present theoretical framework—deriving a highly nonlinear dissipative term in a hyperbolic sine form using cumulant expansion from the linear result near equilibrium—it seems appropriate to define it as the length observed under small force or deformation.

Finally, the non-equilibrium distribution function f associated with the constitutive equation (2.21) can be expressed in the exponential form as follows

$$f(\mathbf{r},t) = n \frac{\exp\left\{-\beta\left[\frac{1}{2}S_0 r^2 - \frac{\boldsymbol{\tau}}{2\mu/\lambda} : (S_0 \mathbf{rr} - k_B T \mathbf{I})\right]\right\}}{\left\langle \exp\left\{-\beta\left[\frac{1}{2}S_0 r^2 - \frac{\boldsymbol{\tau}}{2\mu/\lambda} : (S_0 \mathbf{rr} - k_B T \mathbf{I})\right]\right\}\right\rangle}. \tag{2.23}$$

This form of non-equilibrium distribution function is believed to be the first reported in the literature. Unlike conventional non-equilibrium distribution functions based on the polynomial-based perturbation series, which converge and remain non-negative only within a limited range [59, pp. 77-81], the present form strictly remains non-negative due to its special form, the exponential form. Similar to the case of the softening parameter α, this non-equilibrium distribution function can be utilized in experimental studies on polymer behavior, such as the conformational dynamics of individual polymers in steady shear flow [71].

D. Second-order sinh-type nonlinear coupled constitutive relations (NCCR) for viscoelastic fluids

If the solvent contribution to the extra-stress is included, the conservation law of momentum can be written as

$$\rho \frac{D\mathbf{u}}{Dt} + \nabla p + \mu_s \nabla^2 \mathbf{u} - \nabla \cdot \boldsymbol{\tau} = 0 . \tag{2.24}$$

If the conformation tensor $\mathbf{C} \equiv S_0 \langle \mathbf{rr} f \rangle$, which appears in (2.12) as a second-order moment, is considered instead of the polymer stress $\boldsymbol{\tau}$, the following evolution equation for the thermodynamically-consistent conformation tensor can be derived by starting from (2.21) ($G \equiv nk_BT = \mu / \lambda$)

$$\frac{D\mathbf{C}}{Dt} - \left[(\nabla \mathbf{u})^T \mathbf{C} + \mathbf{C} \nabla \mathbf{u} \right] = -\frac{1}{\lambda} (\mathbf{C} - G\mathbf{I}) q_{2\text{nd}} \left(\alpha \sqrt{(\mathbf{C}/G - \mathbf{I}) : (\mathbf{C}/G - \mathbf{I})} \right). \tag{2.25}$$

If the conformation tensor is defined as a dimensionless quantity, $\mathbf{C} \equiv \boldsymbol{\tau} / (\mu / \lambda) + \mathbf{I}$, (2.25) becomes

$$\frac{D\mathbf{C}}{Dt} - \left[(\nabla \mathbf{u})^T \mathbf{C} + \mathbf{C} \nabla \mathbf{u} \right] = -\frac{1}{\lambda} (\mathbf{C} - \mathbf{I}) q_{2\text{nd}} \left(\alpha \sqrt{(\mathbf{C} - \mathbf{I}) : (\mathbf{C} - \mathbf{I})} \right). \tag{2.26}$$

III. VALIDATION OF THE NON-HOOKEAN SINH-TYPE NCCR MODEL AND DISCUSSIONS

A. Comparison with experimental data

To check the ability of the second-order sinh model to provide fits to experimental rheological data, extensional and shear flows are considered. Table I details the parameters used by Barnes et al. [72] and Ballman [73] in their work and adjustable fit parameters for the NCCR model.

Table I. Experimental parameters for the measurement of the extensional and shear viscosity of a viscoelastic fluid (Polystyrene Melt - PS300K).

Parameter type	Parameters	Extensional flow ($\dot{\varepsilon}$)	Shear flow ($\dot{\gamma}$)
Fluid parameters	Temperature (T)	422 K	
	Molecular weight (M_w)	320 Kg/mole	
	Polydispersity (M_w/ M_n)	2.539	
Parameters used to fit experimental data	Initial polymer viscosity (μ_p)	110.37 Pa·s	18.923 Pa·s
	Average reptation time ($\lambda = \lambda_a$)	67 s	15 s
	NCCR model parameter (α)	1.0	1.0

In the case of uniaxial flow, the velocity gradients can be represented as $\dot{\varepsilon}_1 = \dot{\varepsilon}$, and $\dot{\varepsilon}_2 = \dot{\varepsilon}_3 = -\dot{\varepsilon}/2$, where $\dot{\varepsilon}$ is the extensional rate. At steady-state, the components of the viscoelastic stress tensor (τ_{11} and τ_{22}) can be reduced from (2.21) as

$$\begin{aligned}
&\tau_{11} q_{2\mathrm{nd}}(\kappa_1) = 2\dot{\varepsilon}(\lambda\tau_{11} + \mu), \\
&\tau_{22} q_{2\mathrm{nd}}(\kappa_1) = -\dot{\varepsilon}(\lambda\tau_{22} + \mu), \\
&\text{where } \kappa_1 = \alpha \frac{\sqrt{\tau_{11}^2 + 2\tau_{22}^2}}{\mu/\lambda}.
\end{aligned} \tag{3.1}$$

These nonlinear coupled algebraic equations are then iteratively solved to provide the extensional viscosity, defined as

$$\mu_E \equiv \frac{\tau_{11} - \tau_{22}}{\dot{\varepsilon}} = \frac{3\mu}{\left(q_{2\mathrm{nd}}(\kappa_1) - 2\lambda\dot{\varepsilon}\right)\left(1 + \lambda\dot{\varepsilon} / q_{2\mathrm{nd}}(\kappa_1)\right)}. \tag{3.2}$$

Note that when $q_{2\mathrm{nd}}$ is assumed unity, the extensional viscosity (3.2) is simplified into

$$\mu_E = \frac{3\mu}{(1 - 2\lambda\dot{\varepsilon})(1 + \lambda\dot{\varepsilon})}, \tag{3.3}$$

which is equivalent to the extensional viscosity of the Maxwell-Oldroyd viscoelastic model.

In the case of shear flow, the velocity gradients can be represented as the shear rate $\dot{\gamma}$. At steady-state, the components of the viscoelastic stress tensor (τ_{11} and τ_{12}) can be reduced from (2.21) as ($\tau_{22} = 0$)

$$\begin{aligned}
&\tau_{11} q_{2\mathrm{nd}}(\kappa_1) = 2\lambda\dot{\gamma}\tau_{12}, \\
&\tau_{12} q_{2\mathrm{nd}}(\kappa_1) = \mu\dot{\gamma}, \\
&\text{where } \kappa_1 = \alpha \frac{\sqrt{\tau_{11}^2 + 2\tau_{12}^2}}{\mu/\lambda}.
\end{aligned} \tag{3.4}$$

These nonlinear coupled algebraic equations sharing a common stress constraint with a parabolic type $\tau_{11} = 2\tau_{12}^2\lambda/\mu$ are then iteratively solved to provide the shear viscosity defined as

$$\eta_S \equiv \frac{\tau_{12}}{\dot{\gamma}} = \frac{\mu}{q_{2\mathrm{nd}}(\kappa_1)}. \tag{3.5}$$

Note that when $q_{2\mathrm{nd}}$ is assumed unity, the shear viscosity (3.5) is simplified into

$$\eta_S = \mu, \tag{3.6}$$

which is equivalent to the constant shear viscosity of the Maxwell-Oldroyd viscoelastic model.

The results for the extensional and shear viscosity of a viscoelastic fluid are plotted in Fig. 3 and Fig. 4, respectively. It turns out that the “sinh” second-order NCCR model provides a good fit with the experimental data for both cases. In particular, from Fig. 3, the most important experimental feature in extension flow—the extensional thickening with increasing strain rate followed by extensional thinning—is well-captured by the NCCR model. The extensional thickening and thinning can be explained by the subtle interplay of the second-

order stress-strain rate coupling term $2\dot{\varepsilon}\lambda\tau_{11}$ and the second-order dissipation term $\tau_{11}q_{2\mathrm{nd}}(\kappa_1)$. Under small and intermediate extension, both terms play an important role, as shown in Fig. 3. As the strain rate increases, first the coupling term contributes more than the dissipation term (before reaching the peak), then both terms contribute equally (near the peak), and finally the dissipation term contributes more than the coupling term (after reaching the peak). On the other hand, for very large strain rate, the dissipative term in the hyperbolic sine form becomes dominant (in particular, the $\exp(\kappa_1)$ term, which corresponds to the gain in the number of macromolecules in phase space), ultimately resulting in logarithmic (extensional thinning) asymptotic behavior. This reduction in friction during extensional thinning is known to be a key physical mechanism driving the complex, nonlinear behavior observed in viscoelastic fluids, such as polymer melts or suspensions.

A similar reduction in friction occurs during shear flow, as shown in Fig. 4. The NCCR model accurately captures the main feature of measured shear viscosity: shear thinning at high shear rates. The shear thinning in the new model is described by the nonlinear factor, $\eta_S = \mu / q_{2\mathrm{nd}}(\kappa_1)$, given in (3.5). Because other popular models, such as Giesekus [7], PTT [8], FENE [32, 36, 37] models have similar nonlinearity—a nonlinear factor in $\eta_S = f_{nonlinear}\mu$ being smaller than unity—in shear flow, the new model shares the same behavior with existing models.

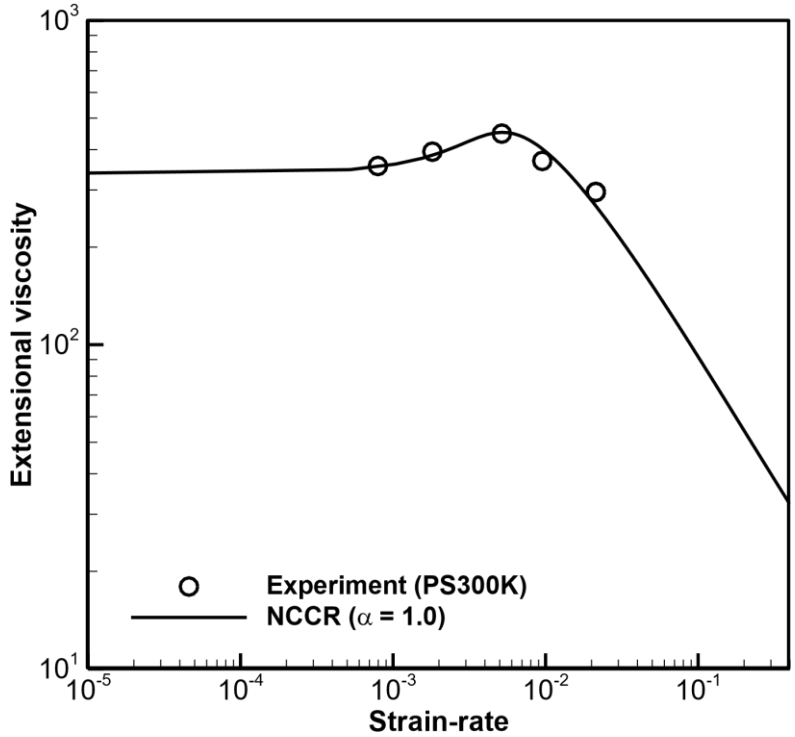


Fig. 3. Comparison of extensional viscosity of "sinh" second-order NCCR model with the measured extensional viscosity for varying strain rate.

