Copyright 2012 Narayanan Ashwin Kumar Bharadwaj
LOW DIMENSIONAL INTRINSIC MATERIAL FUNCTIONS UNIQUELY IDENTIFY RHEOLOGICAL CONSTITUTIVE MODELS AND INFER MATERIAL MICROSTRUCTURE

BY

NARAYANAN ASHWIN KUMAR BHARADWAJ

THESIS

Submitted in partial fulfillment of the requirements for the degree of Master of Science in Mechanical Engineering in the Graduate College of the University of Illinois at Urbana-Champaign, 2012

Urbana, Illinois

Adviser:

Professor Randy H. Ewoldt
Abstract

Rheological material functions are used to form our conceptual understanding of a material response. For a nonlinear rheological response, the associated material functions span a high-dimensional space. A theoretical framework is developed to outline low-dimensional measures for describing asymptotic nonlinear responses in large-amplitude oscillatory shear (LAOS). Nomenclature is introduced to provide physical interpretations for these newly developed intrinsic measures under both shear strain-control (LAOStrain) and shear stress-control (LAOStress) protocols.

Analytical solutions are surveyed for these intrinsic signatures of constitutive model responses to imposed large-amplitude oscillatory shear strain (LAOStrain) and translated into the language of intrinsic Chebyshev coefficients to allow for comparison and conceptual interpretation. Considered constitutive models include that of a third order fluid, corotational Maxwell model, Giesekus model, and other specific models for polymer melts, rodlike polymer solutions, and emulsions. New analytical results are derived for two transient nonlinear-elastic network models; finitely extensible nonlinear elastic (FENE) and wormlike chain (WLC) models. A library of analytical intrinsic LAOStrain fingerprints is thus generated. The intrinsic signatures for all these models are only a function of the imposed frequency and a nonlinear parameter, if any. Interesting sign changes are observed in the intrinsic signatures across constitutive models that help compare and contrast between.

Under a defined deformation protocol, a numerical approach may be required to converge on solutions to constitutive equations that may not have an analytical solution. A robust numerical scheme is thus developed for quick and efficient extraction of intrinsic LAOStrain nonlinearities for nonlinear constitutive models. The proposed numerical algorithm is used to extract intrinsic LAOStrain material functions for the single mode pompom model and the intrinsic signatures are compared for different combinations of the associated nonlinear parameters. With slight modifications, the numerical scheme is applicable for any differential or integral constitutive model. They are equally flexible to accommodate for increased
nonlinearities in the system arising from modifications to constitutive equations in their current form.

The utility of these measures is demonstrated by experimentally measuring the frequency-dependent intrinsic LAOStrain nonlinearities for a polymeric hydrogel (PVA-Borax). Techniques for accurate extraction of the subdominant intrinsic measures are presented. Physical interpretations are provided through the obtained intrinsic signatures of the PVA-Borax system. The four measured intrinsic nonlinear fingerprints are compared with the available analytical and numerical library of intrinsic fingerprints. The matching process identifies a unique constitutive equation, fits the nonlinear model parameter, and implies molecular- and micro-scale structure in the material.
Acknowledgments

I would like to express my deepest gratitude to my advisor Prof. Randy H. Ewoldt for his constant motivation, unwavering support and encouragement throughout this work. This work would not have been possible without his exuberance in my research and expertly guidance whenever needed. I’d like to thank my colleagues Michael, Brendan and Soham for all the invaluable discussions relating to my research. I would also like to thank Prof. Jozef Kokkini for allowing me access to his lab and Dr. Francesca DeVito for her help on my experiments. Furthermore, I would like to thank all my friends and well-wishers for their support.

I’m grateful to my parents for their encouragement to pursue my dreams and equipping me with all that was needed to reach this stage in life. My sister also deserves special mention for the lighthearted discussions that enlivens an otherwise dull day. I’d also like to thank all my family members for their prayers, care and affection which till day have kept me going strong. Last but not the least, I thank god for bestowing me with this opportunity.
Contents

1. Introduction and Background ........................................................................................................... 1
   1.1 Low dimensional representation in nonlinear oscillatory deformation ........................................ 1
   1.2 Pipkin space mapping .................................................................................................................. 4
   1.3 Overview of intrinsic LAOS material functions ........................................................................... 7
2. Theory .............................................................................................................................................. 9
   2.1 Theory for LAOStrain .................................................................................................................. 9
      2.1.1 Time Domain LAOStrain ....................................................................................................... 9
      2.1.2 Deformation domain LAOStrain ......................................................................................... 11
      2.1.3 Interrelations with other measures ..................................................................................... 17
   2.2 Theory for LAOStress ................................................................................................................ 20
3. Experimental Results ....................................................................................................................... 24
   3.1 Materials .................................................................................................................................... 24
   3.2 Linear Viscoelastic Results ......................................................................................................... 26
   3.3 Asymptotic nonlinear results from [LAOStrain] ....................................................................... 28
   3.4 Interpretation of [LAOStrain] fingerprints of PVA-Borax ............................................................ 32
   3.5 Inferring Structure from Intrinsic Measures ............................................................................. 35
4. Library of Intrinsic LAOStrain Fingerprints for Nonlinear Constitutive Models ......................... 37
   4.1 Analytical results based on existing literature ........................................................................... 37
      4.1.1. Third Order fluid .................................................................................................................. 38
      4.1.2. Corotational Maxwell Model ............................................................................................. 39
      4.1.3. Giesekus Model ................................................................................................................... 43
      4.1.4. Integral-Generalized strain measure .................................................................................. 45
4.1.5. Rod like polymers........................................................................................................48
4.1.6. Simple Emulsion..........................................................................................................50
4.2 Transient Network Models ..............................................................................................54
  4.2.1 Finitely Extensible Nonlinear Elastic (FENE) Model..................................................59
  4.2.2 Wormlike chain (WLC) Model..................................................................................63
4.3. Compare and contrast Constitutive Models on [LAOStrain] signatures..........................66

5. **Numerical Simulations** ..................................................................................................75
  5.1 Simulation Algorithm and techniques ............................................................................75
  5.2. Validating Simulations with Analytical results..............................................................82
    5.2.1. Giesekus Model ........................................................................................................82
    5.2.2. Corotational Maxwell Model ..................................................................................82
  5.3. Intrinsic nonlinearities of the Single Mode Pompom model........................................84

6. **Structure-Rheology Connections** ................................................................................92

7. **Conclusions** .................................................................................................................97

References .............................................................................................................................101

Appendix A .............................................................................................................................106
Chapter 1

Introduction and Background

1.1 Low dimensional representation in nonlinear oscillary deformation

Rheological material functions are the starting point to describe intensive material responses to various loading conditions. Descriptive material functions such as linear viscoelastic moduli \( G'(\omega) \) and \( G^*(\omega) \), transient shear viscosity \( \eta^+(t,\gamma) \), and several other measures (Dealy 1995) are used to understand the mechanical properties of complex fluids or solids, but they are not predictive models in themselves. Nonlinear rheological characterization can generate an overwhelming amount of information and material functions, with various measures that each map out a two-dimensional parameter space, e.g. stress relaxation modulus \( G(t,\gamma) \) or the variety of material functions associated with large-amplitude oscillatory shear (LAOS); e.g. see [Giacomin et al. (2011); Hyun et al. (2011), Ewoldt (2013)]. One ever-present challenge is to identify and interpret the most appropriate material function(s) for the material and application of interest.

Reducing abundant information available from nonlinear rheological characterization into meaningful and easily interpretable material measures is important and the work here involves low-dimensional and physically interpretable descriptions of nonlinear viscoelasticity. Particular focus is laid on material functions that can be used to characterize any material of interest, for example solids, liquids, polymers, colloidal suspensions, emulsions and viscoelastic materials. To give our aims context, consider the damping function \( h(\gamma_0) \). The function \( h(\gamma_0) \) is a low-dimensional representation of nonlinear viscoelasticity, but it is a model, not a material function in general. The damping function is used to shift self-similar stress relaxation curves according to \( G(t) = G(t,\gamma_0)/h(\gamma_0) \). Rather

---

1 Adopted from the authors’ work; Ewoldt.R.H. Bharadwaj.A.N, “Low-dimensional intrinsic material functions for nonlinear viscoelasticity,” Rheol. Acta (submitted)
than reporting the full two-dimensional response surface $G(t, \gamma_0)$, one only needs to report the one-dimensional functions $G(t)$ and $h(\gamma_0)$. The convenient use of the damping function is limited to the special case of time-strain separability. As this cannot be generally true for viscoelastic materials, the damping function cannot be used in general and therefore is not a material function.

Asymptotic expansions allow for generally-applicable low-dimensional descriptions that are material functions. For example, intrinsic shear viscosity $[\eta]$ is a material function and represents asymptotic changes to viscosity due to an additive. A particular functional dependence is assumed,

$$\eta(\dot{\gamma}, \phi) = \eta_0(\dot{\gamma}) \left[ 1 + [\eta](\dot{\gamma}) \phi + O(\phi^2) \right]$$  \hspace{1cm} (1.1)$$

where $\phi$ is the volume fraction of additive, $\eta_0(\dot{\gamma})$ is the baseline viscosity, and $O(\phi^2)$ represents terms of order $\phi^2$ and higher. A low-dimensional description is possible within the asymptotic region of $\phi \ll 1$ (the precise limits of which depend on the desired accuracy). In such a region, instead of reporting the two-dimensional function $\eta(\dot{\gamma}, \phi)$, one only needs to report two functions, $\eta_0(\dot{\gamma})$ and $[\eta](\dot{\gamma})$. The magnitude and sign of $[\eta](\dot{\gamma})$ can be a strong function of molecular or microstructural features. Einstein was the first to relate its measurement to molecular dimensions [Einstein (1906); (1911)]. Since then, the intrinsic viscosity $[\eta]$ has been used to infer other micro-, nano-, and molecular-scale features, for example the aspect ratio of carbon nanotubes suspended in solution [Davis et al. (2004)]. The sign of $[\eta]$ is also sensitive to the underlying molecular features. It can be negative, for example, with some polymer melts with nanoparticle additives [Tuteja et al. (2005)].

In addition to inferring structure, the intrinsic shear viscosity has a clear physical interpretation, readily apparent in Eq.(1.1), where it represents a leading-order change in the dissipative resistance to shear flow.

Drawing inspiration from intrinsic viscosity, viscoelastic material functions are sought that capture leading-order nonlinearities in response to deformation; the motive being to obtain a clear physical interpretation and to associate intrinsic responses to structure. The deformation we consider is homogeneous simple shear, and specifically oscillatory shear. An
Oscillatory deformation protocol is powerful owing to its ability to conceptually decompose the response into dissipative effects (viscous or plastic) from the storage effects (elastic), e.g. linear viscoelastic moduli $G'(\omega)$, $G''(\omega)$, or linear viscoelastic compliances $J'(\omega)$, $J''(\omega)$.

In contrast, stress relaxation modulus $G(t, \gamma_0)$ conflates viscous and elastic effects into a single measure, as does the shear stress-controlled creep compliance $J(t, \sigma_0)$. While these conflated material functions are valid, useful, and well defined, in this work we focus on the conceptually decomposed viscoelastic material functions from oscillatory deformation.

Oscillatory deformation imposes a known frequency and amplitude, and therefore covers the two-dimensional viscoelastic response map of timescale and amplitude known as the Pipkin space (Pipkin 1972) (detailed in Section 1.2). When the response is observably nonlinear (i.e. not scaling linearly with the input amplitude), the protocol has been termed large-amplitude oscillatory shear (LAOS). The linear counterpart is known as small-amplitude oscillatory shear (SAOS), when the material moduli do not show any strain amplitude dependence. Well established literature and well defined material measures have motivated rheological characterization in the SAOS regime.

The limit of linear viscoelasticity is arbitrary, depending on the sensitivity to nonlinear deviations. The asymptotic deviation from linearity was considered theoretically by [Onogi et al. (1970)]. Some asymptotic nonlinearities were measured by [Davis and Macosko (1978)] for solid PMMA, and others have followed since. Recently, references have been made to the region of measurable leading-order deviations from linearity as medium-amplitude oscillatory shear (MAOS) [Hyun et al. (2006); Hyun and Wilhelm (2009); Wagner et al. (2011)].

In the spirit of intrinsic viscosity denoted as $[\eta]$, we call the leading-order response region the intrinsic LAOS regime. We will sometimes use the shorthand [LAOS] here, and the associated material functions will also use brackets [ ]. For LAOS, the input amplitude may be either controlled-shear strain amplitude $\gamma_0$ or controlled-shear stress amplitude $\sigma_0$. To distinguish between shear strain-control and shear stress-control tests, we will use the short-hand “LAOStrain” and “LAOStress,” respectively referring to large-amplitude
oscillatory shear strain/stress [Dimitriou et al. (2013), Ewoldt (2013)]. We will use the acronym LAOS when the controlled input need not be specified.

1.2 Pipkin space mapping

The range of the intrinsic nonlinear regime is best shown with a Pipkin space. The Pipkin space typically maps a viscoelastic material response as a function of timescale and loading amplitude [Pipkin (1972)]. For LAOStrain, the two deformation inputs define the Pipkin space: the strain amplitude $\gamma_0$ and the Deborah number $\text{De} = \lambda \omega$, as shown in Figure 1.1.

A line delineating the linear from the nonlinear regime has been drawn by Pipkin and others [Pipkin (1972); Dealy and Wissbrun (1990); Macosko (1994), Giacomin et al. (2011), Ewoldt et al. (2012)]. Such a line can be interpreted as the maximum linear viscoelastic strain amplitude as a function of $\text{De}$. A second line can also be drawn, which shows the limit of the intrinsic nonlinear regime. It is possible to see how intrinsic LAOS nonlinearities make quantitative predictions for the shape of this boundary.

In Figure 1.1 the boundaries for linear, intrinsic nonlinear and nonlinear regimes are identified based on the Giesekus model asymptotic response to LAOStrain. We use the analytical results of [Gurnon and Wagner (2012)] with $\alpha = 0.3$ (converted to our framework in Section 4.1.3. Eq. (4.15)-(4.18). The linear viscoelastic boundary is based on the first occurrence of any 0.1% deviation from linear viscoelasticity. The upper limit of intrinsic nonlinearity is based on 10% deviation. The choice of these deviations is for purposes of illustration. These choices only affect the relative positions of the boundary and not the functional dependence.

The boundaries are drawn by interpreting each intrinsic LAOS material function as a critical amplitude that will generate nonlinearity. For convenience, the comparison is drawn with respect to linear viscoelastic moduli. Consider normalized nonlinearities less than an arbitrary small value $\varepsilon$,

$$
\frac{\text{elastic nonlinearity}}{G'(\omega)} < \varepsilon, \quad \frac{\text{viscous nonlinearity}}{\eta'(\omega)} < \varepsilon.
$$

(1.2)
With the four intrinsic shear stress nonlinearities (see section 2.1.2 for details) we have four possible criteria,

\[
\frac{[e_1](\omega)\gamma_0^2}{G'(\omega)} \leq \varepsilon, \quad \frac{[v_1](\omega)\gamma_0^2}{\eta'(\omega)} \leq \varepsilon,
\]

\[
\frac{[e_3](\omega)\gamma_0^2}{G'(\omega)} \leq \varepsilon, \quad \frac{[v_3](\omega)\gamma_0^2}{\eta'(\omega)} \leq \varepsilon. \tag{1.3}
\]

All of the material functions in Eq.(1.3) depend only on frequency (or Deborah number \( {\text{De}} = \lambda \omega \)), and therefore each equation can be written to define a line for the critical strain amplitude \( \gamma_0^*(\text{De}) \) at which the specified nonlinearity appears an amount \( \varepsilon \). For example, in terms of the first-harmonic elastic nonlinearity, the critical strain amplitude expression is written

\[
\gamma_0^*(\text{De}) = \varepsilon \left( \frac{G'(\text{De})}{[e_1](\text{De})} \right)^{1/2}. \tag{1.4}
\]

A smaller intrinsic nonlinearity corresponds to a larger strain amplitude to generate a nonlinear rheological response. Different critical strain-amplitudes exist for each of the material functions \([e_1](\omega), [e_3](\omega), [v_1](\omega), [v_3](\omega)\). Although an arbitrary choice of \( \varepsilon \) is required, the boundary shapes depend only on the functional form of the frequency-dependent material functions. In Figure 1.1 we choose \( \varepsilon = 0.001 \) for the SAOS limit and \( \varepsilon = 0.1 \) for the [LAOS] limit of intrinsic leading-order nonlinearities (choice being arbitrary). Figure 1.1 does not indicate which type of nonlinearity from Eq.(1.3) occurs first but it is possible to identify this precisely for any specific model choice.

It is clear in Figure 1.1 that the critical strain amplitude is a function of \( \text{De} \). We observe that at high \( \text{De} \) the critical strain is approximately constant, but at low \( \text{De} \) the critical strain scales as \( \gamma_0 \sim \text{De}^{-1} \). This scaling is the signature of a critical Weissenberg number, \( \text{Wi} = \gamma_0 \text{De} \). At moderate \( \text{De} \) the criteria transitions between a critical \( \text{Wi} \) and a critical \( \gamma_0 \).
Also shown in Figure 1.1 are the regions of applicability of typical constitutive models, including the Newtonian, Generalized Newtonian Fluid (G.N.F.), and Second Order Fluid. Illustrative but arbitrary limits on $\text{De}$ are used for these boundaries. Purely viscous models, namely Newtonian and G.N.F. models apply for very small $\text{De}$; here we use $\text{De} \leq 10^{-3}$. The Second Order Fluid is an expansion with respect to $\text{De}$. A $\text{De} \leq 10^{-2}$ is chosen for the Second order fluid as it does not involve shear-thinning, and only captures the terminal viscoelastic regime at low $\text{De}$. The critical $\text{Wi}$ for a second order fluid is chosen to be the same as the limit of the linear viscoelastic regime as it does not predict shear-thinning.
1.3 Overview of intrinsic LAOS material functions

In Chapter 2, it will be that there are the two familiar linear viscoelastic material functions $G'(\omega)$, $G^*(\omega)$, and four intrinsic nonlinear material functions $[e_1](\omega)$, $[e_3](\omega)$, $[v_1](\omega)$, $[v_3](\omega)$ (we use the letter “e” for elastic nonlinearities and “v” for viscous nonlinearities) for a LAOS-train protocol. A power-function expansion allows for a low-dimensional representation for all six of these measures as a function of frequency only. With strain input represented as $\gamma(t) = \gamma_0 \sin\omega t$, it will be shown that the time-domain expansion of shear stress takes the form

$$\sigma(t;\gamma_0,\omega) = \gamma_0 \left[ G'(\omega) \sin\omega t + G^*(\omega) \cos\omega t \right]$$

$$+ \gamma_0^3 \left[ [e_1](\omega) \sin\omega t + \omega[v_1](\omega) \cos\omega t - [e_3](\omega) \sin3\omega t + \omega[v_3](\omega) \cos3\omega t \right]$$

$$+ O(\gamma_0^5)$$

(1.5)

with the notation $[e_3](\omega)$ to show explicitly the frequency dependence. Physical interpretations of these leading-order nonlinearities are revealed by a coordinate transformation from the time domain to the deformation domain, which represents stress as an instantaneous function of the imposed strain and strain-rate. The coefficients can be transformed to the time-domain representation, Eq.(1.5), for ease of signal processing.

Experimentally (Chapter 3), the small changes of the intrinsic regime can be difficult to observe and indeed difficult to measure, but there are inherent benefits in defining intrinsic LAOS material functions. These material measures are free from experimental artifacts accompanying very large deformations, such as nonhomogeneous flow [Ravindranath et al. (2011)], wall slip, edge fracture, instrument inertia and sample inertia. Successful measurement of intrinsic LAOS-train material measures is demonstrated with a model PVA-Borax system (details in Chapter 3). As an example, for a strain amplitude sweep at frequency $\omega = 1$ rad/s, Figure 1.2 shows a $\gamma_0^2$ scaling for the four intrinsic shear nonlinearities, seen when they rise above a torque resolution (shown by dark shaded symbols).
In Chapter 4, we will consider analytical solutions available for intrinsic material functions in LAOStrain. A recent summary of available LAOStrain analytical solutions for different constitutive models is given in Table 1 of [Giacomin et al. (2011)], and another has been recently published [Gurnon and Wagner (2012)]. Analytical solutions for LAOStrain intrinsic nonlinearities for a range of nonlinear constitutive models are presented and their intrinsic signatures are used to compare between them.

Figure 1.2 Experimental strain amplitude sweep of the PVA-Borax system at $\omega = 1$ rad/s. A standard $\gamma^2_0$ scaling can be seen for the four intrinsic shear nonlinearities, shown by dark (more color saturation) symbols corresponding to data above the torque noise floor.

Intrinsic fingerprints for nonlinear models without analytical solutions are obtained numerically (Chapter 5). A library of analytical and numerical intrinsic LAOStrain fingerprints is thus generated. The experimental fingerprints obtained in Chapter 3 are identity matched with the intrinsic fingerprints of constitutive models (developed in the library) that show similar qualitative signatures. Fitting the nonlinear parameter of the identified constitutive model helps infer the inherent microstructure of a chosen material as is discussed (Chapter 6).
Chapter 2

Theory

This chapter details the general theory behind intrinsic material functions for large amplitude oscillatory shear. A theory for LAOStrain intrinsic material functions is developed. A time domain representation is firstly considered and the disadvantages discussed therein. Physically interpretable intrinsic material functions are then defined through a coordinate transformation to a deformation domain, where stress is directly related to the strain and strain rate with time as an internal variable. A theory for LAOSTress material functions is also laid out.