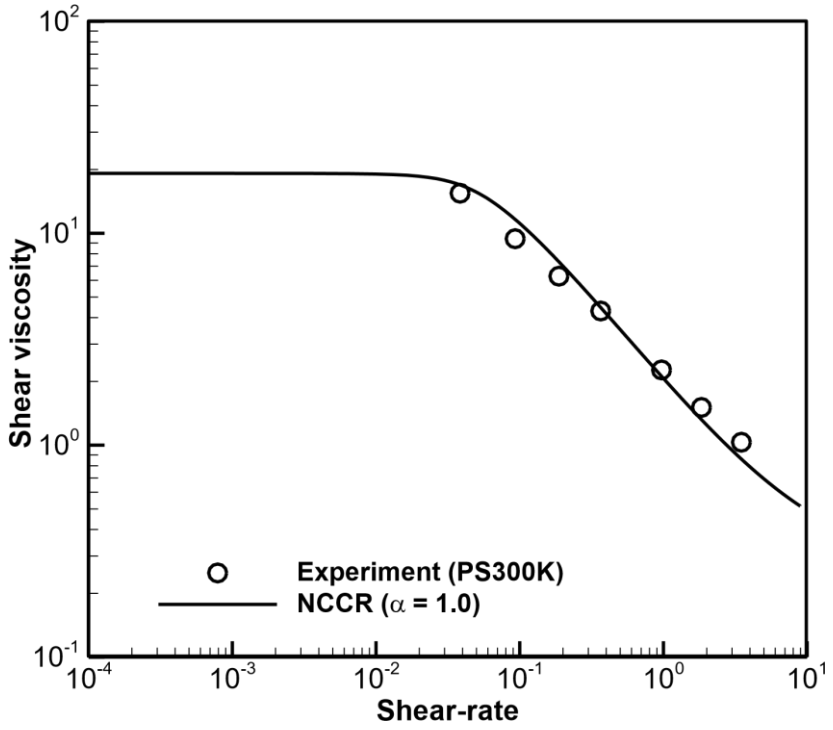


Fig. 4. Comparison of shear viscosity of "sinh" second-order NCCR model with the measured shear viscosity for varying shear rate.

B. Two-dimensional cylinder flow by implementing the new model in OpenFOAM

The numerical implementation of the sinh factor in the constitutive equations was found to be trivial. In the field of rheology, either discrete elastic-viscous stress splitting discontinuous Galerkin (DEVSS/DG) methods [74] or finite volume methods [30, 42] can be easily applied to the new model.

In particular, RheoTool [45, https://github.com/fppimenta/rheoTool], an open-source toolbox based on OpenFOAM®, has become readily available to researchers interested in simulating Newtonian and viscoelastic fluids since 2016. This study implements the newly derived non-Hookean term, $\boldsymbol{\tau}\, q_{2\mathrm{nd}}(\kappa_1)/\lambda$, in OpenFOAM®, in place of the Hookean term, $\boldsymbol{\tau}/\lambda$, in the Maxwell-Oldroyd model. It then analyzes viscoelastic flows around a confined cylinder and verifies its performance by comparing it with other models.

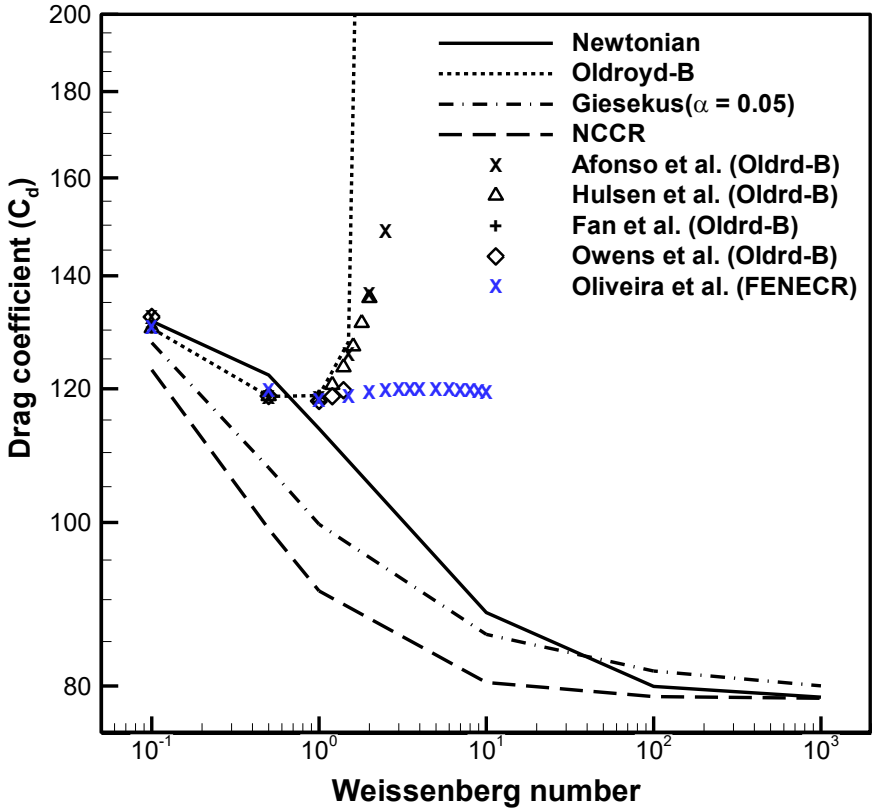


Fig. 5. Comparison of drag coefficients for Newtonian, Oldroyd-B, Giesekus (α=0.05), FENE-CR (Chilcott and Rallison), and second-order NCCR (α=1.0) models for varying Weissenberg numbers at a Reynolds number of 0.0001.

In Fig. 5, the drag coefficients of a cylinder are compared for several models [23, 41, 43, 75-77] for varying Weissenberg numbers at Reynolds number = 0.0001. While the Oldroyd-B model predicts an increase in drag coefficients from Wi=1.0, the new and Giesekus models predict a monotonic decrease in drag coefficients with increasing Weissenberg numbers. On the other hand, the FENE-CR (Chilcott and Rallison) model breaks down around Wi=10 in this viscoelastic flow around a confined cylinder, showing the difficulty in developing a robust model with a solid physical basis, suitable for all flow situations (including not only extensional flow but also contracting and shear flows) and all Weissenberg numbers.

Overall, the results based on OpenFOAM solvers indicate that the new model is free of the HWN problem (up to Wi=1,000, the maximum value considered) for this cylinder flow problem.

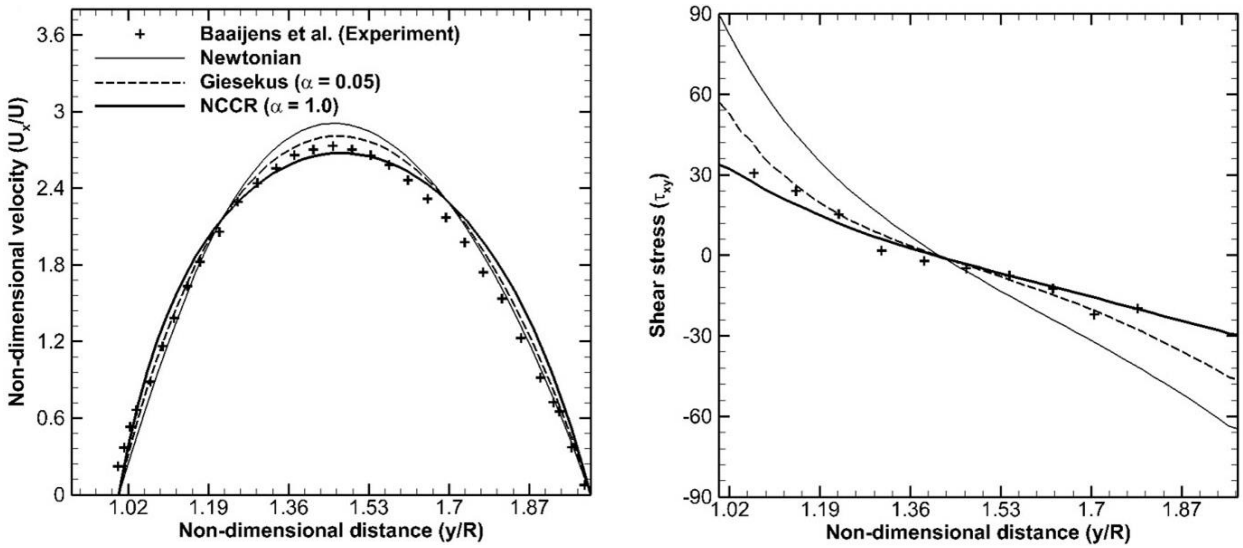


Fig. 6. Comparison of velocity profiles (left) and shear stress distributions (right) along the central line (x/R=0) for the measured data, Newtonian, Giesekus (α=0.05), and second-order NCCR (α=1.0) models, at Wi=0.216 and Re=0.0001.

In Fig. 6, velocity profiles and shear stress distributions along the central line for viscoelastic flows around a confined cylinder are compared for the conditions (Wi=0.216, Re=0.0001, and an extensional viscosity ratio of 0.865) considered in the experimental work of Baaijens et al. [78]. Broadly, the numerical solutions of the NCCR model are in good agreement with experimental data. The maximum velocity values in the present viscoelastic fluid flow are closely related to the shear-thinning properties of the constitutive equations, and the predictions of the new model are closer to experimental data than those of the Newtonian or Giesekus models. This shear-thinning property allows the new model to predict a more reduced shear stress distribution, resulting in better agreement with experimental data.

C. Relationship with existing phenomenological sinh-type models (Ree-Eyring's non-Newtonian and Johnson-Tevaarwerk's electrohydrodynamic), and other popular viscoelastic fluid models (Giesekus, PTT, FENE-P) for simple extensional and contracting flows

The nonlinear sinh models may be found from the viewpoint of phenomenology based on experimental observations. Indeed, such a model already exists, known in the literature as the hyperbolic sine law. The 'sinh' law was basically obtained from the macroscopic consideration, like the semi-empirical reaction rate theory of Eyring in 1936 [54], Ree-Eyring's constitutive model for the non-Newtonian flow of a solid plastic system in 1955 [55], or from best fit to experimental data, like Johnson-Tevaarwerk's constitutive model for the shear behavior of elastohydrodynamic lubrication in 1977-1979 [56, 57].

The Eyring's reaction rate theory [54] considers two neighboring layers of molecules sliding past each other with the perpendicular distance λ_1 ($\lambda_{2,3}$ being the molecule-to-molecule distance in the plane normal to the direction of motion). The shear motion is assumed to occur in a layer, acquiring the activation energy necessary to slip over the potential barrier to the next equilibrium position. The difference in velocity of these two layers ΔV is then proportional to the average distance λ between these equilibrium positions in the direction of motion and the difference in the number of times that a molecule moves in the forward or backward direction in a second, as follows

$$\Delta V = \lambda(k_f - k_b). \tag{3.7}$$

The number of times that a molecule moves in the forward or backward direction may be written as the corresponding specific reaction rate, respectively,

$$k_f = k_1 \exp\left(\frac{\tau}{\tau_1}\right),\ k_b = k_1 \exp\left(-\frac{\tau}{\tau_1}\right). \tag{3.8}$$

Here k_1 is the absolute rate for the transition, τ is the shear stress tending to displace the layer, and τ_1 is defined as $\tau_1 = k_B T / (\lambda_2 \lambda_3 \lambda / 2)$. In (3.8), the force acting on a single molecule is $\tau\lambda_2\lambda_3$, and it acts to lessen the work of passing over the barrier through a distance $\lambda/2$. Accordingly, in the forward direction, the height of the barrier is lowered by the amount $\tau\lambda_2\lambda_3\lambda/2$, while in the backward direction, it is increased by the same amount. Now the velocity difference reduces to

$$\Delta V = \lambda k_1 \left[\exp\left(\frac{\tau}{\tau_1}\right) - \exp\left(-\frac{\tau}{\tau_1}\right)\right] = 2\lambda k_1 \sinh\left(\frac{\tau}{\tau_1}\right). \tag{3.9}$$

From the relation $\Delta V = \dot{\gamma}\lambda_1$ where $\dot{\gamma}$ is the shear rate, Eyring's equation of shear rate can be written as

$$\dot{\gamma} = \frac{1}{\beta}\sinh\left(\frac{\tau}{\tau_1}\right) \text{ or } \tau = \tau_1 \sinh^{-1}(\beta\dot{\gamma}), \tag{3.10}$$

where $\beta = \lambda_1 / (2\lambda k_1)$. Using this relation together with $\tau = \mu_G \dot{\gamma}$, Ree and Eyring [55] obtained the following general expression of viscosity in the non-Newtonian flow of a solid plastic system

$$\mu_G = \tau_1 \beta \frac{\sinh^{-1}(\beta\dot{\gamma})}{\beta\dot{\gamma}}. \tag{3.11}$$

On the other hand, Johnson and Tevaarwerk [56, 57] applied Eyring's phenomenological sinh law to the elastohydrodynamic lubrication problem and demonstrated that the following simple sinh law fits the experimental data,

$$\frac{\mu}{G}\frac{D\boldsymbol{\tau}}{Dt}-\mu\left(\nabla\mathbf{u}^{T}+\nabla\mathbf{u}\right)=-\boldsymbol{\tau}q_{2\mathrm{nd}}\left(\frac{\sqrt{\boldsymbol{\tau}:\boldsymbol{\tau}}}{\tau_{1}}\right), \tag{3.12}$$

where a representative stress τ_1 —an ad-hoc value fit to experimental data—measures the level above which the fluid becomes appreciably nonlinear.

The constitutive equations of complex fluids can be expressed in the following general form:

$$\underset{\substack{\text{Time change}\\ \text{in Lagrangian}}}{\frac{D\boldsymbol{\tau}}{Dt}}+\underset{\substack{\text{High-}\\ \text{order}}}{\text{H.O.}}-\underset{\substack{\text{Stress-strain}\\ \text{rate coupling}\\ \text{(2nd-order)}}}{\left[(\nabla\mathbf{u})^{T}\boldsymbol{\tau}+\boldsymbol{\tau}\nabla\mathbf{u}\right]}-\underset{\substack{\text{Strain rate}\\ \text{(1st-order)}}}{\frac{\mu}{\lambda}(\nabla\mathbf{u}^{T}+\nabla\mathbf{u})}=\underset{\substack{\text{Interaction}\\ \text{(high-order)}}}{-\frac{1}{\lambda}\boldsymbol{\tau}q(\alpha,\lambda,\mu,T,\boldsymbol{\tau})}. \tag{3.13}$$

As explained in Subsection II-B, the balanced treatment of the two high-order terms in the left- and right-hand sides will lead to the closure $\text{H.O.}(\mathbf{rrr})\underset{\text{2nd}}{=}0$ and $\left\langle h^{(1)}C[f]\right\rangle_{\text{2nd}}=-\boldsymbol{\tau}q_{\text{2nd}}\left(\alpha\sqrt{\boldsymbol{\tau}:\boldsymbol{\tau}}/(\mu/\lambda)\right)\Big/\lambda$.

The validity of the theoretically-derived sinh factor given in (2.21) can be demonstrated by comparing it with the phenomenological sinh laws—best fit to experimental data—in Ree-Eyring's model in rheology [55] and the Johnson-Tevaarwerk model in elastohydrodynamic lubrication [56, 57] based on Ree-Eyring's model. Interestingly, there is a parallelism, $G=\mu/\lambda,\ \tau_1/G=1/\alpha$, in interaction terms between this model and the new model (2.21). The only difference is that the parameter τ_1 is an ad-hoc value fit to experimental data, while the parameter α in the new theoretical model is a macromolecular-dependent softening parameter with physical meaning at a molecular level, defined as (2.22).

The relationship of the new model with the Maxwell-Oldroyd viscoelastic model can also be identified: $-\boldsymbol{\tau}q_{\text{2nd}}(\kappa_1)/\lambda$ versus $-\boldsymbol{\tau}/\lambda$. If one accepts the balanced closure of open high-order kinematic and interacting terms, the 3rd-order closure for cumulant expansion $\kappa_1\sinh\left[\kappa_1-\left(\kappa_2/\kappa_1+\kappa_1^2\right)\Big/2\right]$ in (C.15) is not necessary, since the polymer viscoelastic stress is a 2nd-order moment, and the corresponding balanced closure should be H.O.(**rrr**)=0 and $q_{\text{2nd}}(\kappa_1)$, rather than H.O.(**rrr**)=0 and $q_{\text{3rd}}(\kappa_1,\kappa_2)$. However, because more terms will improve the accuracy in the Taylor series expansion of the q_{2nd} term,

$$q_{2nd}(x)=\frac{\sinh x}{x}=1+\frac{1}{3!}x^2+\frac{1}{5!}x^4+\cdots, \tag{3.14}$$

the following form may be more accurate than the Maxwell-Oldroyd and can reduce the appearance of the HWN problem substantially

$$-\frac{1}{\lambda}\boldsymbol{\tau}q_{\text{2nd-cumulant}}\left(\alpha\sqrt{\hat{\boldsymbol{\tau}}:\hat{\boldsymbol{\tau}}}\right)\underset{\text{3rd-Taylor}}{=}-\frac{1}{\lambda}\boldsymbol{\tau}\left(1+\alpha^2\frac{1}{3!}\hat{\boldsymbol{\tau}}:\hat{\boldsymbol{\tau}}\right),\ \text{where}\ \ \hat{\boldsymbol{\tau}}\equiv\frac{\boldsymbol{\tau}}{\mu/\lambda}. \tag{3.15}$$

Note that $q_{2nd}(x)$ is isotropic and does not contain any odd-order terms in x.

There are many popular models in rheology: for example, Giesekus [7,38], Phan-Thien-Tanner (PTT) [8], and FENE-P [39]. All of these models were developed based on sophisticated considerations of both the physical and theoretical aspects of complex fluids. Therefore, a direct comparison with the present model, developed based on the simple dumbbell model, is not straightforward. However, as mentioned in the Introduction, given that the macroscopic properties of polymers can be determined by several large-scale properties of the polymer molecules, it is possible to compare various models for simple one-dimensional contracting and extensional flow in a qualitative way.

The steady-state dimensionless version of (2.21) can be rewritten as ($\hat{\tau}_0$ denoting the dimensionless strain rate; $\hat{\tau}$ denoting $\hat{\tau}_{xx}$; $\hat{\tau}\equiv\tau/(\mu/\lambda)$),

$$-\hat{\tau}\hat{\tau}_0-\hat{\tau}_0=-\hat{\tau}q(\alpha\hat{\tau})\ \ \text{from}\ \ -\left[(\nabla\mathbf{u})^T\boldsymbol{\tau}+\boldsymbol{\tau}\nabla\mathbf{u}\right]-\frac{\mu}{\lambda}(\nabla\mathbf{u}^T+\nabla\mathbf{u})=-\frac{1}{\lambda}\boldsymbol{\tau}q(\alpha,\lambda,\mu,T,\boldsymbol{\tau}). \tag{3.16}$$

The nonlinear factors $q(\alpha\hat{\tau})$ in the interaction terms $-\hat{\tau}q(\alpha\hat{\tau})$ are reduced as, in order of the new model, Giesekus, PTT, and FENE-P

$$\frac{e^{\alpha\hat{\tau}}-e^{-\alpha\hat{\tau}}}{2\alpha\hat{\tau}};\ 1+\alpha\hat{\tau};\ e^{\alpha\hat{\tau}};\ 1+\frac{3}{b}\left(1+\alpha\hat{\tau}\right). \tag{3.17}$$

In the case of Ree and Eyring's phenomenological non-Newtonian model [55], from the non-Newtonian version of (3.16) $-\hat{\tau}_0=-\hat{\tau}q_{2nd}(\alpha\hat{\tau})$—which can be derived by ignoring the stress and strain rate coupling term $-\hat{\tau}\hat{\tau}_0$—the constitutive relation can be expressed as

$$\hat{\tau}=\frac{1}{\alpha}\sinh^{-1}\left(\alpha\hat{\tau}_0\right). \tag{3.18}$$

This is a second-order non-Hookean spring model for non-Newtonian fluids, and its full tensorial form can be written as

$$\hat{\boldsymbol{\tau}} = \frac{\sinh^{-1}\left(\alpha\sqrt{\hat{\boldsymbol{\tau}}_0 : \hat{\boldsymbol{\tau}}_0}\right)}{\alpha\sqrt{\hat{\boldsymbol{\tau}}_0 : \hat{\boldsymbol{\tau}}_0}}\hat{\boldsymbol{\tau}}_0 \text{ where } \hat{\boldsymbol{\tau}}_0 \equiv \lambda(\nabla\mathbf{u}^T + \nabla\mathbf{u}) . \tag{3.19}$$

The characteristics of the new model and its comparison with other popular models in this simplified one-dimensional steady-state condition are summarized in Fig. 7. The most distinctive feature of the new model is *the extensional thickening with increasing strain rate, followed by an extensional thinning region*. This feature, made possible by a subtle interplay between the stress-strain rate coupling $\hat{\tau}\hat{\tau}_0$ and interaction (or dissipation) $\hat{\tau}q_{2nd}(\alpha\hat{\tau})$, was believed to be the essence of many phenomenological observations in the past [72, 77, 79], including in the experimental data used in Fig. 3 of the extensional viscosity obtained by Barnes et al. [72] and Ballman [73]. As shown in Fig. 7 (a), although the range of extensional thickening varies, increasing at small α and decreasing at large α, this trend remains generic for all values of α ($0 < \alpha < \infty$) in the new model, allowing it to encompass a much wider range of viscoelastic fluids with a single softening parameter derived from molecular and thermodynamic considerations.

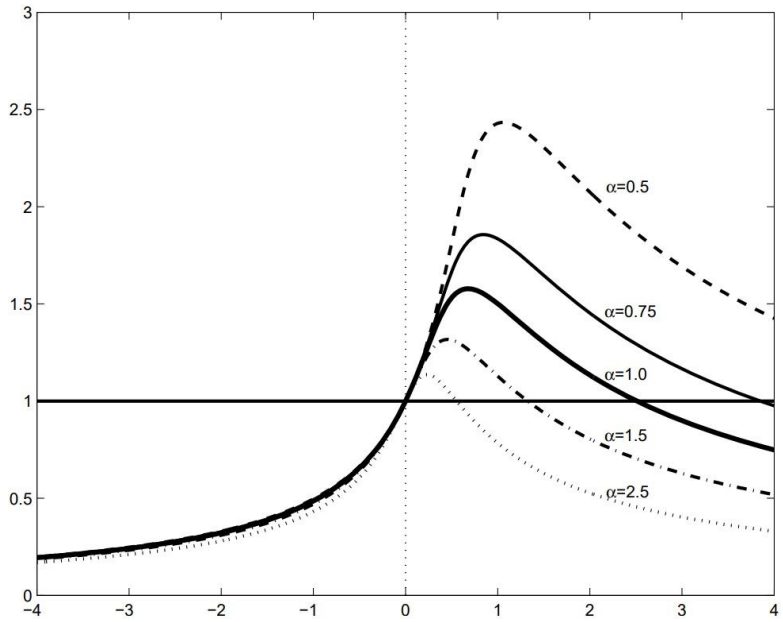
Meanwhile, as discussed in Subsection III-A, for very large strain rates, the $\exp(\alpha|\hat{\tau}|)$ term in the dissipative term $\hat{\tau}q_{2nd}(\alpha\hat{\tau})$ becomes dominant, ultimately resulting in logarithmic asymptotic behavior. Therefore, for very large values of α, the asymptotic behavior is again extensional thinning, but the range of extensional thickening becomes very large, making the new model much closer to other models such as FENE-P, as shown in Fig. 7 (b).