2.1 Theory for LAOStrain

2.1.1 Time Domain LAOStrain

In LAOStrain, it is common convention [Ewoldt (2013)] to represent the input for the shear strain as

\[ \gamma(t) = \gamma_0 \sin \omega t, \]

where \( \gamma_0 \) is the strain amplitude and \( \omega \) is the imposed frequency. This consequently imposes an orthogonal strain rate

\[ \dot{\gamma}(t) = \dot{\gamma}_0 \cos \omega t \]

where \( \dot{\gamma}_0 \) is the strain rate amplitude. The resulting shear stress response can be represented as a Fourier series [Dealy and Wissburn (1990)]

\[ \sigma(t; \omega, \gamma_0) = \gamma_0 \sum_{n: \text{odd}} \left\{ G_n' \left( \omega, \gamma_0 \right) \sin n\omega t + G_n'' \left( \omega, \gamma_0 \right) \cos n\omega t \right\}, \]

1 Adopted from the authors’ work; Ewoldt.R.H, Bharadwaj.A.N, “Low-dimensional intrinsic material functions for nonlinear viscoelasticity,” Rheol. Acta (submitted)
where the Fourier moduli $G'_n(\omega, \gamma_0)$ and $G'^*_n(\omega, \gamma_0)$ are functions of input frequency $\omega$ and strain amplitude $\gamma_0$. The resulting stress signal is assumed to have attained a time-periodic response, or alternance [Giacomin et al (2011); Gurnon and Wagner (2012)], and is shear symmetric, hence the inclusion of only odd-harmonics $n$ in Eq. (2.3) [Hyun et al. (2011)].

An alternate representation of the resultant stress response is an infinite power series expansion in both strain amplitude and frequency [Onogi et al. (1970); Pearson and Rochefort (1982)]

$$
\sigma(t; \omega, \gamma_0) = \sum_{j: \text{odd}} \sum_{n: \text{odd}} \gamma_0^j \left[ G'_{jn}(\omega) \sin(n \omega t) + G'^*_n(\omega) \cos(n \omega t) \right].
$$

(2.4)

It is important to note that the coefficients $G'_{jn}(\omega)$ and $G'^*_n(\omega)$ are only a function of input frequency $\omega$, and all strain-dependence is assumed to originate from the integer power series expansion. In this notation, the linear viscoelastic moduli are represented as $G'(\omega) = G'_{11}(\omega)$ and $G'^*(\omega) = G'^*_{11}(\omega)$. Since the expansion is with respect to dimensionless strain amplitude, the coefficients $G'_{jn}(\omega)$ and $G'^*_n(\omega)$ maintain the dimensions of stress (F/L$^2$), or Pa in SI units. Comparing Eq. (2.3) and Eq.(2.4), the Fourier moduli, which are easier to calculate from measured data, can be related to the power expansion coefficients as

$$
\begin{align*}
G'_{1}(\omega, \gamma_0) &= G'(\omega) + G'_{31}(\omega) \gamma_0^2 + O\left(\gamma_0^4\right) \\
G'^*_{1}(\omega, \gamma_0) &= G'^*(\omega) + G'^*_{31}(\omega) \gamma_0^2 + O\left(\gamma_0^4\right) \\
G'_{3}(\omega, \gamma_0) &= G'_{33}(\omega) \gamma_0^2 + O\left(\gamma_0^4\right) \\
G'^*_{3}(\omega, \gamma_0) &= G'^*_{33}(\omega) \gamma_0^2 + O\left(\gamma_0^4\right).
\end{align*}
$$

(2.5)

In the limit of small amplitude $\gamma_0 \to 0$, the first-harmonic moduli reduce to the linear viscoelastic moduli $G'_{1}(\omega, \gamma_0) \to G'(\omega)$ and $G'^*_{1}(\omega, \gamma_0) \to G'^*(\omega)$.

The first observance of a nonlinear response is captured in Eq. (2.5) by the four $O(\gamma_0^2)$ terms that produce leading-order nonlinearities at finite $\gamma_0$. The physical interpretation of these four intrinsic nonlinearities is not clear from a time-domain representation. A change
of coordinate frame from the time domain to the deformation domain (Figure 2.1) is performed and appropriate orthogonal polynomials are used to define physically-meaningful intrinsic nonlinearities, as detailed in Section 2.1.2.

In many cases, a viscoelastic material is also characterized by viscosity coefficients. For this purpose, a scaling of stress with respect to strain-rate amplitude \( \dot{\gamma}_0 = \gamma_0 \omega \) is considered. The Fourier coefficients can then be represented as dynamic viscosity coefficients

\[
\sigma(t) = \dot{\gamma}_0 \sum_{n: \text{odd}} \left\{ \eta_n^+(\omega, \gamma_0) \sin n \omega t + \eta_n^-(\omega, \gamma_0) \cos n \omega t \right\}.
\]

For this viscous perspective the power function expansion is \( \text{Fan and Bird (1984); Giacomin et al. (2011)} \)

\[
\sigma(t) = \sum_{j: \text{odd}} \sum_{n: \text{odd}} \dot{\gamma}_0^j \left\{ \eta_{jn}^+(\omega) \sin (n \omega t) + \eta_{jn}^-(\omega) \cos (n \omega t) \right\}.
\]

In the expansion with respect to strain-rate, the coefficients \( \eta_{jn}^+(\omega) \) and \( \eta_{jn}^-(\omega) \) have dimensions that depend on the power \( j \). For \( j = 1 \) the dimension are that of viscosity (F.T/L^2), or Pa.s in SI units. But in general the dimensions depend on the index \( j \) as (F.T^j/L^2). Due to these peculiar dimensions, the expansion with respect to dimensionless strain amplitude \( \gamma_0 \) may be preferred, as in Eq.(2.4). It is for this reason that the strain-amplitude expansion will be used in the deformation-domain Chebyshev representation given in the following section, for shear strain-controlled LAOS. We will see that for shear stress-controlled LAOS the expansion is with respect to stress amplitude \( \sigma_0 \), and the peculiar dimensions are unavoidable for the intrinsic coefficients.

**2.1.2 Deformation domain LAOStrain**

Meaningful interpretation of LAOS nonlinearities comes from a coordinate transformation to the deformation domain (Figure 2.1) with time as an internal variable.
Figure 2.1 LAOStrain response of the Giesekus model ($\alpha = 0.3$) at $De = 1$ and $\gamma_0^* = 0.6852$ chosen such that $[|\varepsilon_1|\gamma_0^*/G'] = 0.1$. Representation of the nonlinear response is possible in (a) the time domain as periodic waveforms and in (b) the deformation domain as parametric loops; dashed and dotted lines are elastic stress $\sigma^e(\gamma)$ and viscous stress $\sigma^v(\dot{\gamma})$, respectively. The deformation domain Lissajous curves are more insightful and provide meaningful physical interpretations to each kind of nonlinearity depending on their signs and magnitudes whereas this information is uninterpretable in the time domain representation.

Starting with LAOStrain, we use normalized deformation-domain parameters

$$x \equiv \gamma(t)/\gamma_0 = \sin \omega t$$

$$y \equiv \dot{\gamma}(t)/\gamma_0^* = \cos \omega t$$

(2.8) (2.9)

to represent the total stress $\sigma$ as a superposition of elastic stress $\sigma^e(\gamma)$ and viscous $\sigma^v(\dot{\gamma})$ stresses [Cho et al. (2005)]

$$\sigma(x, y; \omega, \gamma_0) = \sigma^e(x; \omega, \gamma) + \sigma^v(y; \omega, \dot{\gamma}).$$

(2.10)
This decomposition is based on the idea that the elastic and viscous stresses are functions of instantaneous strain $\gamma$ and strain rate $\dot{\gamma}$, respectively. Thus, the decomposed stresses can be represented as single valued functions of strain and strain rate. This interpretation of elastic and viscous stress is well-established in the linear viscoelastic regime, and we therefore expect it to be well-defined for the asymptotic nonlinear regime as well. It is worth remarking that these decomposed measures are not useful at very large deformations, especially for yield stress fluids, in which case local measures of nonlinearities have proven useful [Rogers and Lettinga (2012)], including for LAOSTress [Dimitriou et al. (2013)].

The decomposed stresses in Eq.(2.10) can be represented in terms of orthogonal Chebyshev polynomials of the first kind [Ewoldt et al. (2008)]

$$
\sigma^e(x; \omega, \gamma) = \gamma_0 \sum_{n: \text{odd}} e_n(\omega, \gamma_0) T_n(x) \tag{2.11}
$$

$$
\sigma^v(y; \omega, \dot{\gamma}) = \dot{\gamma}_0 \sum_{n: \text{odd}} v_n(\omega, \gamma_0) T_n(y) \tag{2.12}
$$

where $e_n(\omega, \gamma_0)$ and $v_n(\omega, \dot{\gamma}_0)$ are functions of the LAOS input parameters $\omega$ and $\gamma_0$. The Chebyshev basis functions $T_n(x)$ are defined by the recurrence relation [Abramowitz and Stegun (1964)]

$$
\begin{align*}
T_0(x) &= 1 \\
T_1(x) &= x \\
T_{n+1}(x) &= 2xT_n(x) - T_{n-1}(x).
\end{align*} \tag{2.13}
$$

The third harmonic is the most important for intrinsic (leading order) nonlinearities, $T_3(x) = 4x^3 - 3x$. The Chebyshev coefficients are directly related to the Fourier coefficients of Eq.(2.3) and Eq.(2.6) by the relations for $n$ odd [Ewoldt et al. (2008)].

$$
\begin{align*}
e_n &= G_n'(-1)^{(n-1)/2} = \omega \eta_n'(-1)^{(n-1)/2} \\
v_n &= \frac{G_n''}{\omega} = \eta_n'
\end{align*} \tag{2.14}
$$
Some interpretations of first- and third-harmonic coefficients were given previously (Ewoldt et al. 2008). The first-harmonic material functions $e_1(\omega, \gamma_0) = G'_1(\omega, \gamma_0)$ and $v_1(\omega, \gamma_0) = \eta'_1(\omega, \gamma_0)$ are measures of average elasticity and average dissipation, respectively. They are coefficients of a linear basis response, but this basis response is only equivalent to the linear viscoelastic response of $G'(\omega)$ and $\eta'(\omega)$ in the limit of zero strain amplitude.

The third-harmonic measures add the basis function $T_3(x) = 4x^3 - 3x$, and indicate local changes and distortion of the decomposed stresses. The coefficients $e_3(\omega, \gamma_0)$ and $v_3(\omega, \gamma_0)$ determine the leading order convexity of the decomposed elastic and viscous stresses, respectively. Adding a positive function $T_3(x)$ results in curves with positive convexity for positive instantaneous strains. This convexity of the decomposed elastic curve may indicate strain-dependent stiffening for $e_3(\omega, \gamma_0) > 0$, or softening with $e_3(\omega, \gamma_0) < 0$, whereas for the viscous curve the convexity indicates strain-rate dependent thickening ($v_3(\omega, \gamma_0) > 0$) or thinning ($v_3(\omega, \gamma_0) < 0$) [Ewoldt et al. (2008)]. We qualify this interpretation below when we interpret the response of Figure 2.1 in terms of the intrinsic Chebyshev coefficients.

We now define low-dimensional intrinsic Chebyshev nonlinearities, using an integer power function expansion of $e_n(\omega, \gamma_0)$ and $v_n(\omega, \gamma_0)$ with respect to dimensionless strain amplitude. This is similar to Eq.(2.5) which expands the Fourier coefficients $G'_n(\omega, \gamma_0)$ and $G''_n(\omega, \gamma_0)$. The leading-order Chebyshev expansion, with the inter-relation to the Fourier coefficients, is

$$
\begin{align*}
 e_1(\omega, \gamma_0) &= G'_1(\omega, \gamma_0) = G'(\omega) + [e_1](\omega)\gamma_0^2 + O(\gamma_0^4) \\
 e_3(\omega, \gamma_0) &= -G'_3(\omega, \gamma_0) = [e_3](\omega)\gamma_0^2 + O(\gamma_0^4) \\
 v_1(\omega, \gamma_0) &= \eta'_1(\omega, \gamma_0) = \eta'(\omega) + [v_1](\omega)\gamma_0^2 + O(\gamma_0^4) \\
 v_3(\omega, \gamma_0) &= \eta'_3(\omega, \gamma_0) = [v_3](\omega)\gamma_0^2 + O(\gamma_0^4)
\end{align*}
$$

(2.15)

where the elastic coefficients $G'(\omega)$, $[e_1](\omega)$, $[e_3](\omega)$, and the viscous coefficients $\eta'(\omega)$, $[v_1](\omega)$ and $[v_3](\omega)$ are functions of only frequency $\omega$. 

14
The four nonlinearities of Eq. (2.15) are summarized graphically in Figure 2.2. The nonlinearities are decomposed to show how each independently rotates or bends the Lissajous curves and decomposed stress curves. The first-harmonic nonlinearities each cause rotation of the underlying linear basis function (increasing slope for positive values of \([e_1](\omega)\) and \([v_1](\omega)\)). The underlying basis function is linear, but it changes for each cyclic loading at increasing strain amplitude – this has been termed intercycle nonlinearity [Ewoldt et al. (2008)]. Physically, the rotation is interpreted as changes in the average elasticity or viscosity, revealed when plotted in the domain of stress versus strain or stress versus strain rate.

The third-harmonic intrinsic nonlinearities bend and twist the decomposed stress response, by adding the third-harmonic basis function \(T_3(x) = 4x^3 - 3x\). This basis function represents local deviation from the linear basis function. It tells of the relative differences in local nonlinear effects, relative nonlinearities within a single cycle – this has been called intracycle nonlinearity [Ewoldt et al. (2008)]

We now interpret the Giesekus model response shown in Figure 2.1b at \(De = 1\). At this frequency, the chosen strain amplitude \((\dot{\gamma}_0 = 0.6852)\) resides in the low-dimensional intrinsic LAOS regime. The emergence of nonlinearity changes the shape of the elastic and viscous decomposed stress curves, which is explained by the signs and magnitudes of the intrinsic nonlinearities. The \([e_1]\) nonlinearity dominates in this example (as can be seen from the magnitudes in the inset of Figure 2.2). The negative values of \([e_1]\) and \([e_3]\) signify average elastic softening (clockwise rotation) and instantaneous elastic strain softening (mild distortion) in the decomposed elastic stress curve. Independently, negative \([v_1]\) signifies average viscous thinning (clockwise rotation). Positive \([v_3]\) captures relative local changes separate from the average; \([v_3]>0\) bends the curve such that relative thinning occurs at \(\dot{\gamma} = 0\) and relative thickening at \(\dot{\gamma} = \dot{\gamma}_0\). Since the average change is thinning, \([v_1]<0\), we prefer here to interpret \([v_3]>0\) as an indicator of the location of relatively more thinning, which is near \(\dot{\gamma} = 0\), or equivalently \(\gamma = \pm \gamma_0\).
An important distinction is that Eq.(2.15) does not use a scaling with respect to the linear viscoelastic material functions. Such a scaling is possible, and for example this would result in modifying Eq.(2.15) to take the form (for just the first-harmonic elastic modulus)

$$G'_1(\omega, \gamma_0) = G'(\omega) \left(1 + \frac{[e_1](\omega)}{G'(\omega)} \gamma_0^2 + O(\gamma_0^4)\right).$$  

(2.16)

Figure 2.2 Schematic showing possible nonlinear viscoelastic contributions to LAOStrain deformation. Lissajous curves are normalized by strain amplitude $\gamma_0$ and the linear viscoelastic stress amplitude $\sigma_0$. Each intrinsic nonlinearity is shown separately, each contribution 10% nonlinearity compared to the linear response. Positive values are shown for illustration. Negative values of $[e_1]$ and $[v_1]$ would instead rotate the curves clockwise, and negative values of $[e_3]$ and $[v_3]$ would cause the opposite convexity.

The ratio of $[e_1](\omega)/G'(\omega)$ is analogous to intrinsic viscosity $[\eta](\dot{\gamma})$ of Eq.(1.1). This is certainly a useful quantity as shown in Eq.(1.3). However, this ratio is not suggested as a fundamental material function since it would complicate the definition and also include
numerical errors associated with division involving two measured quantities with finite precision error.

2.1.3 Interrelations with other measures

The four intrinsic material functions can be related to other nonlinear viscoelastic measures, including local measures of nonlinearity introduced by [Ewoldt et al. (2008)]. This gives context to the intrinsic measures and supports their physical interpretation. We also give interrelations with other notation to facilitate conversion to a common framework, which we will do for some published literature results in Chapter 4.

Local measures of nonlinear viscoelasticity were introduced by [Ewoldt et al. (2008)], showing particular locations on Lissajous curves that can be used to define viscoelastic moduli and dynamic viscosities. At the minimum instantaneous strain \( \gamma = 0 \) (equivalent to maximum strain rate \( \dot{\gamma} = \pm \dot{\gamma}_0 \)), the local slope is a measure of elastic modulus,

\[
G'_M \equiv \left( \frac{d\sigma}{d\gamma} \right)_{\gamma=0, \dot{\gamma}=\pm\dot{\gamma}_0} = \sum ne_n(\omega,\gamma_0)(-1)^{(n-1)/2}. \tag{2.17}
\]

A corresponding measure at the largest instantaneous strain \( \gamma = \pm \gamma_0 \) (equivalent to minimum strain rate \( \dot{\gamma} = 0 \)) is also a measure of local elastic modulus

\[
G'_L \equiv \left( \sigma \right)_{\gamma=\pm\gamma_0, \dot{\gamma}=0} = \sum ne_n(\omega,\gamma_0). \tag{2.18}
\]

In terms of the intrinsic elastic nonlinearities, the various measures of elastic modulus are

\[
\begin{align*}
G'_I(\omega,\gamma_0) &= G'(\omega) + \gamma_0^2 [e_1](\omega) + O(\gamma_0^4) \\
G'_M(\omega,\gamma_0) &= G'(\omega) + \gamma_0^2 \{[e_1](\omega) - 3[e_3](\omega)\} + O(\gamma_0^4) \\
G'_L(\omega,\gamma_0) &= G'(\omega) + \gamma_0^2 \{[e_1](\omega) + [e_3](\omega)\} + O(\gamma_0^4).
\end{align*} \tag{2.19}
\]

The average measure \( G'_I(\omega,\gamma_0) \) is influenced only by \([e_1](\omega)\), but the local measures \( G'_M(\omega,\gamma_0) \) and \( G'_L(\omega,\gamma_0) \) are dependent on a combination of \([e_1](\omega)\) and \([e_3](\omega)\), with a
different sign dependence on \([e_j](\omega)\) for each. For finite \([e_3](\omega)\), at leading order, the average measure \(G'_1(\omega, \gamma_0)\) will always lie between \(G'_M(\omega, \gamma_0)\) and \(G'_L(\omega, \gamma_0)\).

Analogous intrinsic relations can be derived for average viscosity \(\eta'_1(\omega, \gamma_0)\), minimum-rate viscosity \(\eta'_M(\omega, \gamma_0)\), and large-rate viscosity \(\eta'_L(\omega, \gamma_0)\). These are functions of intrinsic viscous measures \([v_1](\omega)\) and \([v_3](\omega)\) in the same form as Eq.(2.19).

There are several different measures to characterize a nonlinear response to LAOS, but in the intrinsic regime only four measures are required. This is the power of the low-dimensional representation with intrinsic material functions. Deeper into the nonlinear regime the \(O(\gamma_0^4)\) and higher terms appear, and the local measures of \(G'_M(\omega, \gamma_0)\), \(\eta'_M(\omega, \gamma_0)\), etc. become of increasing importance.

Only four intrinsic nonlinearities are required for the shear response, but various nomenclature exists to represent them, as discussed in Section 2.1.1. Below, inter-relations are given for converting other nomenclature to the Chebyshev nomenclature here, \([e_1](\omega)\), \([e_3](\omega)\), \([v_1](\omega)\), \([v_3](\omega)\). The Chebyshev coefficient representation is preferred as it allows for a physical interpretation [Ewoldt et al. (2008)] and is immune to the trigonometric reference of the input which can cause ambiguous signs of higher-harmonic Fourier coefficients (Ewoldt 2012). Previous work has represented intrinsic nonlinearities in the time-domain, with either the elastic or viscous scaling (Eq.(2.4) or Eq.(2.7)). To convert these results from the Fourier representation to the Chebyshev representation, we use the inter-relation of Eq.(2.14) and compare coefficients of the power function expansions, from Eq.(2.4), Eq.(2.7), and Eq.(2.15). The relation is

\[
\begin{align*}
[e_1](\omega) &= G'_{31}(\omega) = \omega^3 \eta''_{31}(\omega) \\
[e_3](\omega) &= -G'_{33}(\omega) = -\omega^3 \eta''_{33}(\omega) \\
[v_1](\omega) &= \frac{G''_{31}(\omega)}{\omega} = \omega^2 \eta''_{31}(\omega) \\
[v_3](\omega) &= \frac{G''_{33}(\omega)}{\omega} = \omega^2 \eta''_{33}(\omega)
\end{align*}
\] (2.20)
The conversions result in sign changes (to change from the time-domain to the deformation-domain), and factors of $\omega$ which occur for two reasons. First, because the viscous Chebyshev coefficients $v_1(\omega, \gamma_0)$ and $v_3(\omega, \gamma_0)$ are defined by a shear-rate scaling, giving the coefficients dimensions of viscosity. Second, the intrinsic coefficients $[v_1](\omega)$ and $[v_3](\omega)$ also have dimensions of viscosity since the power function expansion is still with respect to the dimensionless strain amplitude $\gamma_0$, Eq.(2.15).