Interestingly, the PTT model also predicts a similar trend, as shown in Fig. 7 (b). Indeed, the new model shares the same qualitative feature with the PTT model (α=0.25). In contrast, some existing models, such as Maxwell-Oldroyd and Giesekus with α=0.5, predict extensional thickening only in this simple flow problem.

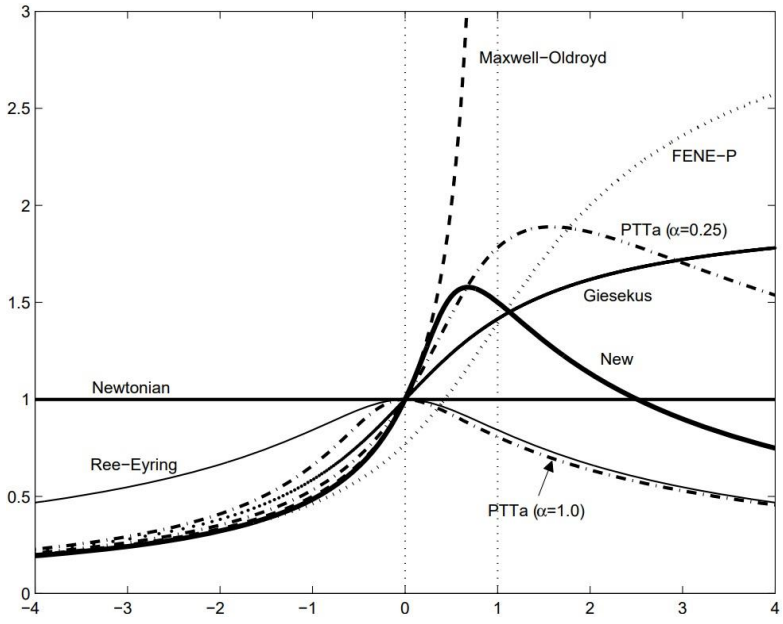
However, the present preliminary results are based on such an oversimplified flow problem (3.16) and a limited number of cases selected from a large pool of adjustable parameters α (and additional b for FENE-P). For example, recent studies [80-83] reported an excellent agreement with experimental data that exhibit the extensional thickening with increasing strain rate, followed by extensional thinning, by additionally taking the flow-induced reduction of the friction coefficient into account in the FENE-PM (Peterlin multimode) model.

Thus, careful consideration and more rigorous analysis will be needed in the future to evaluate the performance of various models thoroughly.

On the other hand, in the contracting flow, all models show essentially the same trend with no exception: contracting thinning.



(a) $\hat{\tau}/\hat{\tau}_0$ in function of $\hat{\tau}_0$



(b) $\hat{\tau}/\hat{\tau}_0$ in function of $\hat{\tau}_0$

Fig. 7. (a) Effect of different α on the extensional ($0 < \hat{\tau}_0$) and contracting ($\hat{\tau}_0 < 0$) viscosity in the NCCR model, (b) comparison with other models: Maxwell-Oldroyd, new (α=1.0), non-Newtonian Ree-Eyring (α=1.0), Giesekus (α=0.5), Phan-Thien-Tanner (PTTa) (α=0.25, 1.0), FENE-P with b=10 (α=1.0). The horizontal and vertical axes represent the strain (force) term $\hat{\tau}_0$ and the normal stress $\hat{\tau}$, respectively.

D. Strictly traceless constitutive equation of the viscoelastic stress

If we accept the following relation noted by Bird et al. [59, p. 16],

$$nk_BT = \frac{1}{3}S_0\left\langle r^2 f^{(eq)}\right\rangle, \tag{3.20}$$

the viscoelastic stress tensor defined in (2.12) becomes a strictly traceless tensor as follows:

$$\boldsymbol{\tau} = S_0\left\langle \mathbf{r}\mathbf{r}f\right\rangle - \frac{1}{3}S_0\left\langle \mathrm{Tr}(\mathbf{r}\mathbf{r})f\right\rangle\mathbf{I} \equiv S_0\left\langle [\mathbf{r}\mathbf{r}]^{(2)}f\right\rangle, \tag{3.21}$$

where the symbol $[\ ]^{(2)}$ stands for a traceless symmetric part of the tensor. By applying the traceless operator to both the left and right sides of the following second-order FP-*m*Boltzmann constitutive equations,

$$\frac{\partial\left\langle \mathbf{r}\mathbf{r}f\right\rangle}{\partial t} - \left[(\nabla\mathbf{u})^T\left\langle \mathbf{r}\mathbf{r}f\right\rangle + \left\langle \mathbf{r}\mathbf{r}f\right\rangle\nabla\mathbf{u}\right] - \frac{4nk_BT}{\varsigma}\mathbf{I} = \left\langle \mathbf{r}\mathbf{r}C\left[f\right]\right\rangle_{2nd}, \tag{3.22}$$

we can derive

$$\begin{aligned}
&\frac{D\boldsymbol{\tau}}{Dt} - \left[(\nabla\mathbf{u})^T\boldsymbol{\tau} + \boldsymbol{\tau}\nabla\mathbf{u}\right] + \frac{2}{3}\mathrm{Tr}(\boldsymbol{\tau}\cdot\nabla\mathbf{u})\mathbf{I} - \frac{\mu}{\lambda}(\nabla\mathbf{u}^T + \nabla\mathbf{u}) = -\frac{1}{\lambda}\boldsymbol{\tau}q_{2\mathrm{nd}}(\kappa_1),\\
&\text{or}\\
&\frac{D\boldsymbol{\tau}}{Dt} - 2\left[\boldsymbol{\tau}\cdot\nabla\mathbf{u}\right]^{(2)} - 2\frac{\mu}{\lambda}\left[\nabla\mathbf{u}\right]^{(2)} = -\frac{1}{\lambda}\boldsymbol{\tau}q_{2\mathrm{nd}}(\kappa_1),\\
&\text{or}\\
&\frac{D\mathbf{C}}{Dt} - 2\left[\mathbf{C}\cdot\nabla\mathbf{u}\right]^{(2)} = -\frac{1}{\lambda}(\mathbf{C}-\mathbf{I})q_{2\mathrm{nd}}\left(\alpha\sqrt{(\mathbf{C}-\mathbf{I}):(\mathbf{C}-\mathbf{I})}\right).
\end{aligned} \tag{3.23}$$

During the derivation, the upper-convective derivative and two identities— $2\left[\nabla\mathbf{u}\right]^{(2)} = (\nabla\mathbf{u}^T + \nabla\mathbf{u})$ and $\mathrm{Tr}(\mathbf{I}\cdot\nabla\mathbf{u})\mathbf{I} = \mathbf{0}$ from the incompressible assumption $\nabla\cdot\mathbf{u} = 0$ —are used. Note that there is a new term $2\mathrm{Tr}(\boldsymbol{\tau}\cdot\nabla\mathbf{u})\mathbf{I}/3$ in the strictly traceless constitutive equation.

The difference between the strictly traceless form (3.23) and the conventional form (2.21) is minor in general, but it brings an interesting result in the case of shear flow, which was considered for the conventional form in Subsection III-A.

At steady-state, the components of the viscoelastic stress tensor can be written for shear flow from (3.23) as follows,

$$\begin{aligned}
\tau_{11} q_{2\mathrm{nd}}(\kappa_1) &= 2\lambda\dot{\gamma}\tau_{12} \underline{-\frac{2}{3}\lambda\dot{\gamma}\tau_{12}}, \\
\tau_{22} q_{2\mathrm{nd}}(\kappa_1) &= \underline{-\frac{2}{3}\lambda\dot{\gamma}\tau_{12}}, \\
\tau_{33} q_{2\mathrm{nd}}(\kappa_1) &= \underline{-\frac{2}{3}\lambda\dot{\gamma}\tau_{12}}, \\
\tau_{12} q_{2\mathrm{nd}}(\kappa_1) &= \lambda\dot{\gamma}\tau_{22} + \mu\dot{\gamma},
\end{aligned} \tag{3.24}$$

where the underlined terms come from the new term. Note that the normal stresses $\tau_{22,33}$ do not vanish anymore. From (3.24), the dissipation function of the traceless viscoelastic stress is then reduced to $\kappa_1 = \alpha\sqrt{3\tau_{11}^2/2 + 2\tau_{12}^2}\,\big/(\mu/\lambda)$. In addition, we can show the existence of a common stress constraint of an elliptic type $-2\tau_{12}^2/3 = \tau_{22}(\mu/\lambda + \tau_{22})$. As a result, we have the following shear viscosity relation and finite first and vanishing second normal differences,

$$\begin{aligned}
\eta_S &\equiv \frac{\tau_{12}}{\dot{\gamma}} = \frac{\mu}{q_{2\mathrm{nd}}(\kappa_1)}\left(1 + \frac{\tau_{22}}{\mu/\lambda}\right), \\
N_1 &\equiv \frac{\tau_{11} - \tau_{22}}{\dot{\gamma}} = \frac{3\tau_{11}}{2\dot{\gamma}} = \frac{2\lambda\tau_{12}}{q_{2\mathrm{nd}}(\kappa_1)}, \\
N_2 &\equiv \frac{\tau_{22} - \tau_{33}}{\dot{\gamma}} = 0.
\end{aligned} \tag{3.25}$$

E. Computational stability of the NCCR model based on the planar stability theory of autonomous dynamical systems

The mathematical characteristics of the new viscoelastic constitutive equations can be further investigated with the help of the planar stability theory of autonomous dynamical systems [84-86, 87, Chap. 3]. For this purpose, (3.23) can be rewritten as

$$\begin{aligned}
&\lambda\frac{D\boldsymbol{\tau}}{Dt} = \boldsymbol{\tau}_0 - f(\boldsymbol{\tau}) \text{ where } \boldsymbol{\tau}_0 \equiv \mu(\nabla\mathbf{u}^T + \nabla\mathbf{u}), \\
&f(\boldsymbol{\tau}) \equiv \boldsymbol{\tau} q_{2\mathrm{nd}}(\kappa_1) - \lambda\left\{\left[(\nabla\mathbf{u})^T\boldsymbol{\tau} + \boldsymbol{\tau}\nabla\mathbf{u}\right] - \frac{2}{3}\mathrm{Tr}(\boldsymbol{\tau}\cdot\nabla\mathbf{u})\mathbf{I}\right\}.
\end{aligned} \tag{3.26}$$

If the tensor $\boldsymbol{\tau}$ is essentially described by two components in simple situations, for example, (τ_{11}, τ_{12}), (3.26) may be regarded as an autonomous planar dynamical system as follows,

$$\lambda \frac{D}{Dt}\begin{bmatrix}\tau_{11}\\ \tau_{12}\end{bmatrix}=\begin{bmatrix}\tau_{11_0}-f_1(\boldsymbol{\tau})\\ \tau_{12_0}-f_2(\boldsymbol{\tau})\end{bmatrix}. \tag{3.27}$$

The evolution (stable or unstable) of (τ_{11},τ_{12})—the stability of an initial value in computations—will then be determined by *the planar stability theory on the phase portrait*. For a Jacobian matrix **A** defined as

$$\mathbf{A}=(-)\begin{bmatrix}\partial f_1/\partial\tau_{11} & \partial f_1/\partial\tau_{12}\\ \partial f_2/\partial\tau_{11} & \partial f_2/\partial\tau_{12}\end{bmatrix}_{\boldsymbol{\tau}=f^{-1}(\boldsymbol{\tau}_0)}, \tag{3.28}$$

the planar stability theory requires that the system under consideration be stable if Tr(**A**)<0 and Det(**A**)>0.