Although four independent intrinsic nonlinearities exist, some studies have chosen to combine the third harmonic terms into a lumped measure [Hyun and Wilhelm (2009)]. In this case the relative intensity of the third harmonic is normalized by the first harmonic, $I_{3l} = I_3 / I_1$. Based on intrinsic regime scaling, a nonlinear coefficient is defined as $Q(\omega, \gamma_0) = I_{3l} / \gamma_0^2$. In the asymptotic limit of small strain amplitudes, or intrinsic LAOS, it is possible to obtain $Q_0(\omega) = \lim_{\gamma_0 \to 0} Q(\omega, \gamma_0)$. Using our notations, we rewrite this lumped intrinsic measure as

$$Q_0 = \frac{\sqrt{|e_1|^2 + (|v_3|\omega)^2}}{\sqrt{G_1^2 + G_1^2}}. \quad (2.21)$$

Such lumped parameters are intrinsic, and can be useful, but they omit first-harmonic nonlinearities, combine the elastic and viscous third-harmonic measures, and remove the sign information. The significance of signs and magnitudes of each intrinsic measure is shown in Chapter 4 where the signatures are used to contrast and compare between constitutive models. Chapter 6 shows experimental fingerprints to demonstrate the importance of these measures in identifying underlying microstructure.

Stress controlled large amplitude oscillatory shear experiments are also considered by rheologists for material characterization. In contrast to a LAOStrain framework where analytical asymptotic solutions exist, there are no available analytical solutions for a LAOStress framework in the intrinsic regime, and hence no definitions. Intrinsic material functions for a LAOStress protocol are defined in the next section.
2.2 Theory for LAOStress

Here, a framework and notation is introduced for interpretation of LAOStress. Choosing the right form to represent the input stress is vital [Ewoldt (2013)] requiring that the input signal be defined as

\[ \sigma(t) = \sigma_0 \cos \omega t. \]  

(2.22)

The strain and strain rate response can be represented as

\[ \gamma(t) = \tilde{\gamma}(\omega, \gamma_0) + \sigma_0 \sum_{n: \text{odd}} \left\{ J'_n(\omega, \sigma_0) \cos n \omega t + J''_n(\omega, \sigma_0) \sin n \omega t \right\} \]  

(2.23)

\[ \dot{\gamma}(t) = \sigma_0 \sum_{n: \text{odd}} \left\{ -\phi'_n(\omega, \sigma_0) \sin n \omega t + \phi''_n(\omega, \sigma_0) \cos n \omega t \right\} \]  

(2.24)

where \( J'_n, J''_n \) are compliances and \( \phi'_n, \phi''_n \) are fluidities. The term \( \tilde{\gamma}(\omega, \gamma_0) \) represents the zeroth harmonic accounting for the possibility of the output strain signal not being centered about zero. An alternate series expansion of the resulting strain in the powers of stress amplitude and frequency is

\[ \gamma(t; \omega, \sigma_0) = \tilde{\gamma}(\omega, \gamma_0) + \sum_{j: \text{odd}} \sum_{n: \text{odd}} \sigma_0^n \left\{ J'_n(\omega) \cos(\omega t) + \phi'_n(\omega) \sin(\omega t) \right\} \]  

(2.25)

which can be expanded as

\[ \gamma(t; \omega, \gamma_0) = \tilde{\gamma}(\omega, \gamma_0) + \sigma_0 \left\{ J'(\omega) \cos \omega t + J''(\omega) \sin \omega t \right\} + \sigma_0^3 \left\{ J'_{31}(\omega) \cos 3\omega t + J''_{31}(\omega) \sin 3\omega t \right\} + O(\sigma_0^5) \]  

(2.26)

where the linear viscoelastic compliances are \( J'(\omega) = J'_{11}(\omega) \) and \( J''(\omega) = J''_{11}(\omega) \). A relation between the Fourier moduli and the power expansion coefficients can be obtained by comparing Eq.(2.23) and Eq.(2.26)
\[ J'_1(\omega, \gamma_0) = J'(\omega) + J'_3(\omega)\sigma_0^2 + O\left(\sigma_0^4\right) \]
\[ J'_1(\omega, \gamma_0) = J''(\omega) + J'_3(\omega)\sigma_0^2 + O\left(\sigma_0^4\right) \]
\[ J'_3(\omega, \gamma_0) = J'_3(\omega)\sigma_0^2 + O\left(\sigma_0^4\right) \]
\[ J''_3(\omega, \gamma_0) = J''_3(\omega)\sigma_0^2 + O\left(\sigma_0^4\right). \] (2.27)

The first-harmonic measures again represent a cyclic average, but physical interpretations for the third-harmonic measures are not yet apparent. For the same reasons stated earlier, a switch is made to the deformation domain framework to introduce a Chebyshev representation \([\text{Ewoldt et al. (2008)}]\) through a harmonic stress input \(\sigma(t)\) made dimensionless as

\[ z = \frac{\sigma(t)}{\sigma_0}. \] (2.28)

The resulting strain response is decomposed into apparent elastic and viscous components,

\[ \gamma = \gamma^e(\sigma) + \gamma^v(\sigma) \] (2.29)

which can be rewritten in a viscous perspective in terms of strain rate as

\[ \dot{\gamma} = \dot{\gamma}^e(\sigma) + \dot{\gamma}^v(\sigma). \] (2.30)

The elastic and viscous decompositions result from the idea that the elastic strain and viscous strain-rate are both instantaneous functions of stress. The Chebyshev representation follows as

\[ \gamma^e(\sigma) = \sigma_0 \sum_{n = \text{odd}} c_n T_n(z) \]
\[ \gamma^v(\sigma) = \sigma_0 \sum_{n = \text{odd}} f_n T_n(z) \] (2.31)

where \(c_n\) stands for compliances and \(f_n\) stands for fluidities. As is the case in LAOStrain control, a direct relationship can be identified between the Fourier and Chebyshev coefficients

\[ c_n = J'_n \]
\[ f_n = n\omega J''_n. \] (2.32)
The leading-order Chebyshev expansion, with the inter-relation to the Fourier coefficients, is

\[
\begin{align*}
  c_1(\omega, \sigma_0) &= J'(\omega, \sigma_0) = J'(\omega) + [c_1](\omega)\sigma_0^2 + O(\sigma_0^4) \\
  c_3(\omega, \sigma_0) &= J'_3(\omega, \sigma_0) = [c_3](\omega)\sigma_0^2 + O(\sigma_0^4) \\
  f_1(\omega, \sigma_0) &= \phi'_1(\omega, \sigma_0) = \phi'(\omega) + [f_1](\omega)\sigma_0^2 + O(\sigma_0^4) \\
  f_3(\omega, \sigma_0) &= \phi'_3(\omega, \sigma_0) = [f_3](\omega)\sigma_0^2 + O(\sigma_0^4),
\end{align*}
\]

(2.33)

where the intrinsic compliances and fluidities are a function of frequency only. The signs are conveniently all positive in this inter-relation, resulting from the choice of a cosine input in Eq.(2.22) rather than a sine input to define the Fourier coefficients [Ewaldt (2013)].

The dimensions of the orthogonal Chebyshev coefficients \( c_n(\omega, \gamma_0) \) are compliance \((L^2/F)\) or \(1/\text{Pa}\) in SI, but the intrinsic compliance coefficients \([c_1](\omega)\) and \([c_3](\omega)\) have dimensions \((L^4/F)\) due to the power function expansion with respect to stress amplitude \(\sigma_0\). There is a similar difference between the dimensions of the orthogonal Chebyshev coefficients \( f_n(\omega, \gamma_0) \) which have dimensions of fluidity, or inverse viscosity \(L^2/(\text{FT})\), and the intrinsic fluidities \([f_1](\omega)\) and \([f_3](\omega)\) having dimensions of \(L^6/(\text{FT}^3)\). Such cumbersome dimensions are not uncommon for intrinsic measures, e.g. when intrinsic viscosity \(\eta\) is defined from an expansion with respect to concentration, rather than volume fraction.

The first-harmonic material functions \([c_1](\omega)\) and \([f_1](\omega)\) encode the average changes of compliance and fluidity as the stress amplitude is increased. As with LAOStrain, these LAOStress measures cause rotation of Lissajous curves (positive is counterclockwise, negative is clockwise). The intrinsic third-harmonics \([c_3](\omega)\) and \([f_3](\omega)\) represent relative nonlinearities within a cycle, as a function of the input stress. Adding a positive third-harmonic basis function \(T_3(z)\) will at high stress cause relatively higher compliance (or fluidity), and at low stress relatively lower compliance (or fluidity). The local changes (intracycle nonlinearities) should be interpreted in the context of the average changes, as indicated by \([c_1](\omega)\) and \([f_1](\omega)\).

There is an important difference here between LAOStress and LAOStrain. In LAOStrain the elastic response is referenced to strain and viscous response to strain-rate,
Eq.(2.11)-(2.12). In LAOStress, there is only one input to reference, the stress $\sigma$, as shown in Eq.(2.31). Moreover, stress is an absolute reference input. Zero stress and maximum stress are clearly defined, in contrast to the strain-input which can be reset by yielding events and confuse the interpretation of local responses as “zero strain”. In this way, LAOStress is perhaps easier to interpret than LAOStrain.

For both LAOStrain and LAOStress, the low-dimensional description of the intrinsic regime is based on the assumption of a power-function expansion of the response. A subtle point is that an integer expansion has been assumed, and this is the case for all known prior work in this area. Such integer expansions may be insufficient for some rheological responses and non-integer power expansions may be required [Ewoldt & Bharadwaj (submitted)]
Chapter 3

Experimental Results

Rheological measurements were performed using a separated motor-transducer ARES-G2 rotational rheometer (TA Instruments). Strain controlled LAOS tests are performed on a transiently crosslinked PVA-Borax system. A cone-plate geometry with a cone diameter of 50 mm was used for these tests. Constant amplitude frequency sweeps are performed to identify a plateau modulus and a steady shear viscosity. Constant frequency strain amplitude sweeps are then performed and frequency dependent intrinsic shear material functions are extracted from the visibly nonlinear response. The intrinsic rheological fingerprints (in terms of the four nonlinearities) of the PVA-Borax are presented as a function of frequency.

3.1 Materials

A mixture of Poly-vinyl alcohol (PVA) and Sodium tetra borate (Borax) was considered for rheometric measurements. A di-diol complexation reaction drives the formation of this mixture, where ion-assisted thermoreversible crosslinks develop between the two diol units of PVA and one borate ion (shown in Figure 3.1). Extensive study of such reversible gels has been undertaken owing to their physical and chemical properties [Kurokawa et al. (1992); Koike et al. (1995); Keita et al. (1995); Lin et al. (2005)]. The choice of this system is motivated by its simplicity and effectiveness, in-as-much as it shows a single relaxation behavior [Koike et al. (1995)] and simultaneously shows nonlinear signatures under LAOS as we will see in Section 3.3.

The mixture preparation protocol was as follows. 99% hydrolyzed PVA with molecular weight $M_w$ ranging from 85,000 – 110,000 was obtained from Sigma Aldrich Chemical Company in granulated form and was dissolved in deionized water to form a 4%
Figure 3.1 PVA-Borax reacts in two stages a) monodiol complexation reaction with a borate ion b) crosslink reaction (di-diol reaction)

stock solution. The dissolution was carried out in two stages: first by dispersing PVA in water by stirring at room temperature and then by continuous stirring at a temperature of 95°C for about 2 hours until a homogeneous transparent solution was obtained. The sample was heated to accelerate the dissolution process, which otherwise was found slow and ineffective at room temperature. The Sodium tetra borate sample, obtained in granulated form from Sigma Aldrich Chemical Company was also mixed under similar conditions to form a 4% stock solution. The stirring was carried out using a magnetic stir rod and throughout the stirring process, the containers were sealed with a layer of plastic film to avoid evaporation losses.

The two solutions were then allowed to cool ambiently and mixed together to form a transient crosslinked complex of PVA/Borax [Koike et al. (1995)] with 2.75 wt.% PVA and 1.25 wt.% Borax (PVA: Borax :: 2.2:1). Mixing was done by transferring measured volumes of each component into a closed test tube and shaking them to the point where each of the components mixed thoroughly with the other. It was noticed that the concentration of PVA drastically affected the viscosity of the resulting mixture and at this concentration (2.75 % PVA) the gel was just at the point where it no longer behaved/flowed like a liquid. The gel was allowed to rest to allow the contents to fully interact and later centrifuged at 3000 rpm for 10 minutes to get rid of trapped air bubbles (CL2 Centrifuge, Thermo Scientific). The
resulting homogeneous mixture was then used for rheometric tests described in following section.

3.2 Linear Viscoelastic Results

Measurements were performed with a separated-motor-transducer rotational rheometer (ARES-G2, TA Instruments) using a cone-plate geometry. A cone geometry is chosen as it imposes a homogeneous strain field that may prevent the sample from rupturing. A large cone radius (50 mm, 0.04 rad) was chosen for better torque sensitivity at lower input strains which assists in accurate extraction of nonlinearities (Section 3.3.2)). To avoid shear heating of the sample, experiments were carried out at a temperature of 25°C maintained by Peltier system in the lower plate. The sample was uniformly coated with mineral oil around its periphery. This layer of mineral oil acts as a barrier between the sample and the external atmosphere and prevents evaporation losses in the course of the test. Significant evaporation losses were observed for tests run on a sample without this coating.

A standard sample loading protocol was followed. The prepared sample (stored in a graduated test tube) was poured onto the temperature controlled bottom plate to form a round puddle. The upper geometry was then lowered at a rate limited by the normal reaction force that the sample generated as it was being deformed. The cap on this limiting normal force was set to a bare minimum (0.3 N) to prevent damage to the sample and the sensitive instrument transducer as the upper geometry squeezed on the material. Care was also taken to confine the puddle to the center of the plate so that the material spread out uniformly and completely occupied the gap before the test was executed. After lowering the geometry, excess sample was trimmed to match the sample radius to the cone radius and mineral oil applied to the outer edge. To be sure that LAOS tests were run on a completely relaxed sample, the axial force of the loaded sample was allowed to relax to a constant value over a zero displacement stress relaxation test for 2700 seconds.

As preliminary tests to identify the linear viscoelastic (SAOS) regime, strain amplitude sweeps were carried out starting from \( \gamma_0 = 0.1\% \) to \( \gamma_0 = 100\% \) at a fixed frequency of \( \omega = 1 \) rad/s. Reverse amplitude sweeps were subsequently performed to check for reversibility. Figure 3.2 shows the strain amplitude sweeps where overlapping data points in
forward and reverse amplitude sweeps confirm reversibility. The response is linear up to $\gamma_0 \sim 1\%$, beyond which slight deviations are observed from a linear behavior.

Figure 3.2 Forward (open circles) and reverse (filled circles) amplitude sweep on the PVA-Borax system. A linear viscoelastic region can be assumed till a $\gamma_0 = 1\%$. Overlapping data points confirm reversibility.

A strain amplitude of $\gamma_0 = 0.1\%$ (from the linear viscoelastic SAOS regime) was chosen for the oscillation frequency sweep, performed from $\omega = 0.01$ to $\omega = 100$ rad/s. Figure 3.3 shows the frequency dependent first harmonic moduli (in symbols). A single mode Maxwell model fits the data reasonably well, particularly at low and high frequencies. This Maxwellian fit (shown as solid lines in Figure 3.3) results in a plateau modulus $G_0 = 700$ Pa and a steady shear viscosity $\eta_0 = 250$ Pa.s which are used to define a characteristic time scale $\lambda = \eta / G = 0.357$ s.

A frequency corresponding to this timescale can alternately be found as $\omega = 1 / \lambda = 2.8$ s$^{-1}$. LAOS tests are performed at frequencies that result in a Deborah number (De) within ten orders of magnitude (on either side of a log scale) of the De corresponding to the characteristic time scale of the material. LAOStrain tests were constant frequency strain amplitude sweeps with 5 points per decade of strain amplitude ranging from 0.1% to 250%. The upper limit of strain amplitude was reduced for high frequency tests (beyond 10 rad/s...
to avoid fracture and slippage of material). The identified values for the plateau modulus (700 Pa) and steady shear viscosity (280 Pa.s) will be used to normalize intrinsic elastic and viscous measures respectively.

![Graph showing oscillation frequency sweep on the PVA-Borax system at $\gamma_0 = 0.1\%$](image)

Figure 3.3 Oscillation frequency sweep on the PVA-Borax system at $\gamma_0 = 0.1\%$. A Maxwell model fit (lines) to the data results in a plateau modulus $G_0$ at high frequencies and steady shear viscosity $\eta_0$ in the terminal regime.

### 3.3 Asymptotic nonlinear results from [LAOStrain]

The raw transient data of the resulting stress response was analyzed using the FT-Rheology package in TRIOS software (TA Instruments) which decomposes the stress signal into its constitutive first and higher harmonic components and gives the Fourier moduli and Chebyshev coefficients. The elastic and viscous intrinsic nonlinearities are reported after normalizing them with the plateau modulus and steady shear viscosity respectively.

For a deformation controlled experiment at a given frequency, measurements at low strain amplitudes are characterized by a small magnitude torque amplitude response. Measurements are meaningful provided the torque amplitude response is beyond the lower limit of torque resolution, or the torque noise floor $T_{\text{noise}}$. This is observed at a specific
magnitude of strain (the magnitude of which may vary with frequency), when the intrinsic nonlinearities clearly rise above the measurement resolution and show an intrinsic power law scaling $\sim \gamma_0^2$. For instance, this asymptotic scaling is observed in the in phase third harmonic stress component

$$\gamma_0 e_3(\omega, \gamma_0) = F_\sigma T_{\text{noise}} + \gamma_0^3 \epsilon_3(\omega) + O(\gamma_0^5)$$

(3.1)

where $F_\sigma$ is the geometry factor to convert torque to stress. For the cone geometry $F_\sigma = 3/(2\pi R^3)$. A form analogous to Eq. (3.1) is used for other intrinsic nonlinear deviations as well. We let $T_{\text{noise}}$ be a free parameter in our fits that in turn determines the emergence of each intrinsic measure from the torque noise floor. For $\omega = 1$ rad/s, we fit $T_{\text{noise}} = 0.917 \, \mu\text{Nm}$ for the $e_3(\omega, \gamma_0)$ signal and $T_{\text{noise}} = 2.683 \, \mu\text{Nm}$ for $v_3(\omega, \gamma_0)$. A minimum torque amplitude criterion is determined using this concept of $T_{\text{noise}}$ that aids in visualizing data. If the torque amplitude associated with the measured quantity is less than the minimum torque, for instance $3 \, \mu\text{Nm}$ for 1 rad/s, the symbols are made less prominent by lighter shading/coloring as can be seen from Figure 3.4.

Figure 3.4 LAOStrain amplitude sweep showing the $\gamma_0^2$ scaling of all four intrinsic nonlinearities for the PVA-Borax system at $\omega = 1$ rad/s. The fit lines for $[e_3](\omega)$ and $[v_3](\omega)$ include a torque noise floor in the form of Eq.(3.1). Data points in the noise floor have modified symbol color (less color saturation), on the condition that the associated torque amplitude is less than $3 \, \mu\text{Nm}$. 
A similar approach is adopted for strain amplitude sweeps at each considered frequency. This extraction process is shown in Figure 3.5. The extracted intrinsic nonlinearities are compiled and presented as a fingerprint for the material as a function of the imposed frequency. These signatures are discussed in the following section.

Figure 3.5 (cont.)
As was discussed in the previous section, frequency dependent intrinsic LAOStrain material functions are extracted for the entire range of frequency. Figure 3.6 shows the frequency-dependent fingerprint of all four intrinsic nonlinearities of the PVA-Borax system.
3.4 Interpretation of [LAOStrain] fingerprints of PVA-Borax

For the experimental measurement, the first harmonic measures are always positive, indicating elastic stiffening and viscous thickening of the average viscoelastic response. These first-harmonic intrinsic measures represent the intercycle nonlinearity as strain amplitude increases [Ewoldt et al. (2008)], causing counter-clockwise rotation of both the viscous and elastic Lissajous curves. The signature of $[e_i](\omega) > 0$ and $[\eta_i](\omega) > 0$ is related to Type II behavior of LAOS, defined by [Hyun et al. (2002)], who also demonstrated this with a PVA-Borax system, at a single frequency. We see that this Type II LAOS behavior occurs across the entire frequency range shown in Figure 3.6.

It is noteworthy that average viscous shear-thickening, $[\eta_i] > 0$, is the asymptotic nonlinearity across the entire range of frequency of Figure 3.6, even for $\lambda \omega \ll 1$. This may
be related to shear-induced increase of physical associations. Similarly, average elastic stiffening, \([e_1] > 0\), is observed for the entire range of frequency. Such stiffening at \(\lambda \omega \gg 1\) may come from inherent elastic nonlinearities of the polymers, non-affine deformation, or geometric nonlinearities of the evolving network. The fact that elastic stiffening persists for \(\lambda \omega \ll 1\), when the network has ample time to relax, suggests that the elastic stiffening is mostly likely due to inherent nonlinear elasticity of the polymeric chains, which start from a stretched state. These first-harmonic nonlinearities give the average intercycle nonlinearity, but further insight comes from the third-harmonics, which we use to interpret whether it is large strain or strain-rate that induces the nonlinearity as a function of frequency.

The third harmonic measures change sign as a function of frequency. Such a signature would be lost with any lumped measure of the third-harmonic intensity \((Q_0 \text{ coefficient defined in Eq. 2.21})\). Figure 3.7 shows that this measure is always positive. Intrinsic third harmonics indicate the instantaneous location of developing nonlinearities, and should be interpreted in the context of the average changes due to \([\epsilon_1](\omega)\) and \([\nu_1](\omega)\). Regarding elasticity of the material, \([\epsilon_1](\omega) > 0\) indicates average stiffening. One should then ask, “At what instantaneous deformations does stiffening occur?” The answer is found in \([e_3](\omega)\).

At high frequency, \([e_3](\omega) > 0\), suggesting positive concavity and a stiffer response at the largest instantaneous strains. At these frequencies, stiffening occurs on average, and specifically at large instantaneous strains. In contrast, at low frequency we see \([\epsilon_3](\omega) < 0\), which gives negative concavity of the elastic stress curve. This can be called strain softening, which is true in some way. But more accurately the material is softer at the largest instantaneous strains, and comparately stiffer at the smallest strains. Interpreted in the context of average stiffening \((|\epsilon_1| > 0)\), negative concavity \((|\epsilon_3| < 0)\) suggests that stiffening occurs at the smallest instantaneous strains, or equivalently, at the largest instantaneous strain rate (since \(\dot{\gamma} = \pm \dot{\gamma}_0\) at \(\gamma = 0\)).

We see that at low frequency the elastic nonlinearity is caused by large rates of deformation, whereas at high frequency it is caused by large strains. This onset of nonlinearity is consistent
Figure 3.7 Frequency-dependent [LAOStrain] fingerprints of the PVA-Borax system. The first-harmonic measures are positive but the third harmonic measures change sign. The lumped intrinsic measure $Q_0$ is always positive

with the Pipkin diagram of Eq. 1.1 for which strain-rate ($\dot{\gamma}$) induces nonlinearity at low frequency, $De \ll 1$, where strain amplitude $\gamma_0$ induces nonlinearity at high frequency ($De \gg 1$). The viscous nonlinearities are driven in the same way. Average thickening
occurs for the entire range of frequency. At small frequency, \( \text{De} = \lambda \omega \leq 0.1 \), the thickening occurs locally at the largest instantaneous strain rates, since \([v_3](\omega) > 0\). At higher frequency, \( \text{De} = \lambda \omega > 0.1 \), the instantaneous location of viscous thickening is the opposite, since \([v_3](\omega) \) change sign. In this high frequency regime, thickening occurs at the minimum instantaneous strain-rate, \([v_3](\omega) < 0\), or equivalently the largest instantaneous strains, since \( \gamma = \pm \gamma_0 \) at \( \dot{\gamma} = 0 \).

It is unclear if these trends of critical \( \text{Wi} \) and critical \( \gamma_0 \) are general for all viscoelastic fluids, experimentally or from constitutive models. What is needed is to survey the existing landscape of constitutive models and create a library of intrinsic nonlinear rheological fingerprints (as detailed in Chapter 4). We anticipate unique intrinsic signatures for different constitutive models. In this way experimental fingerprints, such as Figure 3.6, can be compared with the available library of fingerprints to identify appropriate constitutive models that can help infer composition and morphology from structure-property relations with intrinsic viscoelasticity (as discussed in Chapter 6.)

### 3.5 Inferring Structure from Intrinsic Measures

Intrinsic measures are a low dimensional fingerprint of nonlinear behavior and can help infer molecular topology. In the same spirit of linear viscoelastic moduli \( G' \) and \( G'' \) which can be interpreted independent of a specific constitutive model, these measures can be measured independent of the material under consideration. For example, \([e_1](\omega)\), \([e_2](\omega)\), \([v_1](\omega)\), \([v_3](\omega)\) can be measured for any material system, be it polymers, emulsions, colloids, composites etc. and provide physical interpretations without assuming a constitutive model belonging to that material class.

Material specific interpretations of intrinsic signatures are equally useful as they help develop mathematical constitutive models to describe the material response. For example, with the PVA-Borax system, the dominant nonlinear response is that of \([e_1] > 0\) indicating an elastic stiffening nonlinearity. This can be used to infer that mechanical stiffening (of nonlinear elastic polymers) happens before mechanical softening that occurs due to mechanical breaking of network junctions. This helps build a conceptual model of the
response which informing us in the development of a mathematical model of the response, i.e. a tensorial constitutive equation (Section 4.3).

Macroscopic rheological characterization has been used to infer constitutive model parameters [Gurnon & Wagner (2012)] but it remains to be seen if they can uncover molecular features and establish molecular structure-rheology connections. Linear viscoelastic measurements readily yield characteristic relaxation times and a plateau modulus, but cannot distinguish molecular features such as persistence length, finite extensibility, entanglement topologies etc. On the other hand, the newly defined intrinsic measures directly relate to the internal microstructure and quantify structure related parameters such as the equilibrium end to end distance and persistence length (details in Chapter 6).
Chapter 4

Library of Intrinsic LAOStrain Fingerprints for Nonlinear Constitutive Models

The theory developed for intrinsic LAOStrain material functions (Chapter 2, Section 2.1.2) is applied to rheological constitutive models. A library of intrinsic fingerprints is analytically developed for a range of nonlinear constitutive models using published results from the literature (Section 4.1) and newly derived results (Section 4.2). These fingerprints are used as a tool to qualitatively and quantitatively compare between two or more constitutive models. Physical interpretations are provided by grouping two (or more) constitutive models based on the qualitative similarities in their signatures. Contrasting and uniquely different fingerprints help distinguish between diverse constitutive models available for viscoelastic fluids.

4.1 Analytical results based on existing literature

This section involves converting analytical results (under a LAOStrain protocol) existing in the literature to a common framework of deformation domain intrinsic nonlinearities, as was proposed in Chapter 2. With the newly proposed common framework, we can identify unique fingerprints of different models and interpret the asymptotic nonlinearities in physically meaningful ways.

---

1 Some portions adopted from the author’s work Bharadwaj.A.N, Ewoldt.R.H, “Rheological fingerprints of intrinsic Large amplitude oscillatory shear (LAOS)”, to be submitted to J.Rheol.
4.1.1. Third Order fluid

Ordered fluid expansions have been used to capture small deviations from a Newtonian behavior owing to elastic effects [Bird et al. (1987)]. The stress can be represented as a retarded motion expansion

\[ \tau = b_1 \dot{\gamma} + b_2 \dot{\gamma}_{(2)} + b_1 \left\{ \dot{\gamma}_{(1)} \cdot \dot{\gamma}_{(1)} \right\} + b_3 \dot{\gamma}_{(3)} + b_{12} \left\{ \dot{\gamma}_{(2)} \cdot \dot{\gamma}_{(2)} + \dot{\gamma}_{(2)} \cdot \dot{\gamma}_{(1)} + \dot{\gamma}_{(1)} \cdot \dot{\gamma}_{(1)} \right\} + b_{111} \left( \dot{\gamma}_{(1)} \cdot \dot{\gamma}_{(1)} \right) \dot{\gamma}_{(1)} \] + H.O.T. \tag{4.1}

where \( b_1, b_2, \) etc. are material parameters and \( \dot{\gamma}_{(n)} \) the \( n \)th convected rate of strain tensor [Bird et al. (1987)]. The tensor corresponding to \( n=1 \) is the rate of strain tensor \( \dot{\gamma}_{(1)} = \dot{\gamma} \) and the others are defined through a recurrence relation

\[ \dot{\gamma}_{(n+1)} = \frac{D}{Dt} \dot{\gamma}_{(n)} - \left\{ (\nabla \dot{\gamma}) \cdot \dot{\gamma}_{(n)} + \dot{\gamma}_{(n)} \cdot (\nabla \dot{\gamma}) \right\}. \tag{4.2} \]

For spatially homogeneous simple shear strain rate input \( \dot{\gamma} = \dot{\gamma}_0 \cos \omega t \), Eq. (4.2) reduces to a form

\[ \tau_{12} = \dot{\gamma}_0 \left\{ \left( b_1 - b_3 \omega^2 \right) \cos \omega t - b_2 \omega \sin \omega t \right\} - \dot{\gamma}_0^3 \left\{ 2 \cos^3 \omega t \left( b_{12} + b_{111} \right) \right\} + O(\dot{\gamma}_0^5) \tag{4.3} \]

that can be used to identify material functions

\[ \eta'_{LVE} = b_1 - b_3 \omega^2 \]
\[ \eta''_{LVE} = -b_2 \omega \]
\[ [v_1] = \frac{-3}{2} \omega^2 \left( b_{12} + b_{111} \right) \]
\[ [v_3] = \frac{-1}{2} \omega^2 \left( b_{12} + b_{111} \right) \tag{4.4} \]

in terms of the coefficients in the expansion. The indices (or the sum of the indices) correspond to the order of the expansion. In Eq.(4.4), \( b_1 \) corresponds to the first order contribution, \( b_2 \) to the second order and \( b_{12} \) or \( b_3 \) to the third order. A third order fluid
expansion results only in viscous nonlinearities. It is expected that that consideration of the
next order terms (fourth order) in the retarded motion expansion will add elastic nonlinear
effects and result in elastic nonlinearities \([e_1]\) and \([e_3]\).

The universality of the ordered fluid expansion suggests that Eq. (4.4) should be valid for
any viscoelastic model in the limit of \(De \rightarrow 0\). We therefore expect the scaling behavior
\([v_1] \sim [v_3] \sim \omega^2\) in the terminal regime, with the magnitude of the intrinsic viscous
nonlinearity determined by \((b_{12} + b_{331})\). We will see that all constitutive models presented in
this thesis obey this terminal regime scaling.

**4.1.2. Corotational Maxwell Model**

The corotational Maxwell model was firstly proposed by Zaremba in 1903 and further
references were made by [Dewitt (1955)]. The specific choice of this constitutive model is
motivated by the simplicity in its definition and the existence of analytical solutions for
higher harmonics in the shear stress response under LAOStrain [Giacomin et al. (2011)]. The
unique feature of this model is in it being naturally nonlinear; it eliminates the need for the
definition of a nonlinear parameter to yield a nonlinear response. The corotational Maxwell
model defined as

\[
\tau + \lambda \frac{D\tau}{Dt} = \eta_0 \dot{\gamma}
\]

(4.5)

where \(\eta_0\) is the steady shear viscosity and \(\lambda\) is the relaxation time and the plateau modulus
is \(G_0 = \eta_0 / \lambda\). Eq. (4.5) is different from the Maxwell model through the presence of a
Jaumann derivative (or a corotational derivative)

\[
\frac{D\tau}{Dt} = \frac{\partial \tau}{\partial t} + \frac{1}{2} \left( \omega \cdot \tau - \tau \cdot \omega \right)
\]

(4.6)

defined through the material derivative \(D\tau / Dt\), and the vorticity tensor

\[
\omega = \left( \nabla \mathbf{v} \right) - \left( \nabla \mathbf{v} \right)^T.
\]

(4.7)
It is worth remarking the consideration of other derivatives in attempts of defining arising nonlinearities in a material response. As already mentioned, the upper convected time derivative in place of the Juamann derivative in Eq. (4.5), results in the Upper convected Maxwell (UCM) model. The UCM model predicts time dependence in a viscoelastic response to shear deformation, but no shear stress nonlinearities (though it does give shear normal stress differences). A generalization of the UCM came in the form of the Gordon-Schowalter (G-S) derivative defined by Johnson and Segalman [Johnson and Segalman (1977)]. The Johnson-Segalman (J-S) model is a very general case that under specific conditions reduces to either the upper convected or the corotational Maxwell model. The J-S model predicts shear nonlinearities and it may be possible to obtain explicit expressions for intrinsic LAOSTrain nonlinearities, but no solution has been published yet. Also worth attention is a lower convected derivative, which results in the lower convected Maxwell (LCM) model, but there is no conclusive evidence of the LCM model predicting nonlinearities under LAOS.

For the CM model in LAOSTrain, [Giacomin et al. (2011)] obtain analytical expressions in the form of viscosity coefficients $\eta'_{jn}$ and $\eta''_{jn}$ (defined in Eq. 2.7) upto the fifth harmonic (their Eq. 160 to 171) which we convert to deformation domain intrinsic nonlinearities,

\[
\frac{[\epsilon_1]}{G_0} = \frac{\omega^3 \eta_{33}'}{2} = -\frac{3}{2} \text{De}^4 \left( \frac{1}{(1 + \text{De}^2)(1 + 4\text{De}^2)} \right),
\]

\[
\frac{[\eta_1]}{\eta_0} = \frac{\omega^2 \eta_{31}'}{4} = -\frac{3}{4} \text{De}^2 \left( \frac{1}{(1 + \text{De}^2)(1 + 4\text{De}^2)} \right),
\]

\[
\frac{[\epsilon_3]}{G_0} = -\frac{\omega^3 \eta_{33}''}{2} = \frac{3}{2} \text{De}^4 \left( \frac{(1 - \text{De}^2)}{(1 + \text{De}^2)(1 + 4\text{De}^2)(1 + 9\text{De}^2)} \right),
\]

\[
\frac{[\eta_3]}{\eta_0} = \frac{\omega^2 \eta_{33}''}{4} = -\frac{1}{4} \text{De}^2 \left( \frac{(1 - 11\text{De}^2)}{(1 + \text{De}^2)(1 + 4\text{De}^2)(1 + 9\text{De}^2)} \right).
\]

The above measures are normalized by the plateau modulus $G_0$ and steady shear viscosity $\eta_0 = G_0 \lambda$ which are obtained from Maxwell-type linear viscoelastic response. The intrinsic
nonlinearities in Eq. (4.8)-(4.11) do not have any nonlinear parameter and are only a function of the Deborah Number (De).

The functional dependence of each intrinsic nonlinear measure with De (Eq. (4.8) - (4.11)) is captured in Figure 4.1 and physical interpretations can extended from the observed trends.

![Graphs showing Corotational Maxwell Model with no nonlinear parameter](image)

Figure 4.1 Corotational Maxwell (Single Mode) intrinsic LAOStrain fingerprints. \([e_1]\) and \([v_1]\) are always negative, showing average elastic softening and viscous thinning respectively. Instantaneous changes are kept track through third harmonic measures that change sign with De. Log-log plots in the inset show an asymptotic behavior at the De where the sign change occurs. As indicated, there is no nonlinear parameter for this model.

A negative first harmonic elastic nonlinearity \([e_1]\) indicates average elastic softening, the strength reported by its magnitude, which starts with a small negative value at smaller De and gradually becomes more negative at higher De. Physically, this signals a stronger
average softening at higher frequencies compared to smaller frequencies. With softening
observed on an average, a look at the signs of the third harmonic elastic nonlinearity \( [e_3] \)
gives good perspective of how things soften locally. \( [e_3] \) changes sign as we move from a
smaller to a larger frequency. At smaller frequencies, a positive \( [e_3] \) indicates instantaneous
softening at the smallest instantaneous strains (or largest instantaneous strain rates) and at
higher frequencies, a negative \( [e_3] \) signals instantaneous softening at the largest
instantaneous strains (alternately interpreted as the smallest instantaneous strain rate).

Parallel reasoning is used to interpret the first and third harmonic viscous
nonlinearities. A negative first harmonic viscous nonlinearity \( [v_1] \) indicates average viscous
thinning for all De, the effect of which is seen dominant at intermediate frequencies \((\text{De} \sim 1)\)
. Instantaneous thinning effects can be seen from the third harmonic viscous nonlinearity
\( [v_3] \) which changes from being negative at smaller frequencies to being positive at larger
frequencies. At smaller frequencies, a negative \( [v_3] \) is indicative of local thinning at the
largest instantaneous strain rates (alternately smallest instantaneous strain) and at larger
frequencies, a positive \( [v_3] \) shows maximum local thinning at lower strain rates (or largest
instantaneous strain).

In other words, at low De we see large strain rates causing the viscous nonlinearity.
and at high De it is large strains that cause viscous nonlinearity. Furthermore, at higher
frequencies we expect a dominant elastic response which drives a significant strain governed
third harmonic elastic nonlinearity and at lower frequencies we expect a dominant viscous
response which leads to a significant strain rate governed third harmonic viscous
nonlinearity.

Figure 4.1 (inset) shows the log-log functional behavior for the absolute values of
each nonlinear measure of the CM model. The first and third harmonic elastic nonlinearities
grow as \( \text{De}^4 \) in the terminal regime and gradually approach a plateau at higher frequencies.
The first and third harmonic viscous nonlinearities grow as \( \text{De}^2 \) (as expected from the
ordered fluid expansion) in the terminal regime and decay as \( 1/\text{De}^2 \) at higher frequencies.
Table 4.1 at the end of this chapter shows this limiting behavior for each nonlinearity. The
change of sign for the third harmonic measures is seen as an asymptote in the log-log plot, with the asymptote corresponding to the $De$ where the sign change occurs.

The CM model does not have a nonlinear parameter but give interesting intrinsic fingerprints. This motivates consideration of models that do include nonlinear parameters, and give signatures different from Figure 4.1.

### 4.1.3. Giesekus Model

The Giesekus model was derived by [Giesekus (1982)] to study the nonlinear response of polymers in solution. In this section, the nonlinear response of the Giesekus constitutive equation is examined to strain control large-amplitude oscillatory shear. The Giesekus model is defined by a tensor equation in polymeric stress $\tau$ as

$$\frac{1}{\lambda} \tau + \tau_{(1)} + \frac{\alpha}{\lambda G_0} \tau \cdot \tau = G_0 \gamma$$

(4.12)

where

$$\tau_{(1)} = \frac{\partial \tau + \nabla \tau - (\nabla \nu)^T \cdot \tau - \tau \cdot \nabla \nu}{\partial t}$$

(4.13)

is the upper convected time derivative, $\lambda$ the characteristic relaxation time and $G_0$ the plateau modulus. $\alpha$ is a dimensionless nonlinear parameter also called the mobility factor, varying between 0 and 1. The nonlinearities arise from the individual polymer molecules being stretched and the surrounding solvent has no effect on the nonlinear response. Keeping this in mind, the stresses resulting from the surrounding solvent are not considered when writing the governing equations. For a sinusoidal LAOStrain deformation input $\gamma(t) = \gamma_0 \sin \omega t$ [Gurnon & Wagner (2012)] solved for the asymptotic nonlinearities in terms of an expansion in frequency (index $n$) and strain (index $j$) of the form

$$\tau(t) = \sum_{j} \sum_{n} \left[ A_n^{(j)} \sin(n \omega t) + B_n^{(j)} \cos(n \omega t) \right]$$

(4.14)

where $A$ and $B$ are coefficients for the in-phase and out-of-phase components of stress when compared to the deformation input. Expanding the $\tau_{12}$ component of stress to the
third harmonic and third power of strain, analytical expressions were obtained for the coefficients as a function of the Weissenberg number and Deborah number. The solutions of [Gurnon & Wagner (2012)] are converted to our notations and normalized with the linear viscoelastic plateau modulus $G_0$ and steady shear viscosity $\eta_0$ to obtain

$$[\varepsilon_1] = \frac{A^{(3)}_{2,1}}{G_0 \gamma_0^3} = \alpha \text{De}^4 \frac{(-21 - 41 \text{De}^2 - 8 \text{De}^4 + 4\alpha(4 + 7 \text{De}^2))}{4(1 + \text{De}^2)^3(1 + 4 \text{De}^2)}, \quad (4.15)$$

$$[\varepsilon_3] = \frac{A^{(3)}_{2,3}}{G_0 \gamma_0^3} = -\alpha \text{De}^4 \frac{(-21 - 30 \text{De}^2 + 51 \text{De}^4)}{4(1 + \text{De}^2)^3(1 + 4 \text{De}^2)(1 + 9 \text{De}^2)}, \quad (4.16)$$

$$[\nu_1] = \frac{B^{(3)}_{1,2}}{\eta_0 \omega \gamma_0^3} = -\alpha \text{De}^2 \frac{(9 + 11 \text{De}^2 - 10 \text{De}^4 + 2\alpha(-3 - \text{De}^2 + 8 \text{De}^4))}{4(1 + \text{De}^2)^3(1 + 4 \text{De}^2)}, \quad (4.17)$$

$$[\nu_3] = \frac{B^{(3)}_{1,3}}{\eta_0 \omega \gamma_0^3} = \alpha \text{De}^2 \frac{(-3 + 48 \text{De}^2 + 33 \text{De}^4 - 18 \text{De}^6)}{4(1 + \text{De}^2)^3(1 + 4 \text{De}^2)(1 + 9 \text{De}^2)}. \quad (4.18)$$

The above intrinsic measures are a function of Deborah Number (De) and the nonlinear parameter $\alpha$ which appears as a front factor and within the frequency dependent fraction. The sign change in Eq. (4.16) is required for physical interpretation. It is clear from Eqs. (4.15) to (4.18) that different signatures can be expected for different values of the parameter $\alpha$. Figure 4.2 shows these fingerprints for three different values of $\alpha$. Changing $\alpha$ slightly changes the location of zero crossing for the nonlinearities and results in different absolute magnitudes of each nonlinearity. Figure 4.2 shows this trend where increasing $\alpha$ increases the absolute magnitude of each nonlinearity.

All the four intrinsic nonlinearities change magnitude and zero crossings with a change in the nonlinear parameter $\alpha$. $[\varepsilon_1]$ does not plateau and $[\nu_1]$ and $[\nu_3]$ have additional zero crossings when compared with the CM model. Such distinct signatures when compared with the CM model prompt us to consider signatures of other models.
Figure 4.2 Giesekus Model Intrinsic LAOS Strain fingerprints for different values of the nonlinear parameter $\alpha$. $[e_1]$ is always negative, but the other three nonlinearities change signs with De. The sign changes are seen as asymptotes in the log-log plot (inset of each figure, for $\alpha=0.3$). Increasing $\alpha$ increases the absolute magnitude of each nonlinearity.