In the case of the uniaxial extensional and contracting flows with a velocity field $\mathbf{u}=(\dot{\varepsilon}x,-\dot{\varepsilon}y/2,-\dot{\varepsilon}z/2)$, the dynamical systems (3.26) and (3.27) are simplified into

$$\lambda \frac{D}{Dt}\begin{bmatrix}\tau_{11}\\ \tau_{12}\end{bmatrix}=\begin{bmatrix}2\mu\dot{\varepsilon}-\left(q_{2\mathrm{nd}}(\kappa_1)-\lambda\dot{\varepsilon}\right)\tau_{11}\\ -\left(q_{2\mathrm{nd}}(\kappa_1)-\frac{1}{2}\lambda\dot{\varepsilon}\right)\tau_{12}\end{bmatrix}. \tag{3.29}$$

The corresponding Jacobian matrix becomes

$$\begin{aligned}\mathbf{A}&=\begin{bmatrix}\lambda\dot{\varepsilon}-q_{2\mathrm{nd}}(\kappa_1)-\tau_{11}\dfrac{\partial q_{2nd}(\kappa_1)}{\partial\tau_{11}} & 0\\ -\tau_{12}\dfrac{\partial q_{2nd}(\kappa_1)}{\partial\tau_{12}} & \dfrac{1}{2}\lambda\dot{\varepsilon}-q_{2\mathrm{nd}}(\kappa_1)\end{bmatrix}_{\boldsymbol{\tau}=f^{-1}(\boldsymbol{\tau}_0)}\\ &=\begin{bmatrix}\lambda\dot{\varepsilon}-q_{2\mathrm{nd}}(\kappa_1)-\tau_{11}\dfrac{dq_{2\mathrm{nd}}(\kappa_1)}{d\tau_{11}} & 0\\ 0 & \dfrac{1}{2}\lambda\dot{\varepsilon}-q_{2\mathrm{nd}}(\kappa_1)\end{bmatrix},\end{aligned} \tag{3.30}$$

where $\kappa_1=\alpha\sqrt{3\tau_{11}^2/2}\big/(\mu/\lambda)$, $\tau_{12}=0$ obtained from $\boldsymbol{\tau}=f^{-1}(\boldsymbol{\tau}_0)$ have been applied to the second identity.

This system is always stable because the following relations satisfy the stability conditions Tr(**A**)<0 and Det(**A**)>0 for all extensional and contracting rates $\dot{\varepsilon}$ and all positive values of the softening parameter α,

$$\begin{aligned}\mathrm{Tr}(\mathbf{A})&=\frac{3}{2}\lambda\dot{\varepsilon}-2q_{2nd}(\kappa_1)-\tau_{11}\frac{dq_{2nd}(\kappa_1)}{d\tau_{11}},\\ \mathrm{Det}(\mathbf{A})&=\left[\lambda\dot{\varepsilon}-q_{2\mathrm{nd}}(\kappa_1)-\tau_{11}\frac{dq_{2\mathrm{nd}}(\kappa_1)}{d\tau_{11}}\right]\left[\frac{1}{2}\lambda\dot{\varepsilon}-q_{2\mathrm{nd}}(\kappa_1)\right],\end{aligned} \tag{3.31}$$

by the relations

$$q_{2\mathrm{nd}}(\kappa_1)-\lambda\dot{\varepsilon}=\frac{2\mu\dot{\varepsilon}}{\tau_{11}}>0 \text{ and } \tau_{11}\frac{dq_{2nd}(\kappa_1)}{d\tau_{11}}>0. \tag{3.32}$$

This means that the systems (3.23) or (3.26) always provide a stable, steady-state solution for an initial value in computations in the case of the uniaxial extensional and contracting flows.

IV. CONCLUDING REMARKS

The primary goal of the work was to present a theoretical viscoelastic constitutive equation starting from a master Fokker-Planck kinetic equation with a new Boltzmann-type non-Hookean spring force model. Since its initial heuristic form was first presented in an oral presentation in 2012 [88], the present theory and associated constitutive model have undergone several major conceptual revisions. These include the development of a Boltzmann gain-loss-based non-Hookean spring model and associated kinetic equation (FP-*m*Boltzmann), the theoretical derivation of the dissipation term up to the second order via the second law of thermodynamics (i.e., the non-equilibrium entropy production) and the cumulant expansion-based balanced closure, the derivation of a non-negative non-equilibrium distribution function in the exponential form, and the identification of similarities and differences with the Yamamoto reformation-breakage-based network model.

However, considering the availability of numerous popular models for viscoelastic fluids, many of which have passed extensive experimental validation and numerical verification, adding yet another model would be a reckless and pointless endeavor.

Nevertheless, this new model offers significant theoretical novelty, as it starts from a new perspective based on the Boltzmann 1872 concept of probability and gain-loss, the second law of thermodynamics, and the balanced closure based on the cumulant expansion (rather than the polynomial expansion), which ensures the non-negativity of the non-equilibrium distribution function, regardless of order of closure. Because the new theory provides the non-equilibrium distribution function in the configuration space and rigorous physical meaning to the softening parameter from molecular and thermodynamic perspectives, it opens up the possibility of experimentally measuring the stiffness of macromolecules and improving our understanding of viscoelastic fluids based on the bridge between the macroscopic and microscopic worlds. In addition, while the adjustable parameters in most of the existing methods are valid within a limited range (for example, the Giesekus model is valid only for $0<\alpha<1$), the new theory is valid for all values of α ($0<\alpha<\infty$), enabling a single adjustable parameter with microscopic physical meaning to encompass a much wider range of viscoelastic fluids and flow situations.

Furthermore, its validity can be readily tested nowadays on multidimensional benchmark problems using powerful computational tools, such as OpenFOAM—RheoTool. Taking these factors into account, this study presented a Boltzmann-based non-Hookean spring model and an associated sinh-type NCCR model for viscoelastic fluids, whose validity can now be tested by any researcher in the field with minimal effort by simply implementing a nonlinear factor, $q_{2\mathrm{nd}}\left(\alpha\sqrt{\boldsymbol{\tau}:\boldsymbol{\tau}}/(\mu/\lambda)\right)$, in OpenFOAM or an in-house solver.

Preliminary results based on OpenFOAM solvers indicated that 1) the sinh model is free of the HWN problem for the two-dimensional flow over a confined cylinder up to Wi=1,000, the maximum value considered; 2) it correctly describes the die swell (also known as Barus) effect in the free-surface problem, which will be presented in detail in forthcoming articles [89].

Additionally, the well-known 1955 Ree-Eyring phenomenological law in rheology and the Johnson-Tevaarwerk model in elastohydrodynamic lubrication were shown to be theoretically derivable from the molecular-level description via a probabilistic Boltzmann-type non-Hookean spring force model of gain and loss interaction, together with application of the second law of thermodynamics and cumulant expansion. Thus, a theoretical support of the sinh law is now provided not only for non-Newtonian fluids but also for elastohydrodynamic lubrication.

Meanwhile, without relying on a complicated mathematical derivation based on the second law of thermodynamics and cumulant expansion-based balanced closure, the sinh-type NCCR model can also be derived heuristically from physical insight only. Based on Ree and Eyring's forward and backward concept, required when describing the velocity difference in two neighboring layers of molecules sliding past each other (explained in Subsection III-C), the hyperbolic sine function can be derived from the difference in the number of times a molecule moves forward or backward, which is proportional to the corresponding reaction rate in exponential form.

Likewise, from the Boltzmann concept of gain and loss, the net change in the number of dumbbells can be described heuristically based on gain minus loss, that is, $\exp^{(\mathrm{dissipation})} - \exp^{(-\mathrm{dissipation})}$, so that the leading term of dissipation becomes the hyperbolic sine function.

The present study has been limited to a simple dumbbell model with two beads for simplicity and historical significance in the development of rheological theory. However, this author believes that, owing to the universal

nature of the interaction term based on the gain-and-loss concept, basically the same rationale may be carried over to more complex fluids. From the same perspective, there are striking similarities between the present dumbbell model for viscoelastic fluids and the Boltzmann gas kinetic model, to which his gain-loss concept was first applied. Exploring the similarities and differences between the two models would be an interesting topic.

This theoretical study proposed an adjustable softening parameter that depends on macromolecular property, but did not investigate its effect in detail. In addition, the new model has been applied to two-dimensional flow over a confined cylinder only. It would be interesting to apply it to more complicated flow problems [90-95], such as three-dimensional flow over a sphere and free-surface flows where Weissenberg rod-climbing and die swell (also known as Barus) effects are important. It would also be interesting to investigate the effect of the sinh-type dissipation term on elastic turbulent flows [96, 97] driven by the nonlinear elastic stresses generated by polymers stretched by the flow at the high Weissenberg number above the elastic instability. I hope to report progress on extending the present model to these topics in due course.

ACKNOWLEDGMENTS

This work was supported by the National Research Foundation of Korea (NRF) Grant funded by the Ministry of Science and ICT (RS-2024-00397400), Republic of Korea. The author gratefully acknowledges the help of Dr. Tushar Chourushi, a former graduate student, for producing Figures 3-6. The author expresses sincere gratitude to his colleague, Professor Wook Ryol Hwang (Gyeongsang National University), for introducing him to the high Weissenberg number problem in 2010, which provided a crucial gateway to the study of viscoelastic fluids. The author thanks the reviewers of this article for their valuable and helpful comments.

AUTHOR DECLARATIONS

Conflict of Interest

The author has no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon request.

Appendix A: Cumulant expansion specialized for non-negative probability functions

Fisher [98] used the term "cumulative moment function" in 1929 for what is now known as the cumulant-generating function. The cumulant expansion based on the cumulant-generating function may be regarded as a partial re-summation of the expansion of the interaction term in a series of the parameter Wi, and thus it takes into account highly nonlinear irreversible processes to higher accuracy. It is the expansion method specialized for probability functions $f(x)$ which have the unique properties: 1) it is non-negative, $f(x) \geq 0$ for all x; 2) its area integral is unity, $\int_{-\infty}^{\infty} f(x)dx = 1$; and 3) the value vanishes as x goes to infinity, $\lim_{x \to \pm\infty} f(x) \to 0$.