4.1.4. Integral-Generalized strain measure

[Wagner et al. 2011] study the mechanical response of entangled linear and model comb polymer melts in the [LAOS] regime (they call it the Medium amplitude oscillatory shear or MAOS regime) and represent the stress response as a single integral constitutive equation with time strain separability.

$$\sigma_{xy} = \int_{-\infty}^{t} \dot{\gamma}(t-t')S_{xy}(t,t')dt', \quad (4.19)$$
where \( \dot{m}(t, t') \) is the linear viscoelastic memory function and \( S_{xy} \) is a general strain measure. For small shear deformations, they represent the generalized strain measure as

\[
S_{xy} = \gamma - (\alpha - \beta)\gamma^3 + O(\gamma^5),
\]

(4.20)

where \( \alpha \) is associated with the orientation of the tube segments and \( \beta \) with the stretch of polymer chains. \( \alpha \) and \( \beta \) take different values for different models\(^2\) and govern all arising nonlinearities through the defined strain measure.

For a strain input of the form \( \gamma = \gamma_0 \sin \omega t \), they give the shear stress as a power series expansion up to the third harmonic and provide analytical expressions for the power expansion coefficients as functions of frequency (\( \omega \)), discrete relaxation times and the nonlinear parameters (\( \alpha, \beta \)). For only one relaxation time (pertaining to \( i = 1 \)), we convert the expressions for their moduli to our notation. The linear viscoelastic signatures are equivalent to the Maxwell (and Giesekus) models,

\[
G' = G_0 \left( \frac{Dc^2}{1 + Dc^2} \right)
\]

(4.21)

\[
G'' = G_0 \left( \frac{De^2}{1 + De^2} \right)
\]

where \( G_0 = \frac{24}{5\pi^2} \left( \frac{\rho kT}{N_e} \right) \) is the plateau modulus. The normalized (using \( G_0 \) and \( \eta_0 = \lambda G_0 \)) first harmonic and third harmonic nonlinear measures are

\[
\frac{[e_1]}{G_0} = -9(\alpha - \beta)De^4 \left[ \frac{1}{(1 + De^2)(1 + 4De^2)} \right],
\]

(4.22)

\[
\frac{[e_3]}{G_0} = -9(\alpha - \beta)De^4 \left[ \frac{De^2 - 1}{(1 + De^2)(1 + 4De^2)(1 + 9De^2)} \right]
\]

(4.23)

\(^2\) Doi-Edwards(DE) \( \alpha = 191/420, \beta = 0 \); Doi-Edwards with independent alignment(DE-IA) \( \alpha = 5/21, \beta = 0 \); Linear Material Stress function (L-MSF) \( \alpha = 5/21, \beta = 0 \); Quadratic Material stress function (Q MSF) \( \alpha = 5/21, \beta = 0 \)
\[
\frac{[v_1]}{\eta_0} = \frac{9}{2} (\alpha - \beta) \Delta e^2 \left[ \frac{1}{(1 + \Delta e^2)(1 + 4\Delta e^2)} \right],
\]
(4.24)

\[
\frac{[v_3]}{\eta_0} = \frac{3}{2} (\alpha - \beta) \Delta e^2 \left[ \frac{11\Delta e^2 - 1}{(1 + \Delta e^2)(1 + 4\Delta e^2)(1 + 9\Delta e^2)} \right]
\]
(4.25)

Figure 4.3 shows the intrinsic fingerprints for different models (with different values of the nonlinear quantity \(\alpha - \beta\)) originating from a generalized strain measure. The nonlinear quantity appears only as a front factor in Eqs. (4.22)-(4.25) and therefore affects the absolute magnitude of each nonlinearity, but has no bearing on the location of zero crossing or the scaling behavior. This can be understood in terms of the assumed time strain separability of

Figure 4.3 Integral generalized strain model intrinsic LAOStrain fingerprints. Changing \(\alpha - \beta\) (defined in footnote 2) changes the absolute magnitude of each nonlinearity but not the location of zero crossing. Similar \(\text{De}\) scaling behavior is observed across all models (inset).
this model. In contrast, the Giesekus model (Figure 4.2, Eqs. (4.15)-(4.18)) does not have
time strain separability and the nonlinear term influences the functional shape of the De
dependence and zero crossings. In line with the group of polymer systems considered so far,
we consider a model for rodlike polymers next.

4.1.5. Rod like polymers

[Paul (1969)] incorporated suitable corrections to earlier studies [Kirkwood & Plock
(1956)] on the non-Newtonian behavior of rigid rod like molecules in solution under the
influence of a simple shear strain rate \( \epsilon = \text{Re}\{\dot{\epsilon}_0 \exp(i\omega t)\} \) input. For this deformation
protocol, they obtain an expression for the \( xy \) component of shear stress as

\[
\tau_{xy} = c' \zeta b^2 \text{Re} \left[ \frac{1}{30} \sum_{i=-n}^{n} \frac{\ln \nu_i(2\lambda_0)}{1 + i\omega\tau^2} + \frac{3}{1 + i\omega\tau^2} \sum_{i=-n}^{n} \ln \nu_i(\lambda_0) \right] \dot{\epsilon}_0 \exp(i\omega t)
\]

\[
+ \frac{3\dot{\epsilon}_0^2 \tau^2}{350(1 + \omega^2 \tau^2)} \left\{ \frac{10 - 3\omega^2 \tau^2 + 19i\omega \tau}{(1 + 2i\omega \tau)(5 + 3i\omega \tau)} \sum_{i=-n}^{n} \ln \nu_i(2\lambda_0) \right. \\
\left. - \frac{95 - 51\omega^2 \tau^2 + 158i\omega \tau}{2(1 + i\omega \tau)(1 + 2i\omega \tau)(5 + 3i\omega \tau)} \sum_{i=-n}^{n} \ln \nu_i(\lambda_0) \right\} \dot{\epsilon}_0 \exp(i\omega t)
\]

\[
+ \frac{2 + \omega^2 \tau^2 + i\omega \tau}{70(1 + \omega^2 \tau^2)} \left\{ \frac{2 + \omega^2 \tau^2 + 4i\omega \tau}{2(1 + i\omega \tau)(1 + 2i\omega \tau)(5 + 3i\omega \tau)} \sum_{i=-n}^{n} \ln \nu_i(2\lambda_0) \right. \\
\left. - \frac{19 + 15\omega^2 \tau^2 + 4i\omega \tau}{2(1 + i\omega \tau)(1 + 2i\omega \tau)(5 + 3i\omega \tau)} \sum_{i=-n}^{n} \ln \nu_i(\lambda_0) \right\} \dot{\epsilon}_0 \exp(3i\omega t)
\]

where \( c' \) is the concentration in particles per unit volume and all other symbols retain the
same meanings as defined in [Kirkwood & Plock (1956)]. We represent the summation terms
with \( \lambda_0 \) by \( S_1 \) and \( 2\lambda_0 \) by \( S_2 \) and decompose the expression for shear stress into leading
order terms in strain to obtain the linear viscoelastic moduli as

\[
G' = G_0 \left( \frac{\text{De}^2}{1 + \text{De}^2} \right),
\]

\[
G'' = G_0 \left( \frac{\text{De}^2 + \frac{2S_2}{3S_1} \text{De}}{1 + \text{De}^2} \right).
\]
with the plateau modulus \( G_0 = c'\varepsilon b^2S_1/10\tau \), and a resulting steady shear viscosity \( \eta_0 = G_0\tau \). The linear response looks similar to a Jeffrey model response with \( G'' \) scaling as \( \text{De} \) in the limits of \( \text{De} \to \infty \). The normalized first and third harmonic elastic and viscous intrinsic nonlinearities are

\[
\frac{[\epsilon_1]}{G_0} = \frac{3}{35} \text{De}^4 \left[ \frac{1750 \frac{S_2}{S_1} - 930}{2(1 + \text{De}^2)^2 (1 + 4\text{De}^2)(25 + 9\text{De}^2)} \right] + \frac{3750 \frac{S_2}{S_1}}{2(1 + \text{De}^2)^2 (1 + 4\text{De}^2)(25 + 9\text{De}^2)} \text{De}^2 + \frac{630 \frac{S_2}{S_1} - 1514}{2(1 + \text{De}^2)^2 (1 + 4\text{De}^2)(25 + 9\text{De}^2)} \text{De}^3 + \frac{1350 \frac{S_2}{S_1}}{2(1 + \text{De}^2)^2 (1 + 4\text{De}^2)(25 + 9\text{De}^2)} \text{De}^4 \right]
\]

(4.29)

\[
\frac{[v_1]}{\eta_0} = \frac{3}{35} \text{De}^2 \left[ \frac{2500 \frac{S_2}{S_1} - 475}{2(1 + \text{De}^2)^2 (1 + 4\text{De}^2)(25 + 9\text{De}^2)} \right] + \frac{9500 \frac{S_2}{S_1} - 784}{2(1 + \text{De}^2)^2 (1 + 4\text{De}^2)(25 + 9\text{De}^2)} \text{De}^2 + \frac{5346 \frac{S_2}{S_1} - 21}{2(1 + \text{De}^2)^2 (1 + 4\text{De}^2)(25 + 9\text{De}^2)} \text{De}^4 + \frac{324 \frac{S_2}{S_1}}{2(1 + \text{De}^2)^2 (1 + 4\text{De}^2)(25 + 9\text{De}^2)} \text{De}^4 \right]
\]

(4.30)

\[
\frac{[\epsilon_3]}{G_0} = -\frac{1}{7} \text{De}^4 \left[ \frac{1050 \frac{S_2}{S_1} - 362}{2(1 + \text{De}^2)^2 (1 + 4\text{De}^2)(25 + 9\text{De}^2)} \right] + \frac{2628 \frac{S_2}{S_1} - 80}{2(1 + \text{De}^2)^2 (1 + 4\text{De}^2)(25 + 9\text{De}^2)} \text{De}^2 + \frac{810 \frac{S_2}{S_1} + 90}{2(1 + \text{De}^2)^2 (1 + 4\text{De}^2)(25 + 9\text{De}^2)} \text{De}^4 \right]
\]

(4.31)

\[
\frac{[v_3]}{\eta_0} = \frac{1}{7} \text{De}^2 \left[ \frac{500 \frac{S_2}{S_1} - 95}{2(1 + \text{De}^2)^2 (1 + 4\text{De}^2)(25 + 9\text{De}^2)} \right] + \frac{980 \frac{S_2}{S_1} + 358}{2(1 + \text{De}^2)^2 (1 + 4\text{De}^2)(25 + 9\text{De}^2)} \text{De}^2 + \frac{-1212 \frac{S_2}{S_1} + 261}{2(1 + \text{De}^2)^2 (1 + 4\text{De}^2)(25 + 9\text{De}^2)} \text{De}^4 + \frac{540 \frac{S_2}{S_1}}{2(1 + \text{De}^2)^2 (1 + 4\text{De}^2)(25 + 9\text{De}^2)} \text{De}^4 \right]
\]

(4.32)

It can be observed from Eqs. (4.29) to (4.32) that all intrinsic measures are a function of \( \text{De} \) and a single nonlinear quantity \( S_2/S_1 \) which influences both magnitude and functional dependence on frequency. The nonlinear quantity ranges from 0.5–1 (refer Appendix) with the limits defined by a large number of rigid links or a single large dumbbell respectively. The intrinsic fingerprints for this model are shown in Figure 4.4 for both cases. For different \( S_2/S_1 \), the trends indicate a changing magnitude for each nonlinear measure and a change of location of the zero crossing for \([\epsilon_1]\) & \([v_3]\). The scaling behavior (as shown in the inset
of each subfigure in Figure 4.4) remains unaffected. Also noteworthy is each nonlinearity plateauing in the limits of $\text{De} \to \infty$.

Figure 4.4 Rodlike polymers intrinsic LAOStrain fingerprints. Changing the nonlinear quantity $S_2/S_1$ affects the absolute magnitudes (all measures) and locations of the zero crossings ($[e_1]$ and $[v_3]$). The scaling behavior is unaffected and is shown in the log-log plots (inset).

4.1.6. Simple Emulsion

[Yu et al. (2002)] consider a model for a simple emulsion of dilute immiscible Newtonian ellipsoidal droplets in a Newtonian matrix. The interfacial stress is directly coupled to a second order morphology tensor that represents deformation of the drop interface, and solutions are given for an asymptotic expansion response to LAOStrain. The given solutions are not decomposed into the leading order terms, but these terms can be extracted from their result. With strain input $\gamma(t^*) = \gamma_0 \sin(\omega t^*)$ represented in non-dimensional time
$t^* = t / \tau$, and droplet relaxation time $\tau$, the expression for the oscillatory stress due to the interface is (their Eq.(28)),

$$\sigma_{12}^* = \frac{a_1 \sin \omega t + a_2 \cos \omega t + a_3 \sin 3\omega t + a_4 \cos 3\omega t}{b_0 + b_1 \sin 2\omega t + b_2 \cos 2\omega t + b_3 \sin 4\omega t + b_4 \cos 4\omega t}$$

(4.33)

where the coefficients $a_1 - a_4$ and $b_1 - b_4$ are functions of the capillary number $Ca_0$, $\omega \tau, f_1, f_2$ where

$$Ca_0 = \gamma_0 \omega \tau$$

(4.34)

$$f_1 = \frac{40( p + 1)}{(2p + 3)(19p + 16)},$$

(4.35)

$$f_2 = \frac{5}{2p + 3},$$

(4.36)

where

$$p = \frac{\eta_d}{\eta_m}$$

(4.37)

is the viscosity ratio of the Newtonian droplet to the surrounding Newtonian matrix. To obtain intrinsic LAOS material functions, Eq. (4.33) is expanded and terms of $O(\gamma_0^5)$ are neglected (details of the derivation can be found in the Appendix). The linear viscoelastic storage and loss moduli are

$$G' = G_0 \left( \frac{De^2}{1 + De^2} \right)$$

$$G'' = G_0 \left( \frac{De}{1 + De^2} \right)$$

(4.38)

which clearly represents a Maxwellian response. It is then possible to define a plateau modulus (in the limits of $De \rightarrow \infty$) as

$$G_0 = \frac{2}{3} Kf_2^2$$

(4.39)
The plateau modulus is directly related to the inherent material properties through a parameter $K$ defined as

$$K = \frac{6\Gamma}{5R} \left( \frac{(p+1)(2p+3)\phi}{5(p+1)-(5p+2)\phi} \right)$$

(4.40)

with $\Gamma$ being the surface tension, $R$ the drop radius and $\phi$ the volume fraction. It is also possible to define a steady shear viscosity $\eta_0 = G_0\lambda_b$ where $\lambda_b = \tau / f_1$ is the normalized relaxation time of the interface. The normalized intrinsic nonlinearities for this model are,

$$\left[ \varepsilon_1 \right] = f_2^2 \frac{G_0}{6} \text{De}^4 \left( \frac{1 - \text{De}^2 - 6\text{De}^4}{(1 + \text{De}^2)^3(1 + 4\text{De}^2)} \right),$$

(4.41)

$$\left[ v_1 \right] = -\frac{f_2^2}{2} \text{De}^2 \left( \frac{1 + 4\text{De}^2 + 3\text{De}^4}{(1 + \text{De}^2)^3(1 + 4\text{De}^2)} \right),$$

(4.42)

$$\left[ e_3 \right] = f_2^2 \frac{G_0}{3} \text{De}^4 \left( \frac{2 + \text{De}^2 - \text{De}^4}{(1 + \text{De}^2)^3(1 + 4\text{De}^2)} \right),$$

(4.43)

$$\left[ v_3 \right] = \frac{f_2^2}{12} \text{De}^2 \left( \frac{-2 + 7\text{De}^2 + 6\text{De}^4}{(1 + \text{De}^2)^3(1 + 4\text{De}^2)} \right),$$

(4.44)

where, $f_2$ is as defined in Eq. (4.35). The De defined in Eqs. (4.38)-(4.44) is defined through the normalized relaxation time $\lambda_b$ as $\text{De}=\omega \lambda_b$. The nonlinear parameter $f_2$ appears only as a front factor. Figure 4.5 shows the intrinsic signatures for different values of the nonlinear parameter $f_2$, determined from specific values of the viscosity ratio using Eq.(4.37). For one extreme of an air bubble in water, we calculate $f_2 = 1.65$ (using $p = \eta_d / \eta_m = 0.015$) and for the other extreme of a solid sphere in water, $f_2 = 0$. For two fluids of the same viscosity, $f_2 = 1$. It is clear that different values of this parameter just shifts the curves for each nonlinearity without changing the location of the zero crossing (the location of sign change) or affecting the scaling behavior.
Figure 4.5 Simple emulsion model intrinsic LAOStrain fingerprints for different values of the nonlinear parameter $f_2$. $f_2 = 1$ (matched viscosity) $f_2 = 1.65$ (air bubble). Changing $f_2$ changes the absolute magnitude of each nonlinear measure but not the location of zero crossing or the scaling behavior. The log-log plots (inset) show the scaling behavior.

The intrinsic nonlinear fingerprints provide added information on the microstructure to that obtained from linear viscoelastic measurements. It is evident from Eqs. (4.41)-(4.44) and Figure 4.5 that each intrinsic nonlinearity depends only on the material parameter $f_2$, which directly relates to the viscosity ratio (Eq.4.35). A fit of the parameter $f_2$ to the intrinsic fingerprints lends direct information on the viscosity ratio of the constituent fluids in the emulsion. The linear viscoelastic plateau modulus relates to a combination of material properties (as shown in Eq.4.39). For a known $f_2$ and a known plateau modulus from the linear response, it is possible to calculate explicit values for other material parameters (K, $\Gamma/R$) through relations in Eq.4.39 and Eq4.40.
We have surveyed available analytical solutions for constitutive models from the literature and established a library of intrinsic fingerprints. However, these signatures do not match the experimental signatures of PVA-Borax (Chapter 3, Sections 3.2; 3.3), thus demanding analytical solutions for other constitutive models.

### 4.2 Transient Network Models

In addition to the established library of analytical fingerprints in Section 4.1, new solutions are derived for transient network models where deformation driven changes to the microstructure are related to macroscopic rheology through constitutive equations developed on the basis of microstructure concepts. The complete library of analytical fingerprints is then used to qualitatively (and quantitatively) match the experimental fingerprint of PVA-Borax (Chapter 6).

We consider transient networks comprising of weakly cross-linked nonlinear elastic elements, the nonlinearities arising from these nonlinear springs being stretched affinely by the external macroscopic deformation. Several constitutive models have been developed (see for example [Ewoldt et al. (2011), Ng et al. (2008)]) to determine the instantaneous macroscopic stress resulting from deformation of such transient networks. We choose the single relaxation time model proposed by [Ewoldt et al. (2011)], where an evolution equation is presented for a deformation related microstructural tensor $\mathbf{A}$,

\[
\dot{\mathbf{A}}^{(1)} = \frac{1}{\lambda_0} I - \frac{1}{\dot{\lambda}(\mathbf{A})} \mathbf{A}
\]

where subscript (1) refers to the upper convected time derivative, $1/\dot{\lambda}(\mathbf{A})$ a timescale nonlinearity depicting the rate of network destruction and $1/\lambda_0$ the rate of network creation. Here we simplify the destruction rate $1/\dot{\lambda}(\mathbf{A})$ to be equal to the creation rate $1/\lambda_0$. In transient homogeneous simple shear, the tensorial expression Eq. (4.45) is written as a coupled system of component-wise ordinary differential equations,

\[
\frac{dA_{11}}{dt} - 2\dot{\gamma}(t)A_{12} = \frac{1}{\lambda_0} (1 - A_{11})
\]

(4.46)
\[
\frac{dA_{22}}{dt} = \frac{1}{\lambda_0} (1 - A_{22})
\]

(4.47)

\[
\frac{dA_{33}}{dt} = \frac{1}{\lambda_0} (1 - A_{33})
\]

(4.48)

\[
\frac{dA_{12}}{dt} - \dot{\gamma}(t)A_{12} = -\frac{1}{\lambda_0} (A_{12})
\]

(4.49)

which can be solved analytically under initial conditions of \( A_{11} = A_{22} = 1 \) and \( A_{12} = 0 \) at \( t = 0 \) to obtain explicit expressions for individual components of the tensor \( A \) as

\[
A_{22} = A_{33} = 1
\]

(4.50)

\[
A_{12}(\omega t; \gamma_0, De) = \gamma_0 \left[ \frac{De^2}{1 + De^2} \sin \omega t + \frac{De}{1 + De^2} \cos \omega t \right]
\]

(4.51)

\[
A_{11}(\omega t; \gamma_0, De) = 1 + \gamma_0^2 \left[ \left( \frac{De^2}{1 + De^2} \right) \left( \frac{2De^2}{1 + 4De^2} \right) \left\{ \cos 2\omega t + \frac{\sin 2\omega t}{2De} \right\} + \left( \frac{De^2}{1 + De^2} \right) \left( \frac{2De^2}{1 + 4De^2} \right) \left\{ \sin 2\omega t + \frac{\cos 2\omega t}{2De} \right\} \right]
\]

(4.52)

We consider an alternance state response and hence neglect transient terms when arriving at expressions in Eq.(4.51) and Eq.(4.52).

If the orientation and extension along each elastic element is represented by an end to end vector \( \mathbf{Q} \) and the force along that element as \( \mathbf{F}_s \), it is possible to represent the macroscopic stress from an ensemble of elastic elements with a number density \( n \) as [Bird (1987b)]

\[
\tau = n \langle \mathbf{Q} \mathbf{F}_s \rangle
\]

(4.53)

The elastic force \( \mathbf{F}_s \) can be modeled as a nonlinear elastic spring,

\[
\mathbf{F}_s = H(Q)\mathbf{Q}
\]

(4.54)
where \( H(Q) = Hf(Q) \) with \( H \) as the linear Hookean spring constant and \( f(Q) \) a model specific nonlinear multiplicative factor in which \( f_{eq} = 1 \) at equilibrium.

Eq. (4.53) can then be written as

\[
x = n\langle H(Q)QQ \rangle
\]

(4.55)

which can be written as

\[
x = nH(Q)\langle QQ \rangle
\]

(4.56)

if a closure approximation of the Peterlin form is made. The stretch \( Q \) is written in the form of the microstructural tensor \( A \) as follows

\[
A = \frac{\langle QQ \rangle}{Q_{eq,i}^2}
\]

(4.57)

where \( Q_{eq,i} \) is the vector component of the end to end vector in its equilibrium state, with the index \( i \) representing the coordinate directions. The macroscopic stress can then be written as a function of the microstructural tensor \( A \) as

\[
x = nH(Q)Q_{eq,i}^2 A
\]

(4.58)

The magnitude of the total stretch \( Q \) (which we call \( |Q| \)) is related to the scalar invariant of microstructural tensor \( A \) as

\[
tr(A) = \frac{Q_{1}^2 + Q_{2}^2 + Q_{3}^2}{Q_{eq,i}^2} = \frac{|Q|^2}{Q_{eq,i}^2}
\]

(4.59)

From the solutions obtained for the components of \( A \) in Eqs. (4.50) we can then write

\[
|Q|^2 = Q_{eq,i}^2 (2 + A_{11})
\]

(4.60)

The stress tensor in Eq. (4.58) can then be rewritten using Eq. (4.60) as

\[
x = nH(A_{11})Q_{eq,i}^2 \frac{A}{A}
\]

(4.61)

We rewrite Eq.(4.61) as
\[ \tau = G(A_{11})A_{11} \]  
(4.62)

where the multiplicative factor is given by

\[ G(A_{11}) = nH(A_{11})Q_{0}^{2} \]  
(4.63)

For a model choice of one’s preference, the nonlinear front factor \( G(A_{11}) \) is thus observed to be a function of the 11 component of stretch \( (A_{11}) \) an explicit expression for which is obtained in Eq. (4.52). The shear component of stress \( \tau_{12} \) can then be calculated as

\[ \tau_{12} = G(A_{11})A_{12} \]  
(4.64)

Eq.(4.64) is a general form for stress that is applicable to any choice of constitutive model. A linear elastic plateau modulus \( G_{0} \) can be defined in the limits of small strain amplitude

\[ G_{0} = \lim_{\gamma_{0} \to 0} G(A_{11}) \]  
(4.65)

As already defined, it is possible to obtain intrinsic shear material functions from a representation of stress as a power series expansion in the leading order of strain amplitude. To obtain such a form we expand the front factor \( G(A_{11}) \) as a Taylor series about \( \gamma_{0} \to 0 \)

\[ G(A_{11}) = G(A_{11})\bigg|_{\gamma_{0} = 0} + \frac{\gamma_{0}}{1!} \frac{dG(A_{11})}{d\gamma_{0}}\bigg|_{\gamma_{0} = 0} + \frac{\gamma_{0}^{2}}{2!} \frac{d^{2}G(A_{11})}{d\gamma_{0}^{2}}\bigg|_{\gamma_{0} = 0} + O(\gamma_{0}^{3}) \]  
(4.66)

We specifically write

\[ \frac{dG(A_{11})}{d\gamma_{0}} = \frac{dG(A_{11})}{dA_{11}} \frac{dA_{11}}{d\gamma_{0}} \]  
(4.67)

which reduces (4.66) to the form

\[ G(A_{11}) = G_{0} + \frac{\gamma_{0}}{1!} \frac{dG(A_{11})}{dA_{11}}\bigg|_{\gamma_{0} = 0} \frac{dA_{11}}{d\gamma_{0}}\bigg|_{\gamma_{0} = 0} + \frac{\gamma_{0}^{2}}{2!} \frac{d}{d\gamma_{0}} \left( \frac{dG(A_{11})}{dA_{11}} \frac{dA_{11}}{d\gamma_{0}} \right)\bigg|_{\gamma_{0} = 0} + O(\gamma_{0}^{3}) \]  
(4.68)

For the specific form \( A_{11} \) in Eq.(4.52), Eq. (4.68) reduces to

57
\[
G(A_1) = G_0 + \frac{\gamma_0^2}{2} \left[ \frac{dG(A_1)}{dA_1} \bigg|_{\gamma_0=0} \cdot \frac{d^2A_1}{d\gamma_0^2} \bigg|_{\gamma_0=0} \right] + O(\gamma_0^3)
\] (4.69)

The expression for \( A_{12} \) derived in Eq. (4.51) is now used in Eq. (4.64) resulting in

\[
\tau_{12} = G(A_1_1)\gamma_0 \left\{ \frac{De^2}{1+De^2} \sin \omega t + \frac{De}{1+De^2} \cos \omega t \right\}
\] (4.70)

Eq. (4.69) is made use of in Eq. (4.70), and the shear stress \( \tau_{12} \) is written in the leading order of strain amplitude \( \gamma_0 \). We call \( N = \frac{1}{G_0} \frac{dG(A_1)}{dA_1} \bigg|_{\gamma_0=0} \) and define a steady shear viscosity \( \eta_0 = \lambda G_0 \) to obtain explicit forms for the normalized material functions as

\[
\frac{G'}{G_0} = \frac{De^2}{1+De^2}
\] (4.71)

\[
\frac{G''}{G_0} = \frac{De}{1+De^2}
\]

\[
\frac{[\epsilon_1]}{G_0} = N \left( \frac{De^4 \left( 5De^2 + 2 \right)}{(1+De^2)^2 \left( 1+4De^2 \right)} \right)
\] (4.72)

\[
\frac{[\nu_1]}{\eta_0} = \frac{3}{2} N \left( \frac{De^3 \left( 3De^2 + 1 \right)}{(1+De^2)^2 \left( 1+4De^2 \right)} \right)
\] (4.73)

\[
\frac{[\epsilon_3]}{G_0} = N \left( \frac{De^4 \left( De^2 - 2 \right)}{(1+De^2)^2 \left( 1+4De^2 \right)} \right)
\] (4.74)

\[
\frac{[\nu_3]}{\eta_0} = \frac{N}{2} \left( \frac{De^2 \left( 1 - 5De^2 \right)}{(1+De^2)^2 \left( 1+4De^2 \right)} \right)
\] (4.75)

For a linear case, it can be noted that \( \frac{dG(A_1)}{dA_1} \bigg|_{\gamma_0=0} = G_0 \) and hence \( N = 1 \). Time strain separability is noted in Eqs.(4.72)-(4.75) with the nonlinearity being a front factor. This was
also observed with integral model with generalized strain measure and the model for emulsions.

### 4.2.1 Finitely Extensible Nonlinear Elastic (FENE) Model

We start by modeling each element as finitely extensible nonlinear elastic (FENE) [Bird article, Bird (1987b)] and represent the total elastic force in the element as

\[ F_s(Q) = H(Q)Q \]  \hspace{1cm} (4.76)

where a functional form is chosen for the forcing function that best represents the force that it carries by

\[ H(Q) = H \frac{1}{1 - \left(\frac{Q}{L}\right)^2}, \]  \hspace{1cm} (4.77)

where \( Q \) is the stretch along the element, \( L \) its finite extensibility and \( H \) is the linear Hookean spring constant defined in the limits of \( Q \to 0 \).

\[ H = \frac{3}{2} \frac{kT}{b_L} \]  \hspace{1cm} (4.78)

where \( b_L \) is the Kuhn length and \( T \) the temperature. The finite extensibility \( L \) is dictated by the contour length of the chain element between two crosslink points. It is clear from Eq.(4.77) that the force diverges when the stretch \( Q \) approaches its finite extensibility \( L \). Eq. (4.63) can then be rewritten for the FENE model as

\[ G(A_{11}) = nQ_{eq,i}^2H \left( \frac{1}{1 - \frac{Q_{eq,i}^2(A_{11} + 2)}{L^2}} \right) \]  \hspace{1cm} (4.79)

It is possible from Eq. (4.65) and Eq. (4.79) to write an explicit expression for the linear plateau modulus as
\[ G_0 = nQ^2_{eq,H} H \left( \frac{1}{1 - \frac{|Q^2_{eq}|}{L^2}} \right) \]  

The equilibrium stretch \( Q_{eq} \) is related to its finite extensibility \( L \) [Bird (1987b)] through

\[ \frac{\langle Q^n \rangle_{eq}}{\langle Q^{n-2} \rangle_{eq}} = \frac{n+1}{n+b+3} \frac{L^2}{}, \quad (4.81) \]

where \( b \) is a nondimensional finite extensibility parameter defined through the Hookean spring constant \( (H) \) and temperature \( (T) \) as

\[ b = \frac{HL^2}{kT} \quad (4.82) \]

and is generally between 30-300 [Bird (1987b)]. In this equilibrium state, the vector component of the end to end vector by \( Q_{eq,i} \) is then obtained as

\[ \langle QQ \rangle_{eq,i} = \frac{1}{b+5} L^2 \quad (4.83) \]

It should be noted that the expression obtained in Eq. (4.83) is valid only for \( Q_{eq}/L << 1 \), with larger values yielding unphysical results for \( b \). An explicit form for the plateau modulus \( G_0 \) is obtained by using Eq. (4.82) and Eq. (4.83) in Eq. (4.80)

\[ G_0 = nkT \left( \frac{b}{b+2} \right) \quad (4.84) \]

Eq. (4.83) is used to write Eq. (4.79) in terms of the finite extensibility parameter \( b \)

\[ G(A_{11}) = nkT \frac{b}{b+3-A_{11}} \quad (4.85) \]

A specific form can then be obtained for the nonlinear front factor \( N \) as

\[ N = \frac{1}{G_0} \frac{dG(A_{11})}{dA_{11}} \bigg|_{\gamma_0=0} = \frac{1}{(b+2)} \quad (4.86) \]
It is to be noted that Eq. (4.86) requires a large value of $b$ owing to the restriction imposed by Eq. (4.83) that relates $Q_{eq}^2$ to $b$.

For convenience, we re-write the forms of the intrinsic measures

$$[e_1] = \frac{1}{G_0 (b+2)} \left( \frac{\text{De}^4 (5\text{De}^2 + 2)}{(1 + \text{De}^2)^2 (1 + 4\text{De}^2)} \right),$$

(4.87)

$$[e_2] = \frac{1}{G_0 (b+2)} \left( \frac{\text{De}^4 (\text{De}^2 - 2)}{(1 + \text{De}^2)^2 (1 + 4\text{De}^2)} \right),$$

(4.88)

$$[v_1] = \frac{3}{2} \frac{1}{\eta_0 (b+2)} \left( \frac{\text{De}^2 (3\text{De}^2 + 1)}{(1 + \text{De}^2)^2 (1 + 4\text{De}^2)} \right),$$

(4.89)

$$[v_2] = \frac{1}{\eta_0 (b+2)} \left( \frac{\text{De}^2 (1 - 5\text{De}^2)}{(1 + \text{De}^2)^2 (1 + 4\text{De}^2)} \right),$$

(4.90)

and see from Eqs. (4.87)-(4.90) that each of the four nonlinearities depend on De and the finite extensibility parameter $b$. It is seen from Figure 4.6 and Figure 4.7 that changing $N$ only changes the magnitudes of the nonlinearities but does not affect the location of zero crossing. This is demonstrated with the limiting values of $b = 30$ and $b = 300$.

Interesting conclusions can also be drawn with this formulation. The intrinsic fingerprints depend only on $b$ but the plateau modulus $G_0$ conflates $n$ and $b$. By fitting $b$ to the intrinsic LAOStrain fingerprints and using the linear viscoelastic results, it is possible to calculate $n$, the number of crosslink points. However, the form of Eq. (4.86) developed here is not generally applicable and requires reconsideration of the form for Eq. (4.82) that relates $Q_{eq,i}^2$ to $b$. This is indeed possible and considered part of future work in this area. It is also worth remarking that overall softening of the network has been modeled by keeping track of network dissociation through a softening parameter $\alpha$ [Ewoldt et al. (2008)].
Figure 4.6 FENE model intrinsic LAOSStrain fingerprints for $b=30$ and $b=300$. The magnitudes of the nonlinearities change with the nonlinear parameter $b$.

Figure 4.7 FENE model intrinsic LAOSStrain fingerprints for $b=30$ and $b=300$, shown on a log-log scale. The magnitudes of the nonlinearities change with $b$ but the De scaling remains same.
The intrinsic nonlinearities for a model with simultaneous softening and stiffening show the same functional dependence with De as in Eqs. (4.87)- (4.90). However, the nonlinear quantity \( N \) is a combination of \( \alpha \) and \( b \) and governs the signs and magnitudes of each nonlinear measure. The De scaling for each nonlinear measure is summarized in Table 4.1 and 4.2.

4.2.2 Wormlike chain (WLC) Model

The wormlike chain (WLC) model has also been used to model transient networks but largely for stiffer polymers. We study this using an approximate version of the force law as suggested by [Marko & Siggia (1995)],

\[
F = \frac{F_s \xi_p}{kT} = \frac{Q}{L} + \frac{1}{4} \left(1 - \frac{Q}{L}\right)^2 - 1, \tag{4.91}
\]

where \( L \) is the contour length and \( \xi_p \) the persistence length of the element between two network junctions (or crosslink points) and \( F_s \) the scalar component of force that the element carries. \( Q \) here represents the end to end vector between the ends of the element terminated by crosslinks. This force law has been shown to match experimental results on stretched single strand DNA molecules [Smith et al. (1992)]. The force in Eq. (4.91) can be vectorized by multiplying with a unit vector in the direction of \( Q \)

\[
\frac{F_s}{4 \xi_p} = \frac{kT}{4 \xi_p} \left[ \frac{1 - \left(1 - \frac{Q}{L}\right)^2}{Q \left(1 - \frac{Q}{L}\right)^2 + \frac{1}{L}} \right] Q. \tag{4.92}
\]

Eqn. (4.92) can be rewritten in the form \( F_s(Q) = H(Q)Q \) where

\[
H(Q) = H_s \left[ \frac{1 - \left(1 - \frac{Q}{L}\right)^2}{Q \left(1 - \frac{Q}{L}\right)^2 + \frac{1}{L}} \right]. \tag{4.93}
\]
where $H_e$ is the linear Hookean spring constant found in the limits of small extensions, i.e. in the limits of $Q \to 0$,

$$H_e = \frac{3kT}{2\xi_p L}$$

(4.94)

It can be seen from Eq. (4.92) that the force in the elastic element diverges when the extension is of the order of the contour length between crosslinks. It is also evident that any nonlinear response of the element to stretch is introduced by the forcing function $H(Q)$.

The mean squared end to end distance $\langle r_{ee}^2 \rangle$ of a chain element can be evaluated in terms of its persistence length and contour length [Boal (2002)] by accounting for the exponential decay of correlations between tangent vectors along it,

$$\langle r_{ee}^2 \rangle = 2\xi_p L - 2\xi_p^2 \left(1 - e^{-\frac{L}{\xi_p}}\right).$$

(4.95)

Which we rewrite to define a dimensionless parameter $R$ as

$$R = \frac{\langle r_{ee}^2 \rangle}{L^2} = 2\frac{\xi_p}{L} - 2\frac{\xi_p^2}{L^2} \left(1 - e^{-\frac{L}{\xi_p}}\right).$$

(4.96)

Under equilibrium (when no forces act on the chain element), the orientation of the chain element is such that it maximizes its configurational entropy. In this configuration, we represent the equilibrium end to end distance of a chain element through the vector component of the end to end vector $Q$, which we denote by $Q_{eq,i}$, with the index $i$ representing the three coordinate directions. $Q_{eq,i}$ is directly related to the vector component of $\langle r_{ee}^2 \rangle$ through

$$Q_{eq,i}^2 = \langle r_{ee}^2 \rangle_i = \frac{1}{3} \langle r_{ee}^2 \rangle.$$ 

(4.97)

From the definition of $A$, it follows that
\[
\text{tr}(A) = \text{tr}(<QQ>) = \frac{Q_{11}^2 + Q_{22}^2 + Q_{33}^2}{\langle r_{ee}^2 \rangle_i} = \left\langle \frac{Q}{r_{ee}^2} \right\rangle_i,
\]

which can be used to write an expression for the forcing function as a function of the microstructural tensor \(A\)

\[
H(A) = H_e \left[ \sqrt{\frac{<r_{ee}^2>}{3}} \, \text{tr}(A) \right] + \frac{1}{4} \left( 1 - \sqrt{\frac{<r_{ee}^2>}{3}} \, \text{tr}(A) \right)^2 - 1 \quad \left( 4.99 \right)
\]

which can be re-expressed in terms of the dimensionless parameter \(R\) as,

\[
H(A) = H_e \left[ \frac{R}{\sqrt{3}} \sqrt{\text{tr}(A)} + \frac{1}{4} \left( 1 - \frac{R}{\sqrt{3}} \sqrt{\text{tr}(A)} \right)^2 - 1 \right] \quad \left( 4.100 \right)
\]

We see from Eq.(4.96) and Eq. (4.100) that the nonlinear forcing term \(H(A)\) is a function of the normalized persistence length \(\xi_p / L\), the only nondimensional nonlinear parameter.

The plateau modulus can be obtained as (Eqs. (4.63))

\[
G_0 = \lim_{\gamma_0 \to 0} G(A) = n \left\langle r_{ee,i}^2 \right\rangle H_e \left( \frac{(R-1)^2(4R-1)+1}{4(R-1)^2} \right) \quad \left( 4.101 \right)
\]

and the nonlinear quantity \(N\)

\[
N = \left. \frac{1}{G_0} \frac{dG(A)}{dA_{11}} \right|_{\gamma_0=0} = \frac{R}{3(R-1)} \left( \frac{2(R-1)^3-1}{(R-1)^2(4R-1)+1} \right) \quad \left( 4.102 \right)
\]

We then obtain expressions for the normalized material functions as,

\[
\frac{G'}{G_0} = \frac{De^2}{1 + De^2}, \quad \frac{G''}{G_0} = \frac{De}{1 + De^2} \quad \left( 4.103 \right)
\]
\[
\frac{[e_1]}{G_0} = \frac{R}{3(R-1)} \left( \frac{2(R-1)^3 - 1}{(R-1)^2 (4R-1)+1} \right) \left( \frac{\text{De}^4 (5\text{De}^2 + 2)}{(1+\text{De}^2)^2 (1+4\text{De}^2)} \right)
\]

(4.104)

\[
\frac{[e_2]}{G_0} = \frac{R}{3(R-1)} \left( \frac{2(R-1)^3 - 1}{(R-1)^2 (4R-1)+1} \right) \left( \frac{\text{De}^4 (\text{De}^2 - 2)}{(1+\text{De}^2)^2 (1+4\text{De}^2)} \right)
\]

(4.105)

\[
\frac{[v_1]}{\eta_0} = \frac{R}{2(R-1)} \left( \frac{2(R-1)^3 - 1}{(R-1)^2 (4R-1)+1} \right) \left( \frac{\text{De}^2 (3\text{De}^2 + 1)}{(1+\text{De}^2)^2 (1+4\text{De}^2)} \right)
\]

(4.106)

\[
\frac{[v_2]}{\eta_0} = \frac{R}{6(R-1)} \left( \frac{2(R-1)^3 - 1}{(R-1)^2 (4R-1)+1} \right) \left( \frac{\text{De}^2 (1-5\text{De}^2)}{(1+\text{De}^2)^2 (1+4\text{De}^2)} \right)
\]

(4.107)

Figure 4.8 shows the intrinsic fingerprints for different values of $\xi_p / L$. A significant jump in the values of the nonlinearities can be observed when $\xi_p / L$ approaches 1, that is to the length of the contour. In this limit of large $\xi_p / L$, the element starts to behave more like a rigid rod and the equilibrium length of a chain element approaches the chain contour length. This is shown in Figure 4.9 (a) where the nonlinear parameter $R$ approaches 1 with increasing $\xi_p / L$. However, in the limits of $R \rightarrow 1$ the front factor $N$ for each nonlinearity approaches infinity as shown in Figure 4.9(b), thus contributing to large magnitudes for each nonlinearity.

### 4.3. Compare and contrast Constitutive Models on [LAOStrain] signatures

A library of intrinsic fingerprints is generated from the analytical expressions obtained for the constitutive models analyzed in the previous section. Two (or more) fingerprints are grouped together if they show similar signatures, be it in their shape or changes in sign with frequency. Figure 4.10 shows one such grouping of the [LAOS] fingerprints of the corotational Maxwell model, a special case of the Doi-Edwards (DE) model (where $\alpha = 5/21$ and $\beta = 0$)
Figure 4.8 WLC Model intrinsic fingerprints as a function of $\frac{\xi_p}{L}$. Increasing $\frac{\xi_p}{L}$ increases the magnitudes of each nonlinearity. Dashed lines denote negative values.

Figure 4.9 a) The parameter $R$ approaches 1 as $\frac{\xi_p}{L}$ increases b) The front factor for the nonlinearities ($N = f(R)$) diverges in the case of a rigid rod corresponding to $R \rightarrow 1$. 

67
and the model for emulsions. The similarity in the fingerprints of the DE model with the Corotational Maxwell model is striking, inasmuch the Corotational Maxwell model is also a single integral model with the memory function defined as \( \dot{m} \approx \frac{dG(t)}{dt} \). The emulsion model and DE model, despite representing the behavior of two completely different materials, predict similar physical behavior in the nonlinear intrinsic regime. This is enlightening for one could never have imagined comparing the behavior of two completely different materials.