Let $p(x)$ be the probability distribution of x. The l-th moment of this probability distribution is defined as the expectation value of x^l:

$$\left\langle x^l \right\rangle = \int x^l p(x)dx \,, \tag{A.1}$$

and the moment-generated function as the expectation value of e^{ax}

$$\left\langle e^{ax} \right\rangle = \int e^{ax} p(x)dx \,. \tag{A.2}$$

The following relations hold for the power series and derivatives:

$$\left\langle e^{ax} \right\rangle = \sum_{l=0}^{\infty} \frac{a^l}{l!} \int p(x)x^l dx = \sum_{l=0}^{\infty} \frac{a^l}{l!} \left\langle x^l \right\rangle \quad \text{or} \quad \left\langle x^l \right\rangle = \left[\frac{d^l}{da^l} \left\langle e^{ax} \right\rangle \right]_{a=0} . \tag{A.3}$$

The logarithm of the characteristic function is called the cumulant-generating function, and its series coefficients $\kappa_l^{(+)}$ in the Taylor expansion for a are called cumulants of the variable x:

$$\ln \left\langle e^{ax} \right\rangle = \sum_{l=0}^{\infty} \frac{a^l}{l!} \kappa_l^{(+)} \quad \text{or} \quad \kappa_l^{(+)} = \left[\frac{d^l}{da^l} \ln \left\langle e^{ax} \right\rangle \right]_{a=0} . \tag{A.4}$$

Expressions for cumulants in terms of moments may be obtained directly from the definition and equation (A.3), for example:

$$\begin{aligned} \kappa_1^{(+)} &= \left[\frac{d}{da} \ln \left\langle e^{ax} \right\rangle \right]_{a=0} = \left[\frac{1}{\left\langle e^{ax} \right\rangle} \frac{d}{da} \left\langle e^{ax} \right\rangle \right]_{a=0} = \left[\frac{d}{da} \left\langle e^{ax} \right\rangle \right]_{a=0} = \left\langle x \right\rangle, \\ \kappa_2^{(+)} &= \left[\frac{d^2}{da^2} \ln \left\langle e^{ax} \right\rangle \right]_{a=0} = \left[-\frac{1}{\left\langle e^{ax} \right\rangle^2} \left(\frac{d}{da} \left\langle e^{ax} \right\rangle \right)^2 + \frac{1}{\left\langle e^{ax} \right\rangle} \frac{d^2}{da^2} \left\langle e^{ax} \right\rangle \right]_{a=0} = \left\langle x^2 \right\rangle - \left\langle x \right\rangle^2, \quad \cdots. \end{aligned} \tag{A.5}$$

It should be noted that $\left\langle e^{ax}\right\rangle =1$ for $a=0$. Then the relationship between moments and cumulants may be summarized as follows:

$$\left\langle e^{ax}\right\rangle =\sum_{l=0}^{\infty}\frac{a^l}{l!}\left\langle x^l\right\rangle =\exp\left[\sum_{l=1}^{\infty}\frac{a^l}{l!}\kappa_l^{(+)}\right]. \tag{A.6}$$

Appendix B: Cumulant expansion versus polynomial expansion

The essential difference between the cumulant and polynomial expansions may be highlighted by considering a simple exponential function. From (A.6) with setting $a=1$, the polynomial expansion is written as

$$\left\langle e^{x}\right\rangle_{\text{polynomial}} =1+\left\langle x\right\rangle+\frac{1}{2!}\left\langle x^2\right\rangle+\frac{1}{3!}\left\langle x^3\right\rangle+\cdots, \tag{B.1}$$

while the cumulant expansion is written as

$$\left\langle e^{x}\right\rangle_{\text{cumulant}} =e^{\left[\kappa_1+\frac{1}{2!}\kappa_2+\frac{1}{3!}\kappa_3+\cdots\right]} =e^{\left[\langle x\rangle+\frac{1}{2!}\left(\left\langle x^2\right\rangle-\langle x\rangle^2\right)+\cdots\right]}. \tag{B.2}$$

Then relationships between the post- and pre-values can be expressed as

$$\begin{aligned}
&\frac{1}{2}\left(\left\langle e^{x}\right\rangle-\left\langle e^{-x}\right\rangle\right)\Big]_{\text{polynomial}} =\left\langle x\right\rangle+\frac{1}{3}\left\langle x^3\right\rangle+\cdots \underset{\text{2nd}}{=}\left\langle x\right\rangle,\\
&\frac{1}{2}\left(\left\langle e^{x}\right\rangle-\left\langle e^{-x}\right\rangle\right)\Big]_{\text{cumulant}} =e^{\left(\frac{1}{2!}\left(\left\langle x^2\right\rangle-\langle x\rangle^2\right)+\cdots\right)}\frac{1}{2}\left[e^{\left(\langle x\rangle+\cdots\right)}-e^{\left(-\langle x\rangle+\cdots\right)}\right]\underset{\text{2nd}}{=}\sinh\left\langle x\right\rangle.
\end{aligned} \tag{B.3}$$

Therefore, the ratio of the cumulant expansion to the polynomial expansion becomes

$$\frac{\frac{1}{2}\left(\left\langle e^{x}\right\rangle-\left\langle e^{-x}\right\rangle\right)\Big]_{\text{cumulant}}}{\frac{1}{2}\left(\left\langle e^{x}\right\rangle-\left\langle e^{-x}\right\rangle\right)\Big]_{\text{polynomial}}}\underset{\text{2nd}}{=}\frac{\sinh\left\langle x\right\rangle}{\left\langle x\right\rangle}=1+\frac{1}{3!}\left\langle x\right\rangle^2+\frac{1}{5!}\left\langle x\right\rangle^4+\cdots. \tag{B.4}$$

This factor will remain essential for all the interaction systems based on the gain-and-loss concept.

Appendix C: Derivation of sinh-type dissipation term via second law of thermodynamics and cumulant expansion

With further introduction of notations and dimensionless variables (*y* being the post-interaction value of *x*; *n* being the number density; *l* being a characteristic macromolecular length),

$$\bar{\sigma}_{ne}=\frac{\sigma_{ne}}{k_B/g},\ g=\frac{\lambda}{nl^3}\left(\frac{2k_BT}{S_0}\right)^{3/2},\ \bar{\mathbf{r}}=\mathbf{r}\sqrt{\frac{S_0}{k_BT}},\ \langle A\rangle_{ne}\equiv\left\langle f^{(eq)}A(\bar{\mathbf{r}})\right\rangle, \tag{C.1}$$

the non-equilibrium entropy production can be expressed as

$$\begin{aligned}\sigma_{ne}&=-k_B\langle \ln f\ C[f]\rangle=\frac{1}{T}\left\langle\left[\frac{1}{2}S_0r^2+\sum_{n=1}^{\infty}X^{(n)}:h^{(n)}-N\right]C[f^{(eq)}\exp(-x)]\right\rangle\\&=\frac{1}{4T\lambda}\left\langle f^{(eq)}(x-y)\left[\exp(-y)-\exp(-x)\right]\right\rangle,\end{aligned} \tag{C.2}$$

or

$$\bar{\sigma}_{ne}=\frac{1}{4}\left\langle(x-y)\left[\exp(-y)-\exp(-x)\right]\right\rangle_{ne}. \tag{C.3}$$

This form of mathematical equation is suitable for cumulant expansion. It can further be cast into

$$\begin{aligned}&\bar{\sigma}_{ne}=\frac{1}{4}\left[R^{(+)}(a)-R^{(-)}(a)\right]_{a=1},\\&R^{(+)}(a)\equiv\left\langle(x-y)\left[\exp(-ay)-1\right]\right\rangle_{ne},\ R^{(-)}(a)\equiv\left\langle(x-y)\left[\exp(-ax)-1\right]\right\rangle_{ne}.\end{aligned} \tag{C.4}$$

Here, the parameter a is introduced as a bookkeeping index. After expansion in a series of $R^{(\pm)}(a)$, it will be set $a=1$.

The relationship between moments $\langle x^l\rangle$ and cumulants $\kappa_l^{(\pm)}$ in the cumulant expansion may be summarized as follows (refer to Appendix A as well as Eu [64, 65, 67], Meeron [99], Kubo [100], and Appendix B of Myong [63] for details):

$$\left\langle e^{ax}\right\rangle=\sum_{l=0}^{\infty}\frac{a^l}{l!}\left\langle x^l\right\rangle=\exp\left[\sum_{l=1}^{\infty}\frac{a^l}{l!}\kappa_l^{(+)}\right]. \tag{C.5}$$

Using (A.6), (C.4) can be written as

$$\begin{aligned}&\bar{\sigma}_{ne}=\kappa_1^2q(\kappa_1^{(\pm)},\kappa_2^{(\pm)},\cdots)\ \text{where}\ \kappa_1\equiv\frac{1}{2}\left\langle\left\langle(x-y)^2\right\rangle_{ne}\right\rangle^{1/2},\\&q(\kappa_1^{(\pm)},\kappa_2^{(\pm)},\cdots)\equiv\frac{1}{2\kappa_1}\left\{\exp\left[\sum_{l=1}^{\infty}\frac{(-1)^l}{l!}\kappa_l^{(+)}\right]-\exp\left[\sum_{l=1}^{\infty}\frac{(-1)^l}{l!}\kappa_l^{(-)}\right]\right\},\end{aligned} \tag{C.6}$$

where the leading (1st-mean, 2nd-variance, 3rd-skewness) cumulants $\kappa_{1,2,3}^{(\pm)}$ are given by the moments of reduced interaction integrals $\kappa_{1,2,3}$

$$\kappa_1^{(\pm)} = \mp\kappa_1,\ \kappa_2^{(\pm)} = \mp\frac{\kappa_2}{\kappa_1} - \kappa_1^2,\ \kappa_3^{(\pm)} = \mp\frac{\kappa_3}{\kappa_1} - 3\kappa_2 \mp 2\kappa_1^3, \tag{C.7}$$

and

$$\kappa_1 = \frac{1}{2}\left\{\left\langle (x-y)^2 \right\rangle_{ne}\right\}^{1/2},\ \kappa_2 = \frac{1}{4}\left\{\left\langle (x-y)\left(x^2-y^2\right)\right\rangle_{ne}\right\},\ \kappa_3 = \frac{1}{4}\left\{\left\langle (x-y)\left(x^3-y^3\right)\right\rangle_{ne}\right\}. \tag{C.8}$$

In addition, when the distribution function (2.19) is inserted into the definition of non-equilibrium entropy production, the interacting term $\mathbf{\Lambda}^{(n)}$ is shown to be directly related to the non-equilibrium entropy production σ_{ne},

$$\sigma_{ne} \equiv -k_B \left\langle \ln f\ C[f] \right\rangle = -k_B \left\langle -\beta \sum_{n=1}^{\infty} X^{(n)} h^{(n)} C[f] \right\rangle = \frac{1}{T}\sum_{n=1}^{\infty} X^{(n)} \left\langle h^{(n)} C[f] \right\rangle = \frac{1}{T}\sum_{n=1}^{\infty} X^{(n)} \mathbf{\Lambda}^{(n)}\ . \tag{C.9}$$

Now the explicit form of the interacting term $\mathbf{\Lambda}^{(n)}$ can be derived from (C.6) and (C.9) by calculating the first reduced interaction integral κ_1 in terms of $X^{(n)}$; since x appearing in κ_1 consists of a sum of various moments, $x \equiv \beta\left(\sum_{n=1}^{\infty} X^{(n)} h^{(n)} - N\right)$, with the definition $\Delta h^{(n)} = h^{(n)} - h^{(n)*}$, κ_1^2 may be expressed as a quadratic form of X,

$$\kappa_1^2 = \frac{1}{4}\sum_{n,l=1}^{\infty} \left\langle \left(X^{(n)}\Delta h^{(n)} + X_2^{(n)}\Delta h_2^{(n)}\right)\left(X^{(l)}\Delta h^{(l)} + X_2^{(l)}\Delta h_2^{(l)}\right)\right\rangle_{ne}\ . \tag{C.10}$$

On rearrangement of the terms, it may become

$$\kappa_1^2 = \sum_{n,l=1}^{\infty} X^{(n)} R_{12}^{(nl)} X_2^{(l)}\ , \tag{C.11}$$

where $R_{12}^{(nl)}$ are scalar coefficients made up of interaction brackets of $h^{(n)}$ and $h_2^{(l)}$. After comparing (C.6), (C.9), (C.11),

$$\bar{\sigma}_{ne} = \kappa_1^2 q(\kappa_1^{(\pm)}, \kappa_2^{(\pm)}, \cdots) = \beta g \sum_{n=1}^{\infty} X^{(n)} \mathbf{\Lambda}^{(n)} = \sum_{n,l=1}^{\infty} X^{(n)} R_{12}^{(nl)} X_2^{(l)} q(\kappa_1^{(\pm)}, \kappa_2^{(\pm)}, \cdots), \tag{C.12}$$

the following interaction term, consistent with the second law of thermodynamics, can be derived;

$$\mathbf{\Lambda}^{(n)} = \frac{1}{\beta g}\sum_{l=1}^{\infty} R_{12}^{(nl)} X_2^{(l)} q(\kappa_1^{(\pm)}, \kappa_2^{(\pm)}, \cdots)\ . \tag{C.13}$$

Finally, the unknown conjugate variables $X^{(n)}$, which were first introduced in (2.19) of the non-equilibrium distribution function, need to be determined in terms of macroscopic variables, consistent with the laws of thermodynamics.