The sign changes in the intrinsic measures of the Giesekus model make its signature unique and compel comparison with signatures of other models. A comparison with the signatures

![Figure 4.10](image)

Figure 4.10  Comparison of fingerprints for the emulsions model, generalized integral model (shown here for the Doi-Edwards model) and corotational Maxwell model. The fingerprints show strikingly similar shapes and sign changes with \( \text{De} \). However, the magnitudes of these measures differ.

corotational Maxwell model is shown in Figure 4.11. The elastic nonlinearities of the Giesekus model show the same qualitative behavior as the CM model with similar shapes and change of signs. However, the dissimilarities in the viscous signatures are
striking. $[v_1]$ show similar trends for the both models up to $\text{De} \sim 1$, but a change of sign is observed at large $\text{De}$ for the Giesekus model. On the other hand, $[v_3]$ show opposite signs at small and large $\text{De}$ for both models.

Remarkable qualitative similarities are observed in the intrinsic fingerprints of some models, but faint differences tell them apart. The CM model shows similar functional dependence with $\text{De}$ as the FENE model and the WLC model. They have a single zero crossing point (sign change), but have opposite signs for the nonlinear measures. Figure 4.12 shows this comparison for the CM model and FENE model. These similarities or differences are subtle and this distinction could never have been made with lumped measures of nonlinearity such as the normalized third harmonic nonlinearity, $Q_0$ coefficient [Hyun et al. (2007), Hyun & Wilhelm (2009), Wagner et al. (2011)].
Figure 4.12 FENE model signatures compared with corotational Maxwell model signatures. Opposite signs are observed for all intrinsic measures.

Figure 4.13 $Q_0$ coefficient for the FENE and CM model. This measure is always positive and loses all interesting trends observed in Figure 4.12.
We derive this coefficient for the CM model (Refer Appendix for details on derivation) and obtain

\[
Q_0 = \frac{\text{De}^2}{2(1+4\text{De}^2)(1+9\text{De}^2)} \sqrt{\frac{9\text{De}^6 + \frac{49}{4}\text{De}^4 + \frac{7}{2}\text{De}^2 + \frac{1}{4}}{1+\text{De}^2}}. \tag{4.108}
\]

This measure conflates elastic and viscous measures and loses vital physical information in the process. It is always positive and loses all sign information that gave insight into frequency dependent average and instantaneous changes. It is clear from Eq. (4.108) that \(Q_0\) is always positive, unlike the newly defined intrinsic measures which change signs with \(\text{De}\). As reported in earlier literatures [Hyun and Wilhelm (2008)], we see from Figure 4.13 that \(Q_0\) scales as \(\text{De}^2\) in the limits of small \(\text{De}\).

Quantitative differences can be used to distinguish between two qualitatively similar signatures. This is seen in Figure 4.10 where the intrinsic signatures for the three constitutive models (simple emulsion, DE and CM) are qualitatively similar but magnitudes of are entirely different. In most cases, the magnitude of a nonlinear measure directly relates to a nonlinear parameter defined for that model (the exception being the CM model which is nonlinear from the very definition of the corotational derivative). Changing the nonlinear parameter changes the magnitudes of the intrinsic measures. This is demonstrated by comparing the magnitudes of the nonlinearities of the two cases of rodlike polymers (Figure 4.4) a dumbbell type polymer (nonlinear parameter \(S_2/S_1 = 1\)) being more nonlinear than a polymer molecule modeled as an infinite rod (\(S_2/S_1 = 0.5\)).

Table 4.1 and 4.2 list out the \(\text{De}\) limiting behavior for the intrinsic nonlinearities of each considered constitutive model. Across all models, the first harmonic elastic and viscous nonlinearities show similar scaling behavior with \(\text{De}\). \([e_1]\) scales as \(\text{De}^4\) in the limits of \(\text{De} \to 0\) and approaches a constant in the limits of \(\text{De} \to \infty\); \([v_1]\) scales as \(\text{De}^2\) in the \(\text{De} \to 0\) and approaches zero as \(\text{De}^{-2}\) with increasing \(\text{De}\). The third harmonic measures also show similar scaling behavior; the exception coming from \([e_3]\) for the Giesekus model that shows a \(\text{De}^{-2}\) scaling at large \(\text{De}\).
The effectiveness of the newly developed LAOStrain intrinsic material functions in contrasting nonlinear constitutive models is conspicuous in our demonstration. However, the analysis in this chapter is restricted only to constitutive models which can be solved analytically to obtain explicit expressions for these measures. Furthermore, only two models (Giesekus and rodlike polymers) are not time-strain separable. To extend the analysis into other nonlinear constitutive models (where there are no existing analytical solutions), a numerical approach is required. This motivates discussions in the following chapter, where details are provided on numerical extraction of LAOStrain nonlinearities for constitutive models.
Table 4.1: Limiting behavior of the first harmonic intrinsic nonlinearities \([e_1]\) and \([v_1]\) at high and low Deborah number for different constitutive models. The scaling of these coefficients with \(De\) is the same for all models listed.

Note: The parameter \(N\) is defined in Eq. (4.86) for the FENE model and Eq. (4.102) for the WLC model.

<table>
<thead>
<tr>
<th>MODEL</th>
<th>(\lim_{De \to 0} [e_1])</th>
<th>(\lim_{De \to \infty} [e_1])</th>
<th>(\lim_{De \to 0} [v_1])</th>
<th>(\lim_{De \to \infty} [v_1])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corotational Maxwell</td>
<td>(-\frac{3}{2}GDe^4)</td>
<td>(-\frac{3}{8}G)</td>
<td>(\frac{3}{4}\eta De^2)</td>
<td>(-\frac{3}{16}\eta \frac{1}{De^2})</td>
</tr>
<tr>
<td>Giesekus ((\eta_e = 0))</td>
<td>(\alpha G(-21+11\alpha)) (4) (De^4)</td>
<td>(-\frac{1}{2}\alpha G)</td>
<td>(\alpha \eta (9-6\alpha)) (4) (De^2)</td>
<td>(-\alpha \eta (8\alpha - 5)\frac{1}{8} \frac{1}{De^2})</td>
</tr>
<tr>
<td>Integral, Generalized strain</td>
<td>(-\frac{216}{5\pi^2} \frac{\rho KT}{N_e} (\alpha - \beta) De^4)</td>
<td>(-\frac{54}{5\pi^2} \frac{\rho KT}{N_e} (\alpha - \beta))</td>
<td>(-\frac{108}{5\pi^2} \frac{\rho KT \lambda}{N_e} (\alpha - \beta) De^2)</td>
<td>(-\frac{27}{4} \frac{\rho KT \lambda}{N_e} (\alpha - \beta) \frac{1}{De})</td>
</tr>
<tr>
<td>Simple Emulsions</td>
<td>(-\frac{K}{6} f_2^4)</td>
<td>(-\frac{K}{9} f_2^4)</td>
<td>(-\frac{Kf_2^4}{3} \lambda_0 De^2)</td>
<td>(-\frac{K\lambda_0 f_2^4}{4} \frac{1}{De^2})</td>
</tr>
<tr>
<td>Rod like polymers</td>
<td>(\frac{3G_0}{175} \left( \frac{S_2}{S_1} - \frac{93}{93} \right) De^4)</td>
<td>(\frac{51 S_2}{35 S_1} \eta_0)</td>
<td>(\frac{3\eta_0}{70} \left( \frac{S_2}{S_1} - \frac{19}{19} \right) De^2)</td>
<td>(\frac{27 S_2}{70 S_1} \eta_0)</td>
</tr>
<tr>
<td>FENE Stiffening &amp; WLC</td>
<td>(2G_0, N De^4)</td>
<td>(\frac{5}{4} G_0 N)</td>
<td>(\frac{3}{2} \eta_0 N De^2)</td>
<td>(\frac{9}{8} \eta_0 N \frac{1}{De^2})</td>
</tr>
</tbody>
</table>
Table 4.2: Limiting behavior of the third harmonic intrinsic nonlinearities $[e_3]$ and $[v_3]$ at high and low Deborah number for different constitutive models. The scaling is distinct for $[e_3]$ of the Giesekus model at $De \to \infty$, but otherwise all models shown have the same scaling behavior for these coefficients.

<table>
<thead>
<tr>
<th>MODEL</th>
<th>$[e_3]$</th>
<th>$[v_3]$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lim_{De \to 0}$</td>
<td>$\lim_{De \to \infty}$</td>
</tr>
<tr>
<td>Corotational Maxwell</td>
<td>$\frac{3}{2}G_0De^4$</td>
<td>$-\frac{1}{24}$</td>
</tr>
<tr>
<td>Giesekus ($\eta_\infty = 0$)</td>
<td>$-\frac{\alpha G_0(-21+16\alpha)}{4}De^4$</td>
<td>$-\frac{\alpha G_0(17+4\alpha)}{48}De^2$</td>
</tr>
<tr>
<td>Integral, Generalized strain</td>
<td>$\frac{216\rho KT}{5\pi^2 N_e}(\alpha-\beta)De^4$</td>
<td>$-\frac{6\rho KT}{5\pi^2 N_e}(\alpha-\beta)De^2$</td>
</tr>
<tr>
<td>Simple Emulsions</td>
<td>$\frac{4Kf_0^4}{9}De^4$</td>
<td>$-\frac{Kf_0^4}{18}$</td>
</tr>
<tr>
<td>Rod like polymers</td>
<td>$-\frac{G_0}{175}\left{\frac{525 S_2}{S_1}-181\right}$</td>
<td>$\frac{5G_0}{28}\left{\frac{S_2}{S_1}+1\right}$</td>
</tr>
<tr>
<td>FENE Stiffening &amp; WLC</td>
<td>$-2G_0NDe^4$</td>
<td>$\frac{1}{4}G_0N$</td>
</tr>
</tbody>
</table>
Chapter 5

Numerical Simulations

A robust numerical algorithm is developed for quick and efficient extraction of LAOStrain nonlinearities for a given nonlinear constitutive model. For validation, the developed algorithm is implemented on the Giesekus model and the single mode corotational Maxwell model and the numerically obtained fingerprints are compared with analytical fingerprints obtained in Chapter 4. The single mode pompom model is numerically simulated with the established algorithm and its intrinsic signatures obtained for different nonlinear parameters.

5.1 Simulation Algorithm and techniques

The governing constitutive equations for a model are generally represented as tensorial equations in the resulting stress ($\tau$) response or stretch ($A$) of the network elements. For a strain controlled transient oscillatory input of the form $\gamma = \gamma_0 \sin \omega t$, this general form can be expanded and expressed as component wise ordinary differential equations. In most cases, these differential equations are coupled, non-homogeneous and nonlinear and may not be solvable analytically, thus calling for a numerical approach to arrive at a solution.

We seek asymptotic material functions for nonlinear constitutive models under strain controlled oscillatory deformation. We choose to obtain them numerically in MATLAB 7.10 (R2010a). Component wise ODEs in stress (or stretch) are defined along with model parameters that belong to the model. A .dat file keeps track of the values of the model parameters. The ODEs are solved using standard built in numerical solvers in MATLAB.

The choice of the ODE solver is determined by the stiffness of the system of differential algebraic equations in hand. Nonstiff equations are solved easily with one step solvers like ODE45s, based on an explicit Runge-Kutta 4-5 scheme. Stiff equations on the other hand require multistep solvers like ODE15s (or ODE23s), which are variable order
solvers based on numerical differentiation formulas. For solving stiff equations, ODE15s was chosen over other stiff solvers for its accuracy and efficiency.

MATLAB also offers good flexibility in letting the user define options for an ODE solver to approach a solution efficiently. These options are carefully set to accelerate the solution for our (stiff) ODEs without compromising on their accuracy. One such option was with error tolerances for the solution from the ODE solver. For our simulations, the relative and absolute tolerances were each set to a strict $10^{-10}$ expecting the values for the intrinsic measures to be small. A tolerance stricter than this could have been set, but there were no inherent benefits in terms of the accuracy of the solution. More so, it seemed to have an adverse effect on computational efficiency and simulation time.

Most MATLAB solvers vary step size (variable time stepping) to produce solutions within the defined error tolerances. For our simulations, we discretize the input strain signal with $2^7 = 128$ points per cycle and force the ODE solver to take as many steps per cycle of strain simulated. Forcing time steps may affect the efficiency of the solver but a discretized signal is easy to process with a Fourier transform discussed later. It is easy to see the resulting shear stress data having $2^7 = 128$ points per cycle. It is worth remarking that in striving for accuracy of data at higher frequencies, it is easy to get misled into choosing a higher number of points per cycle (ppc) for the strain input (or stress output). But this has no bearing on the accuracy of the solution and only adds to computation time. The choice of 128 ppc (and none higher) is motivated by these observations.

The stress signals are analyzed in a state of alternance (theoretically when the stress amplitude shows no time dependence). In our simulations, a state of alternance is considered attained if the changes in the first-harmonic moduli (both elastic and viscous) for two subsequent cycles are less than $10^{-10}$ %. This strict tolerance may increase computation time but it helps in accurate extraction of asymptotic nonlinearities with small absolute magnitudes (in comparison to first harmonic measures). Figure 5.1 shows a schematic showing an alternance state response which can be identified by comparing the first harmonic moduli for two consecutive cycles. This state is observed beyond a particular number of simulated cycles ($N_{alternance}$, shown in red in Figure 5.1).
At a given strain amplitude (input), the number of simulated cycles for an alternance state response can be represented as a function of the frequency alone (a nondimensional Deborah number (De) in our case, another input parameter). We propose an approximate Figure 5.1 Time dependent stress signal attaining alternance after $N_{\text{alternance}}$ cycles. Alternance implying changes in the first-harmonic for two subsequent cycles are less than $10^{-10}$ %.

De dependent criterion to arrive at $N_{\text{alternance}}$. For a steady state stress response, the time period for a single oscillation of imposed strain should at least be greater than the relaxation time of the material (represented by a constitutive model) under consideration. For an alternance state response for stress at a given frequency, we propose simulating $N_{\text{alternance}}$ cycles of strain such that the total time period of oscillation ($T$) be greater than some number ($x$) times the relaxation time ($\lambda$) of the material. This can be written as

$$
(N_{\text{alternance}})T \geq x\lambda
$$

(5.1)

For a frequency $\omega$, the time period of oscillation $T = 2\pi / \omega$. The magnitude of $x$ increases as the alternance definition becomes more stringent. Eq. (5.1) then reduces to give a De dependent criteria for $N_{\text{alternance}}$ as


\[ N_{\text{alternance}} = \left( \frac{x}{2 \pi} \right) \text{De}. \] (5.2)

For a given \( x \), Eq. (5.2) shows a linear dependence of \( N_{\text{alternance}} \) with \( \text{De} \), which is particularly well obeyed at higher frequencies. We show the validity of Eq. (5.2) with results from simulations on specific nonlinear constitutive models.

\( N_{\text{alternance}} \) shows a strain amplitude dependence that is not explicitly discernible in Eq. (5.2). We demonstrate this dependence by simulating the single mode pompom model (model description in Section 5.3) and the Giesekus model (model description in Section 5.2). For the Single mode pompom model (rendered \textit{moderately nonlinear} with appropriate choice of model parameters), \( N_{\text{alternance}} \) is observed to be independent of the input strain amplitude. Figure 5.2(a) shows this trend for the Single mode pompom model, where \( N_{\text{alternance}} \) grows with increasing \( \text{De} \) but is seen to be independent of the strain amplitude.

On the other hand, Figure 5.2(a) shows a similar growth in \( N_{\text{alternance}} \) with \( \text{De} \) for the nonlinear Giesekus model (model parameter \( \alpha = 0.3 \)), but a strong strain amplitude dependence is conspicuous at higher strains \( (\gamma_0 = 10) \). This strain amplitude dependence of \( N_{\text{alternance}} \) for nonlinear models can be explained physically through the parameter \( x \) in Eq. (5.2).

For both models, \( N_{\text{alternance}} \) is frequency independent up to \( \text{De} \sim 0.4 \), but increases with increasing frequency thereafter. We had predicted this arbitrariness in the frequency dependence of \( N_{\text{alternance}} \) earlier and accounted for it by simulating one cycle at a time and comparing the first harmonic moduli of the simulated cycle with that of the previous cycle. In the terminal regime (small \( \text{De} \)) a minimum of 3 cycles of input strain amplitude was required (as shown by the fit in Figure 5.2 (a)) for an alternance state stress response. This
Figure 5. 2 Single mode pompom model a) $N_{\text{alternance}}$ shows no De dependence up to De~0.4 but scales directly with De at higher frequencies. $N_{\text{alternance}}$ shows no strain amplitude dependence for all De b) The number of relaxation times approaches a constant at higher frequencies (calculated as 11 from Eq.(5.2)).

Figure 5.3 Giesekus Model ($\alpha = 0.3$) a) $N_{\text{alternance}}$ shows no De dependence up to De~0.4, but a strong strain amplitude dependence appears when $\gamma_0 = 10$ b) The number of relaxation times ($\gamma_0$) plateaus at high De but shows a strong $\gamma_0$ dependence. (calculated as 25 for small $\gamma_0$ and 4 for $\gamma_0 = 10$ from Eq. (5.2))
minimum criterion could however change with a change in the precision sought when comparing the first harmonic moduli of two consecutive cycles.

We use Eq. (5.2) to fit data at large De by choosing $\chi$ as a free parameter in our fits. For the pompom model, a good fit is obtained at higher frequencies for $\chi = 14$ for all strain amplitudes. The fit is shown in Figure 5. 2(a) and Figure 5. 2(b) confirms $\chi$ approaching a constant value at larger De. A fit to the Giesekus model (Figure 5.3) however results in two different values for $\chi$, one for the overlapping response at smaller strain amplitudes ($\chi = 25$) and one for the deviatoric response at the higher strain amplitude ($\chi \approx 4.5$). A smaller value of $\chi$ translates into a smaller number of relaxation times and hence a smaller number of cycles (as shown in Eq. (5.2)) before an alternance state response is attained. This is shown in Figure 5.3 (b) where the number of relaxation times ($\chi$) is seen decreasing with increasing $\gamma_0$. Physically, the material relaxation time decreasing with increasing $\gamma_0$ is apparent through its direct relation with viscosity; at large strains, the response being nonlinear and the Giesekus model predicting shear thinning.

A nonlinear stress signal is characterized by higher harmonics in its frequency domain response. A transformation of the time domain stress signal to a frequency domain facilitates extraction of the constituent higher harmonics through a discrete Fourier transform (DFT). As the time domain signal was discretized with $2^n$ data points per cycle, a Fast Fourier Transform (FFT) algorithm can used without errors for this purpose. The FFT is an accelerated DFT that saves on computation time. Odd harmonics (first and third in particular) of the stress signal are then extracted and converted to deformation domain Chebyshev coefficients. The first harmonic nonlinearities are extracted by subtracting out the linear (SAOS) contribution at the smallest simulated strain amplitude for each frequency. Considering these intrinsic measures are observed in leading order of strain amplitude, the simulations are optimized such that venturing into higher strain amplitudes (than required) is avoided. This is particularly achieved by terminating the simulation once a $\gamma_0^2$ scaling is observed for each intrinsic measure. Figure 5.4 summarizes the simulation process as a flow chart.
Figure 5.4 Flow chart summarizing the simulation process involved in extraction of intrinsic nonlinearities
5.2. Validating Simulations with Analytical results

The algorithm proposed for numerical simulations (Section 5.1) is validated by directly applying it to constitutive models with readily available analytical solutions for intrinsic measures (Section 4.1). Numerically obtained intrinsic fingerprints are then compared with analytical intrinsic fingerprints. The Giesekus model and Corotational model are considered for this purpose.

5.2.1. Giesekus Model

The Giesekus Model ($\alpha = 3$, neglecting solvent viscosity) is defined in Section 4.2.3. For homogeneous simple shear flow, component wise differential equations can be written for the non-dimensional stress as

\[
\frac{d\tau^*_1}{dt} = 2\dot{\gamma}\tau^*_2 - \frac{\tau^*_1}{\lambda} \left( \tau^*_2 + \tau^*_2 \right) \frac{\alpha}{\lambda} \\
\frac{d\tau^*_2}{dt} = -\frac{\tau^*_1}{\lambda} \left( \tau^*_2 + \tau^*_2 \right) \frac{\alpha}{\lambda} \\
\frac{d\tau^*_{12}}{dt} = \dot{\gamma} \left( \tau^*_{12} - 1 \right) - \frac{\tau^*_1}{\lambda} \left( \tau^*_1 + \tau^*_2 \right) \frac{\alpha}{\lambda}. \tag{5.3, 5.4, 5.5}
\]

This system of equations is coupled, nonhomogeneous and nonlinear. For a strain input $\dot{\gamma} = \gamma_0 \sin \omega t$ and nonlinear parameter $\alpha = 3$, Eqs. (5.3) to (5.5) are solved numerically using a stiff ODE solver (ODE15s). The intrinsic nonlinearities are extracted in the technique summarized in the flowchart of Figure 5.4 (see Section 5.1 for details). Figure 5.5 compares the results of the simulations with the analytical fingerprints derived in Section 4.2.2. (Eq. 4.17-4.20). The simulation results capture every signature shown by the analytical results.