One way to achieve this is to generalize the equilibrium Gibbs ensemble theory—providing the relationship between thermodynamic variables and the partition functions—to non-equilibrium processes. Such a non-equilibrium generalization was already developed by Eu [67], and the leading order approximate solution may be expressed as

$$X^{(1)} = -\frac{\boldsymbol{\tau}}{2\mu/\lambda}. \tag{C.14}$$

Here, the viscoelastic stress $\boldsymbol{\tau}$ is defined as the Kramers expression [21, 59],

$$\boldsymbol{\tau} \equiv S_0 \langle \mathbf{r}\mathbf{r} f \rangle - nk_B T\mathbf{1}.$$

Note that the molecular representation corresponding to Kramer's viscoelastic stress is $h^{(1)} = S_0\mathbf{r}\mathbf{r} - k_B T\mathbf{1}$. Then, after the interaction approximation $R_{12}^{(11)} = 2\beta g\mu/\lambda$, equation (C.14), and the leading order cumulant expansion $q_{2nd}(\kappa_1^{(\pm)})$,

$$\bar{\sigma}_{ne} = \frac{\kappa_1}{2}\left\{\exp\left[\kappa_1 - \frac{1}{2}\left(\frac{\kappa_2}{\kappa_1} + \kappa_1^2\right) + \cdots\right] - \exp\left[-\kappa_1 + \frac{1}{2}\left(\frac{\kappa_2}{\kappa_1} - \kappa_1^2\right) + \cdots\right]\right\} \underset{\text{2nd}}{=} \kappa_1 \sinh\kappa_1. \tag{C.15}$$

are applied, the resulting equation of (C.13) can be expressed in the following form with the nonlinear hyperbolic sine factor:

$$\boldsymbol{\Lambda}^{(1)} \equiv \frac{1}{\lambda}\left\langle h^{(1)}\left(f^* - f\right)\right\rangle \underset{\text{2nd}}{=} -\frac{1}{\lambda}\boldsymbol{\tau} q_{\text{2nd}}(\kappa_1), \tag{C.16}$$

where

$$q_{\text{2nd}}(\kappa_1) = \frac{\sinh\kappa_1}{\kappa_1},\ \kappa_1 = \alpha\frac{\sqrt{\boldsymbol{\tau}:\boldsymbol{\tau}}}{\mu/\lambda},\ \alpha = \frac{t_p}{\lambda},\ t_p = \frac{1}{2\lambda}\beta g\mu. \tag{C.17}$$

REFERENCES

[1]C. L. M .H. Navier, *Mémoirs de l'Académie des Sciences de l'Institut de France. t. vi* (Paris, 1822).

[2]J. C. Maxwell, "On the dynamical theory of gases," Philos. Trans. Roy. Soc. Lond. **159**, 49-88 (1867).

[3]L. Boltzmann, "Further studies on the thermal equilibrium of gas molecules," Sitzungsberichte Akademie der Wissenschaften **66**, 275-370 (1872).

[4]C. Truesdell and R. G. Muncaster, *Fundamentals of Maxwell's Kinetic Theory of a Simple Monatomic Gas* (Academic Press, New York,1980).

[5]C. Truesdell and W. Noll, *The Non-Linear Field Theories of Mechanics* (Springer, Heidelberg, 2003).

[6]J. G. Oldroyd, "On the formulation of rheological equation of state," Proc. Roy. Soc. Lond. A **200**, 523-541 (1950).

[7]H. Giesekus, "Die elastizität von flüssigkeiten," Rheol. Acta **5**, 29-35 (1966).

[8]N. Phan-Thien and R. I. Tanner, "A new constitutive equation derived from network theory," J. Non-Newtonian Fluid Mech. **2**, 353-365 (1977).

[9]R. G. Larson, *Constitutive Equations for Polymer Melts and Solutions* (Butterworths, Boston, 1988).

[10]R. B. Bird and J. M. Wiest, "Constitutive equations for polymeric liquids," Ann. Rev. Fluid Mech. **27**, 169-193 (1995).

[11]R. S. Myong, "Thermodynamically consistent hydrodynamic computational models for high-Knudsen-number gas flows," Phys. Fluids **11**, 2788-2802 (1999).

[12]R. S. Myong, "A computational method for Eu's generalized hydrodynamic equations of rarefied and microscale gasdynamics," J. Comput. Phys. **168**, 47-72 (2001).

[13]J. M. Reese, M. A. Gallis, and D. A. Lockerby, "New directions in fluid dynamics: Non-equilibrium aerodynamic and microsystem flows," Philos. Trans. R. Soc. London, Ser. A **361**, 2967-2988 (2003).

[14]R. S. Myong, "A full analytical solution for the force-driven compressible Poiseuille gas flow based on a nonlinear coupled constitutive relation," Phys. Fluids **23(1)**, 012002 (2011).

[15]N. T. P. Le, H. Xiao, and R. S. Myong, "A triangular discontinuous Galerkin method for non-Newtonian implicit constitutive models of rarefied and microscale gases," J. Comput. Phys. **273**, 160-184 (2014).

[16]R. S. Myong, "Theoretical description of the gaseous Knudsen layer in Couette flow based on the second-order constitutive and slip-jump models," Phys. of Fluids **28-1**, 012002 (2016).

[17]R. Hooke, *De Potentia Restitutiva, or of Spring. Explaining the Power of Springing Bodies*, London, 1678.

[18]M. J. Crochet and K. Walters, "Numerical methods in non-Newtonian fluid mechanics," Ann. Rev. Fluid Mech. **15**, 241-260 (1983).

[19]R. Keunings, "On the high Weissenberg number problem," J. Non-Newtonian Fluid Mech. **20**, 209-226 (1986).

[20]J. M. Rallison and E. J. Hinch, "Do we understand the physics in the constitutive equation?," J. Non-Newtonian Fluid Mech. **29**, 37-55 (1988).

[21]R. G. Owens and T. N. Phillips, *Computational Rheology* (Imperial College Press, London, 2002).

[22]R. Fattal and R. Kupferman, "Constitutive laws of the matrix-logarithm of the conformation tensor," J. Non-Newtonian Fluid Mech. **123**, 281-285 (2004).

[23]M. A. Hulsen, R. Fattal, and R. Kupferman, "Flow of viscoelastic fluids past a cylinder at high Weissenberg number: stabilized simulations using matrix logarithms," J. Non-Newtonian Fluid Mech. **127**, 27-39 (2005).

[24]M. Renardy, "A comment on smoothness of viscoelastic stresses," J. Non-Newtonian Fluid Mech. **138(2-3)**, 204-205 (2006).

[25]B. Thomases and M. Shelley, "Emergence of singular structures in Oldroyd-B fluids," Phys. Fluids **19**, 103103 (2007).

[26]M. Bajaj, M. Pasquali, and J. R. Prakash, "Coil-stretch transition and the breakdown of computations for viscoelastic fluid flow around a confined cylinder," J. Rheol. **52(1)**, 197-223 (2008).

[27]J. R. Prakash, "Micro and macro in the dynamics of dilute polymer solutions: convergence of theory with experiment," Korea-Aust. Rheol. J. **21(4)**, 245-268 (2009).

[28]P. Becherer, W. van Saarloos, and A. N. Morozov, "Stress singularities and the formation of birefringent strands in stagnation flows of dilute polymer solutions," J. Non-Newtonian Fluid Mech. **157(1-2)**, 126-132 (2009).

[29]A. M. Afonso, M. A. Alves, and F. T. Pinho, "Purely elastic instabilities in three-dimensional cross-slot geometries," J. Non-Newtonian Fluid Mech. **165(13-14)**, 743-751 (2010).

[30]X. Chen, H. Marschall, M. Schäfer, and D. Bothe, "A comparison of stabilisation approaches for finite-volume simulation of viscoelastic fluid flow," Int. J. Comput. Fluid Dyn. **27(6-7)**, 229-250 (2013).

[31]A. M. Afonso, *Further Developments on Theoretical and Computational Rheology* (Ph.D. Thesis, Universidade Do Porto, 2010).

[32]H. R. Warner, Jr., "Kinetic theory and rheology of dilute suspensions of finitely extendible dumbbells," Ind. Eng. Chem. Fundam., **11(3)**, 379-387 (1972).

[33]M. Yamamoto, "The visco-elastic properties of network structure I. general formalism," J. The Physical Society of Japan **11(4)**, 413-421 (1956).

[34]A. S. Lodge, "The isotropy of Gaussian molecular networks and the stress-birefringence relations for rubberlike materials cross-linked in stressed states," Kolloid-Zeitsehrifl, Band **171**, 46-51 (1960).

[35]F. W. Wiegel, "A network model for viscoelastic fluids," Physica **42(1)**, 156-164 (1969).

[36]R. B. Bird, P. J. Dotson, and N. L. Johnson, "Polymer solution rheology based on a finitely extensible bead-spring chain model," J. Non-Newtonian Fluid Mech. **7(2-3)**, 213-235 (1980).

[37]R. Keunings, "On the Peterlin approximation for finitely extensible dumbbells," J. Non-Newtonian Fluid Mech. **68(1)**, 85-100 (1997).

[38]M. Kroger, "Simple models for complex nonequilibrium fluids," Phys. Rep. **390**, 453-551 (2004).

[39]M. Davoodi, K. Zografos, P. J. Oliveira, and R. J. Poole, "On the similarities between the simplified Phan-Thien–Tanner model and the finitely extensible nonlinear elastic dumbbell (Peterlin closure) model in simple and complex flows," Phys. Fluids **34**, 033110 (2022).

[40]P. L. Bhatnagar, E. P. Gross, and M. Krook, "A model for collision processes in gases. I. Small amplitude processes in charged and neutral one-component systems," Phys. Rev. **94 (3)**, 511-525 (1954).

[41]Y. Fan, R. I. Tanner, and N. Phan-Thien, "Galerkin/least-square finite-element methods for steady viscoelastic flows," J. Non-Newtonian Fluid Mech. **84(2-3)**, 233-256 (1999).

[42]M. Alves, F. Pinho, and P. J. Oliveira, "The flow of viscoelastic fluids past a cylinder: finite-volume high-resolution methods," J. Non-Newtonian Fluid Mech. **97(2-3)**, 207-232 (2001).

[43]P. J. Oliveira and A. I. Miranda, "A numerical study of steady and unsteady viscoelastic flow past bounded cylinders," J. Non-Newtonian Fluid Mech. **127(1)**, 51-66 (2005).

[44]F. Habla, A. Obermeier, and O. Hinrichsen, "Semi-implicit stress formulation for viscoelastic models: Application to three-dimensional contraction flows," J. Non-Newtonian Fluid Mech. **199**, 70-79 (2013).

[45]F. Pimenta, and M. A. Alves, "RheoTool," OpenFOAM Toolbox (2016), accessed October 15, 2025. https://github.com/fppimenta/rheoTool.

[46]J. L. Favero, A. R. Secchi, N. S. M. Cardozo, and H. Jasak, "Viscoelastic flow analysis using the software OpenFOAM and differential constitutive equations," J. Non-Newtonian Fluid Mech. **165 (23-24)**, 1625-1636 (2010).

[47]F. Habla, H. Marschall, O. Hinrichsen, L. Dietsche, H. Jasak, and J. L. Favero, "Numerical simulation of viscoelastic two-phase flows using OpenFOAM," Chem. Eng. Sci. **66** (2011) 5487–5496.

[48]F. Pimenta and M. A. Alves, "Stabilization of an open-source finite-volume solver for viscoelastic fluid flows," J. Non-Newtonian Fluid Mech. **239**, 85-104 (2017).

[49]F. Pimenta and M. A. Alves, "A coupled finite-volume solver for numerical simulation of electrically-driven flows," Comput. Fluids **193**, 104279 (2019).

[50]T. Chourushi, "Effect of fluid elasticity on the numerical stability of high-resolution schemes for high shearing contraction flows using OpenFOAM," TAML **7(1)**, 41-51 (2017).

[51]T. Chourushi, "A high resolution equi-gradient scheme for convective flows," Appl. Math. Comput. **338**, 123-140 (2018).

[52]S. Meburger, M. Niethammer, D. Bothe, and M. Schäfer, "Numerical simulation of non-isothermal viscoelastic flows at high Weissenberg numbers using a finite volume method on general unstructured meshes," J. Non-Newton. Fluid Mech. **287**, 104451 (2021).

[53]M. A. Alves, P. J. Oliveira, and F. T. Pinho, "Numerical methods for viscoelastic fluid flows," Annu. Rev. Fluid Mech. **53**, 509-541 (2021).

[54]H. Eyring, "Viscosity, plasticity, and diffusion as examples of absolute reaction rates," J. Chem. Phys. **4**, 283-291 (1936).

[55]T. Ree and H. Eyring, "Theory of non-Newtonian flow. I. Solid plastic system," J. Appl. Phys. **26**, 793-800 (1955).

[56]K. L. Johnson and J. L. Tevaarwerk, "Shear behaviour of elastohydrodynamic oil films," Proc. Roy. Soc. Lond. A **356**, 215-236 (1977).

[57]J. L. Tevaarwerk and K. L. Johnson, "The influence of fluid rheology of traction drives," J. of Lubrication Tech. **101(3)**, 266-273 (1979).

[58]H. Giesekus, "A simple constitutive equation for polymer fluids based on the concept of deformation-dependent tensorial mobility," J. Non-Newtonian Fluid Mech. **11**, 69-109 (1982).

[59]R. B. Bird, C. F. Curtiss, R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids, Volume 2: Kinetic Theory* (2nd Edition, Wiley-Interscience, 1987).

[60]T. Gombosi, *Gaskinetic Theory* (Cambridge University Press, 1994).

[61]R. B. Bird and A. J. Giacomin, "Polymer fluid dynamics: Continuum and molecular approaches," Annu. Rev. Chem. Biomol. Eng. **7**, 479-507 (2016).

[62]O. Malaspinas, *Lattice Boltzmann Method for the Simulation of Viscoelastic Fluid Flows* (Ph.D. Thesis, Ecole Polytechnique Fédérale de Lausanne, 2009).

[63]R. S. Myong, "On the high Mach number shock structure singularity caused by overreach of Maxwellian molecules," Phys. Fluids **26(5)**, 056102 (2014).

[64]B. C. Eu, "A modified moment method and irreversible thermodynamics," J. Chem. Phys. **73**, 2958-2969 (1980).

[65]B. C. Eu, *Kinetic Theory and Irreversible Thermodynamics* (Wiley, New York, 1992).

[66]M. Al-Ghoul and B. C. Eu, "Generalized hydrodynamics and shock waves," Phys. Rev. E **56**, 2981-2992 (1997).

[67]B. C. Eu, *Nonequilibrium Statistical Mechanics: Ensemble Method* (Kluwer Academic Publishers, Dordrecht, 1998).

[68]B. C. Eu, *Transport Coefficients of Fluids* (Springer, Heidelberg, 2006).

[69]L. Onsager, "Reciprocal relations in irreversible processes. I," Phys. Rev. **37**, 405-426 (1931).

[70]C. A. Bippes, A. D. L. Humphris, M. Stark, D. J. Müller, and H. Janovjak, "Direct measurement of single-molecule visco-elasticity in atomic force microscope force-extension experiments," Eur. Biophys. J. **35**, 287-292 (2006).

[71]D. E. Smith, H. P. Babcock, and S. Chu, "Single-polymer dynamics in steady shear flow," Science **283(5408)**, 1724-1727 (1999).

[72]H. A. Barnes and G. P. Roberts, "A simple empirical model describing the steady-state shear and extensional viscosities of polymer melts," J. Non-Newtonian Fluid Mech. **44**, 113-126 (1992).

[73]R. Ballman, "Extensional flow of polystyrene melt," Rheologica Acta, **4(2)**, 137-140 (1965).

[74]W. R. Hwang, M. A. Hulsen, and H. E. H. Meijer, "Direct simulations of particle suspensions in a viscoelastic fluid in sliding bi-periodic frames," J. Non-Newtonian Fluid Mech. **121(1)**, 15-33 (2004).

[75]A. M. Afonso, M. A. Alves, F. T. Pinho, and P. J. Oliveira, "Flow of viscoelastic fluids around a confined cylinder: Comparison of standard and log-conformation stress formulations," National Conference on Numerical Methods in Fluid Mechanics and Thermodynamics, University of Aveiro, Portugal (2008).

[76]R. G. Owens, C. Chauvière, and T. N. Philips, "A locally-upwinded spectral technique (LUST) for viscoelastic flows," J. Non-Newtonian Fluid Mech. **108**, 49-71 (2002).

[77]J. Aho, Rheological Characterization of Polymer Melts in Shear and Extension: Measurement Reliability and Data for Practical Processing (Ph.D. Thesis, Tampere University of Technology, 2011).

[78]F. P. Baaijens, H. P. Baaijens, G. W. Peters, and H. E. Meijer, "An experimental and numerical investigation of a viscoelastic flow around a cylinder," J. Rheology **38(2)**, 351-376 (1994).

[79]Y. P. Seo and Y. Seo, "A simple constitutive model describing the steady state shear viscosity and its prediction of the first normal stress function in shear flow," Polymer **53(5)**, 1058-1062 (2012).

[80]Y. Matsumiya, H. Watanabe, Y. Masubuchi, Q. Huang, and O. Hassager, "Nonlinear elongational rheology of unentangled Polystyrene and Poly(*p-tert*-butylstyrene) melts," Macromolecules **51(23)**, 9710-9729 (2018).

[81]G. Ianniruberto, A. Brasiello, and G. Marrucci, "Modeling unentangled Polystyrene melts in fast elongational flows," Macromolecules **52(12)**, 4610-4616 (2019).

[82]G. Ianniruberto, G. Marrucci, and Y. Masubuchi, "Melts of linear polymers in fast flows," Macromolecules **53(13)**, 5023-5033 (2020).

[83]H. Watanabe, Y. Matsumiya, and T. Sato, "Revisiting nonlinear flow behavior of Rouse chain: Roles of FENE, friction-reduction, and Brownian force intensity variation," Macromolecules **54(8)**, 3700-3715 (2021).

[84]L. Perko, *Differential Equations and Dynamical Systems* (Springer-Verlag, New York, 1991).

[85]R. S. Myong and P. L. Roe, "Shock waves and rarefaction waves in magnetohydrodynamics: I. A model system," J. Plasma Phys. **58**, 485-519 (1997).

[86]R. S. Myong and P. L. Roe, "Shock waves and rarefaction waves in magnetohydrodynamics: II. The MHD system," J. Plasma Phys. **58**, 521-552 (1997).

[87]E. Kreyszig, *Advanced Engineering Mathematics* (8th Ed., John Wiley & Sons, New York, 1999).

[88]R. S. Myong, "On singularity of the UCM and Oldroyd-B models in viscoelastic fluids: Resolving the high-Weissenberg number problem," The 65th Annual Meeting of the APS Division of Fluid Dynamics, M19.002 (2012).

[89]T. Chourushi and R. S. Myong, "High Weissenberg number behavior of the Oldroyd-B, Giesekus, and Myong's NCCR models in viscoelastic flow over a confined cylinder," Unpublished (2026) .

[90]M. Zamani-Taghizadeh-Rabe, M. Norouzi, A. B. Nejad, A. Minaeian, and M. H. Izadifard, "Three-dimensional Phan-Thien-Tanner viscoelastic flows around a sphere," Phys. Fluids **37**, 013114 (2025).

[91]A. Arshadi, M. Nili-Ahmadabadi, A. Minaeian, M. Norouzi, and M. Y. Ha, "Flow and heat transfer in Phan-Thien–Tanner viscoelastic fluid around a rotating hot cylinder in a square enclosure," Phys. Fluids **35**, 093109 (2023).

[92]S. Raffi, A. Chauhan, and C. Sasmal, "Combined effects of fluid elasticity and plasticity on flow past a rotating circular cylinder," Phys. Fluids **37**, 023133 (2025).

[93]I. S. Novikau, S. S. Kantorovich, and S. A. Altmeyer, "Viscoelastic flow instability in planar shear flow," Phys. Fluids **37**, 063109 (2025).

[94]L. Peng, Y. Hao, R. Liu, and J. Li, "Electro-osmotic flow instability of viscoelastic fluids in a nanochannel," Phys. Fluids **36**, 103127 (2024).

[95]K. D. Housiadas and A. N. Beris, "Lubrication approximation of pressure-driven viscoelastic flow in a hyperbolic channel," Phys. Fluids **35**, 123116 (2023).

[96]A. Groisman and V. Steinberg, "Elastic turbulence in a polymer solution flow," Nature **405**, 53-55 (2000).

[97]V. Steinberg, "Elastic turbulence: An experimental view on inertialess random flow," Annu. Rev. Fluid Mech. **53**, 27-58 (2021).

[98]R. A. Fisher, “Moments and product moments of sampling distributions,” Proc. Lond. Math. Soc. (2) **30**, 199-238 (1929).

[99]E. Meeron, “Series expansion of distribution functions in multicomponent fluid systems,” J. Chem. Phys. **27**, 1238-1246 (1957).

[100]R. Kubo, “Generalized cumulant expansion method,” J. Phys. Soc. Jpn. **17**, 1100-1120 (1962).