5.2.2. Corotational Maxwell Model

The corotational Maxwell is defined in Section 4.2.1. There are no nonlinear parameters in the definition and the nonlinearities are a result of the inclusion of the
Jaumann derivative. For homogeneous simple shear flow, component wise differential equations can be written for the non-dimensional stress

\[ \frac{d\tau^*_{11}}{dt} = \dot{\gamma}\tau^*_{12} - \frac{\tau^*_{11}}{\lambda} \]  
(5.6)

\[ \frac{d\tau^*_{22}}{dt} = -\dot{\gamma}\tau^*_{12} - \frac{\tau^*_{22}}{\lambda} \]  
(5.7)

\[ \frac{d\tau^*_{12}}{dt} = \dot{\gamma}\left(1 - \frac{(\tau^*_{11} - \tau^*_{22})}{2}\right)\tau^*_{12} - \frac{\tau^*_{12}}{\lambda}. \]  
(5.8)

For a strain input \( \gamma = \gamma_0 \sin \omega t \) Eqs. (5.6) to (5.8) are solved numerically using ODE15s, a stiff ODE solver. The technique for extraction of intrinsic nonlinearities is as summarized in the flowchart shown in Figure 5.4 (see Section 5.1 for details on extraction). Figure 5.6 compares the results of the simulations with the analytical fingerprints translated in Section 4.2.2 (Eq. 4.10-4.13) from [Giacomin et al. (2011)]. The simulation results capture every signature shown by the analytical results, thus validating the accuracy of the simulations in extracting these measures.
5.3. Intrinsic nonlinearities of the Single Mode Pompom model

In this section, the numerical scheme is used to generate the intrinsic LAOStrain fingerprint for a constitutive model without a known analytical solution. The pompom model was proposed by [Macleish and Larson (1998)] based on a tube model for entangled polymers melts. The pompom molecule comprises of a backbone with \( q \) dangling arms. It is characterized by the molecular weight of the backbone \( M_b \) and net molecular weight of all arms \( M_a \). Normalized molecular weights for the backbone \( s_b = M_b / M_e \) and arms \( s_a = M_a / M_e \) can be obtained by choosing the entanglement molecular weight \( M_e \) as a normalization factor. In short, there are three nonlinear parameters to consider, namely \( q, s_a, s_b \).

The single mode pompom model is defined in its differential form [Macleish and Larson (1998)] by an orientation tensor \( S(t) \) related to a stretch tensor \( A(t) \) and the backbone orientation scalar \( \lambda(t) \)

\[
S(t) = \frac{A(t)}{\sqrt[3]{|A(t)|}}
\]  

Figure 5.6 Corotational Maxwell LAOStrain intrinsic fingerprints extracted from numerical simulations (symbols) compared with analytical fingerprints (lines, background). Open symbols show negative values. A perfect match is observed between simulation and analytical results.
\[
\frac{\partial}{\partial t} A(t) = (\nabla v) A + A (\nabla v)^T - \frac{1}{\tau_b} \left( A - \frac{1}{3} I \right)
\]  \tag{5.10}

\[
\frac{\partial}{\partial t} \lambda = \lambda \left( (\nabla v) \cdot S \right) - \frac{1}{\tau_s} (\lambda - 1) e^{[\nu^*(\lambda - 1)]}
\]  \tag{5.11}

where \( \nu^* = 2/\q \) and \( \tau_b, \tau_s \) are relaxation times related through

\[
\frac{\tau_b}{\tau_s} = \frac{4}{\pi^2} s_b \phi_b
\]  \tag{5.12}

where \( \phi_b \) is the molecular mass fraction of the backbone defined by

\[
\phi_b = \frac{s_b}{2qs_a + s_b}
\]  \tag{5.13}

Eq. (5.11) includes the modification suggested by [Blackwell et al. (2000)] on local branch point displacements. The stress calculator for the total stress tensor \( \sigma \) is given by

\[
\sigma = 3G\phi_b^2 \lambda^2 (t) S(t)
\]  \tag{5.14}

where \( G \) is the plateau modulus. For homogeneous simple shear flow, the component wise differential equations for the stretch can be written as

\[
\frac{dA_{11}}{dt} = 2\gamma A_{12} - \frac{1}{\tau_b} \left( A_{11} - \frac{1}{3} \right)
\]  \tag{5.15}

\[
\frac{dA_{12}}{dt} = \phi A_{12} - \frac{A_{12}}{\tau_b}
\]  \tag{5.16}

\[
\frac{dA_{22}}{dt} = -\frac{1}{\tau_b} \left( A_{22} - \frac{1}{3} \right)
\]  \tag{5.17}

\[
\frac{dA_{33}}{dt} = -\frac{1}{\tau_b} \left( A_{33} - \frac{1}{3} \right)
\]  \tag{5.18}
\[
\frac{d\lambda}{dt} = \lambda \dot{\gamma} \left( \frac{A_{12}}{A_{11} + A_{22} + A_{33}} \right) - \frac{4}{\pi^2} \frac{\lambda b \phi_b}{\tau_b} (\lambda - 1) e^{[\nu^{(\lambda-1)}]} 
\]

(5.19)

For a strain input \( \gamma = \gamma_0 \sin \omega t \) Eqs. (5.15) to (5.19) are solved numerically using a fourth order Runge Kutta scheme (ODE45s). Intrinsic nonlinearities are extracted and Figure 5.7 shows the intrinsic signatures for \( s_a = 2, s_b = 10, q = 2 \) as a function of \( \text{De} \), defined using the backbone relaxation time (\( \tau_b \)).

![Figure 5.7 Pompom model (single mode) LAO strain intrinsic fingerprints. Open symbols are negative values. A similar scaling behavior with De is observed for the elastic and viscous nonlinearities. Signatures are similar to the Giesekus model with the exception of \( [\nu_1] \) that does not change signs with De.](image)

It can be seen from Figure 5.7 that \([e_1]\) and \([\nu_1]\) are always negative indicating average elastic softening and viscous thinning respectively. \([e_3]\) and \([\nu_3]\) change signs with frequency. The third harmonic measures are interpreted in the context of the first harmonic measures. \([e_3]\) is positive at smaller frequencies indicative of elastic softening at the smallest instantaneous strains and turns negative at lower frequency indicating elastic softening at largest instantaneous strains. A negative \([\nu_3]\) at small and large frequencies keeps track of viscous thinning at the largest instantaneous strain rates and a positive \([\nu_3]\) at intermediate frequencies (\( \text{De} \sim 1 \)) represent viscous thinning at the smallest instantaneous strain rates. The nonlinear parameters are now changed and it is seen if this affects the signatures.
There are several possible combinations of the three nonlinear parameters \((q, s_a, s_b)\) and it will be interesting to observe changes in signatures as a function of these nonlinear parameters, if any. For purposes of demonstration we consider a particular combination of nonlinear parameters [Hyun et al. (2013)] where we retain \(s_a, s_b\) as constants and vary the number of arms \(q\). Figure 5.8 shows the linear viscoelastic moduli \(G'_i, G''_i\) plotted with De for \(s_a=2, s_b=10\) and \(q=2, 3, 4\). Both \(G'_i\) and \(G''_i\) decrease with an increasing number of arms. Physically, [Hyun et al. (2013)] attribute this to a decrease in the effective entanglement number with an increasing number of arms. The plateau modulus \((G_0 = \lim_{De \to \infty} G')\) and the steady shear viscosity \((\eta_0 = \lim_{De \to 0} G'/\omega)\) also decrease with an increase in the number of arms. This trend is important to capture as we use \(G_0\) and \(\eta_0\) to normalize elastic and viscous measures respectively.

![Figure 5.8 Single mode pompom \(G'_i, G''_i\) with De for different number of arms \((q)\). The plateau modulus \((G_0)\) and steady shear viscosity \((\eta_0)\) decrease with increasing \(q\).](image)

87
Figure 5.9 Single mode pompom model for $s_a = 2$, $s_b = 10$ and different $q$ a) Intrinsic signatures as a function of $De$. $[e_1]$ and $[v_1]$ are always negative. $[e_3]$ and $[v_3]$ change signs with $De$. b) Lumped intrinsic measure $Q_0$ is always positive. Increasing $q$ decreases the absolute magnitudes of each nonlinear measure.
Figure 5.9 shows the intrinsic signatures of the pompom model for \( s_a=2, s_b=10 \) and \( q=2, 3, 4 \). \([e_1]\) is always negative and plateaus at higher frequencies, but its absolute magnitude decreases with increasing \( q \). Physically, a negative \([e_1]\) represents average elastic softening, with this effect decreasing in magnitude with increasing \( q \) over the whole range of frequencies. It is also observed that \([e_1]\) plateaus at higher De. A plateauing \([e_1]\) is particularly advantageous as it can be extracted accurately from experiments. However, the extraction of the lumped measure \( Q_0 \) at the same regime is difficult owing to its steadily decreasing trend at higher frequencies (Figure 5.9 (b)).

\([e_3]\) starts positive at lower frequencies and turns negative at higher frequencies. Interestingly, \([e_3]\) does not plateau at higher frequencies as was observed with the signatures of the Giesekus model. The effect of increasing \( q \) results in smaller absolute magnitudes of \([e_3]\). Changing \( q \) does not change the basic shape of the curves but does change the location of the zero crossing (zoomed in inset of \([e_3]\) signature in Figure 5.9(a)). \([e_3]\) corresponding to \( q=4 \) crosses zero first followed by \( q=3 \) and \( q=2 \). Although we do not show results for other values of \( q \), it can be concluded from observed trends that increasing \( q \) will result in smaller values of \([e_3]\), with the sign change occurring at smaller values of De. In the context of \([e_1]\) being negative and \([e_3]\) being positive at lower De, this would mean elastic softening at smallest instantaneous strains at lower frequencies, but the range of frequency over which this phenomena occurs reducing with increasing \( q \). At higher frequencies, \([e_3]\) is negative and indicates elastic softening at the largest instantaneous strains. But increasing \( q \) results in this behavior being observed over a larger range of frequency than observed with a smaller value of \( q \).

Trends observed with the viscous intrinsic measures are equally interesting. \([v_1]\) is always negative with its absolute magnitude decreasing with increasing \( q \). This physically denotes average viscous thinning over the whole range of frequencies and this effect diminishing with increasing \( q \). \([v_3]\) switches signs twice (zoomed in inset of \([v_3]\)) with the
measure corresponding to the largest \( q \) crossing zero first in both cases. Physical interpretations can be provided in the context of \([v_1]\). A negative \([v_3]\) at lower and higher \( \text{De} \) denoting viscous thinning at the largest instantaneous strain rates with the effect of increasing \( q \) being resulting in a the reduction of the range of occurrence of this effect on the frequency domain. A positive \([v_3]\) at intermediate \( \text{De} \) reveals viscous thinning at the smallest intermediate strain rates with the effect of increasing \( q \) increasing the range of frequency over which this effect occurs.

Hyun et al 2013 relate the timescale for relaxation of the backbone to the local maxima observed in the lumped \( Q_0 \) measure (Figure 5.9). Interestingly, we observe two local maxima for \([e_3]\) and a single local maximum for \([v_1]\) and \([v_3]\) but we restrain from attributing these observations to any timescale of relaxation of the polymeric molecule.

We obtain rich information from the decomposed intrinsic signatures by changing just one nonlinear parameter (\( q \)). The pompom model is laden with two other nonlinear parameters (\( s_a, s_b \)) and multiple combinations of all three parameters are possible without violating physicality. [Hyun et al. (2013)] consider several combinations for these nonlinear parameters and provide physical interpretations through the lumped \( Q_0 \) measure. As we demonstrate, a single curve \( Q_0 \) may not be as powerful a tool as the decomposed intrinsic measures for fitting these three nonlinear parameters independently. This motivates future work to generate a collection/library of intrinsic signatures for meaningful combinations of the three nonlinear parameters that can help provide richer physical interpretations.

The numerical approach developed here is robust and applicable to any nonlinear differential or integral constitutive model describing complex material behavior or material behavior under complex flow conditions. For example, constitutive models developed for granular flows [Kamrin (2010)] involve partial differential equations (PDEs) to describe nonlocal or boundary effects (that arise in homogeneous simple shear). A natural modification to converge on solutions to such conditions may need replacing the ODE solver block with a PDE solver block (and other suitable modifications as necessary) but still treating the stress outputs the same as in the flowchart of Figure 5.4. Work in this area will
also involve extending the current numerical structure to obtain solutions for integral models. This may involve replacing ODE solvers with other integral solver structures. However, integral models may be easier to solve and hence be less computationally expensive.

Modifications to constitutive models have been proposed to incorporate experimental observations. For example, real experiments under homogeneous simple shear kinematics involve geometry specific stress gradients resulting due to shear banding effects [Zhou et al. (2010)]. Under such conditions, stress diffusion becomes important and diffusion terms are included in the defining constitutive model. Such modifications have been recently proposed to the Giesekus model to predict the rheological behavior of shear banding fluids [Helgeson et al. (2009)]. Further complications arise for experiments at higher frequencies. Under such conditions one has to account for inertia of the sample and the propagation of shear waves at frequencies higher than the inverse timescale of the viscoelastic wave propagation thus rendering the assumption of simple shear kinematics invalid. These modifications add to the complexity of the constitutive equations in their current form and demand a numerical approach to converge on a solution. The numerical techniques developed here are adaptable to complexities that might arise in the modified form of the constitutive model and are capable of delivering quick and accurate solutions of desired material functions under a defined (stress or strain) protocol.

Having established a complete library of analytically and numerically obtained intrinsic fingerprints, we are well poised to scout for constitutive model signatures similar to those obtained experimentally for PVA-Borax. A possible identity match can help fit the corresponding model parameters and give insight to the inherent microstructure of the model system in hand. This is addressed in detail in the following chapter.
Chapter 6

Structure-Rheology Connections

Macroscopic deformation brings about changes to the microstructure of a complex material which fundamentally influence the rheology. Effective material functions successfully bridge the macroscopic response of the material to its underlying microstructure and provide physical interpretation through their signs and magnitudes (similar to intrinsic shear viscosity $[\eta(\dot{\gamma})]$ as discussed in Section 1.1). The signs and magnitudes of the four material functions of intrinsic viscoelasticity deliver meaningful physical interpretations (Chapter 2) and are sensitive to structure of a model system in hand.

Intrinsic LAOStrain material functions were experimentally measured for a model PVA-Borax system in Chapter 3. A library of intrinsic LAOStrain fingerprints were developed analytically (in Chapter 4) and through numerical simulations (in Chapter 5) for nonlinear rheological constitutive models. This chapter involves identifying a constitutive model with qualitatively similar intrinsic signatures as that of the experimental fingerprint. Interpretations of the microstructure are then made by fitting the nonlinear parameter affiliated with the identified constitutive model.

Experimental fingerprints for the PVA-Borax system are reported in Section 3.2 and physical interpretations given therein. From the database of analytically obtained intrinsic fingerprints (Chapter 4), we aim to identify a constitutive model with qualitatively similar signatures as that obtained experimentally for the PVA-Borax system. Several interesting observations follow in this process of identity matching. Figure 6.1 shows one such attempt where the fingerprints of the corotational Maxwell model are compared with the experimental fingerprint. A remarkable qualitative similarity is observed with the corotational Maxwell model with similar shapes and normalized magnitudes in the nonlinear signatures. The elastic measures $[e_1](\omega)$ and $[e_3](\omega)$ seem to plateau for $\textbf{De} = \lambda \omega \gg 1$. $[v_3](\omega)$ also has similarities in shape including the location of the zero-crossing for $\lambda \omega < 1$. The striking
Figure 6.1 Opposite signs are observed when comparing the measured fingerprint of the PVA-Borax system (symbols, $\lambda = 0.357$ s ) to the corotational Maxwell model analytical results (lines). The signs are mismatched, but the frequency-dependent magnitudes are remarkably similar. The CM model does not have a nonlinear parameter and therefore cannot fit the experimental data.

contrast to the CM model is the shift in signs of all of the four intrinsic nonlinearities. There is no nonlinear parameter affiliated with the CM model to bring about a sign change of nonlinearities, considering the nonlinearities arise from the corotational derivative operator. This prompts scouting for other constitutive models with similar intrinsic signatures and possibly nonlinear parameters that can extend physically meaningful interpretations.

From the assembled library of intrinsic nonlinear fingerprints, only one class of model can qualitatively match the signs of the experimental PVA-Borax gel: the transient network models (FENE & WLC model). These models show excellent qualitative similarity with the same signs and similar shapes as that of the experimental fingerprints. These are better than the CM model in that they show the same sign changes with frequency but also carry a
nonlinear parameter which can be fit to the experimental data to reveal insight into molecular features. Figure 6.2 shows the fit of the transient network models (FENE & WLC) to the experimental data.

It can be seen that the experimental fingerprint of \([e_1]\) plateaus at high frequencies as is the case for \([e_1]\) for the FENE model. The experimental \([e_3]\) also shows a plateau at higher frequency, but remains a subdominant response compared to \([e_1]\) and hence not a first choice for the nonlinear parameter fit. The fit results in the nonlinear parameter \(N = 0.5\). A molecular perspective can be developed by relating \(N\) to either the finite

![Experimental fingerprints vs. Transient network models](image)

Figure 6.2. Fingerprint matching of the four intrinsic LAOSTrain nonlinearities, showing the measured fingerprint of the PVA-Borax system (symbols, \(\lambda = 0.357\) s) and the fit to the analytically obtained intrinsic nonlinearities for a transient network model (lines; Eqs. 4.72-4.74). Fit of the single nonlinear quantity \(N\) results in a normalized persistence length \(\xi_p / L = 0.26\) and \(b = 0\).
extensibility parameter $b$ or the normalized persistence length $\xi_p/L$ through the relations developed between them in Eq.(4.86) and Eq.(102). We had obtained $N = 1/(b + 2)$ that results in the finite extensibility parameter $b = 0$. This value for $b$ is unphysical owing to the choice of Eq.(4.81) that is valid only for small values of $|Q|^2/L^2$. One should typically expect values of $b$ to fall within the range of $30 \leq b \leq 300$ [Bird (1987b)]. This preliminary exercise (involving the CM model and FENE model) motivates consideration of a constitutive model that can qualitatively match the experimental fingerprint and simultaneously provide physically interpretable information on the inherent microstructure through its affiliated nonlinear parameter.

We now choose to model the molecular nonlinearity in the PVA-Borax system through the worm like chain (WLC) model. Analytical solutions are obtained for intrinsic LAOStrain material functions of the WLC model in Eqs.(4.104)-(4.107). The analytical form of each nonlinear measure for the WLC model is different from the FENE model through the nonlinear front factor $N$ that directly relates to the normalized equilibrium distance

$$R = \sqrt{\langle r_{ee}^2 \rangle}/L$$

as defined in Eq. 4.99. Figure 6.2 shows the fit of the WLC model with the single fitting parameter $N = 0.5$. Although this fits the experimental data reasonably well, the fit is not perfect as is observed with the shifts for $[\overline{\nu_3}]/\eta_0$ with De. A suitable improvement may be consideration of a multi-mode model to fit data. This value of $N$ when used in Eq.(4.102) results in $R = 0.621$. This physically means a non-zero end-to-end distance before the chains are stretched by the external deformation. It is intuitive that any asymptotic nonlinear deviation away from this equilibrium state can be captured with the help of the intrinsic nonlinearities derived for the WLC model.

The nonlinearities were considered to arise from such stretched elements and a specific form for $R$ was chosen that connected directly with parameters characterizing the molecular makeup of that element. Eq.(4.96) shows this connection between $R$ and the normalized persistence length $\xi_p/L$. With the value obtained for $R$ by fitting the experimental data, the normalized persistence length can be calculated as $\xi_p/L = 0.26$. A direct comparison of $\xi_p/L$ is possible from available literature. For example, persistence length of PVA has been estimated by single molecule testing on an isolated elastic element.
modeled as a wormlike chain [Li et al. (1999)]. Those single molecule studies were performed with AFM testing on PVA in 0.2 M NaCl aqueous solution. For the initial deviation from nonlinearity, they fit $\xi_P = 1.0\text{nm}$ and $l_c = 842\text{ nm}$, where $l_c$ is the contour length of the polymer. It should be noted that the length of the element between crosslinks $L$ will be shorter than the total chain contour length $l_c$. In our analysis we assume an affine deformation of the network, but acknowledge that non-affine deformation has also been implicated in explaining nonlinearities [Storm et al. (2005), Wen et al. (2012)] and is equally plausible. Non-affine models are worth considering as future work, to see if a unique signature is available for the intrinsic LAOS material functions. Analytical results can be attempted first (as with the library populated in Chapter 4), or numerical techniques used, following the algorithm described in Chapter 5.

This chapter establishes the potency of macroscopic rheological measurements to directly relate to underlying microstructure. This is successfully done by employing intrinsic nonlinear rheological signatures as a tool to connect with the microstructural origins of the model system in hand. One can see the opportunities of this technique by considering the ease of macroscopic rheometry and the utility of reverse engineering molecular and microstructural features of complex fluids and soft solids. This motivates next steps that will involve extraction of intrinsic fingerprints for other transient physical gels that might give a response more complicated that the PVA-Borax model system. Other variants of this model system can also be considered, as well as other material-specific constitutive models for which asymptotic nonlinearities depend on specific molecular topology or hierarchical structure in the material.
Chapter 7

Conclusions

The contributions of this thesis can be summarized as follows.

Chapter 2 introduces a new theory for asymptotic material functions under shear strain controlled and shear stress controlled large amplitude oscillatory shear. Section 2.1.2 introduces four LAOStrain intrinsic measures decomposed as elastic and viscous components:

\[ e_1(\omega) \] - First harmonic elastic nonlinearity; positive \( e_1(\omega) \) represents average elastic stiffening and negative \( e_1(\omega) \) average elastic softening.

\[ e_3(\omega) \] - Third harmonic elastic nonlinearity; positive \( e_3(\omega) \) represents instantaneous elastic stiffening and negative \( e_3(\omega) \) instantaneous elastic softening.

\[ v_1(\omega) \] - First harmonic viscous nonlinearity; positive \( v_1(\omega) \) represents average viscous thickening and negative \( v_1(\omega) \) average viscous thinning.

\[ v_3(\omega) \] - Third harmonic viscous nonlinearity; positive \( v_3(\omega) \) represents instantaneous viscous thickening and negative \( v_3(\omega) \) instantaneous viscous softening.

The above measures are functions of the imposed frequency \( \omega \) and provide meaningful physical interpretations of the leading order nonlinear behavior. Interrelations of intrinsic LAOStrain measures to other nonlinear measures [Ewoldt et al. (2008)] are provided in Section 2.1.2. Section 2.1.3. introduces four intrinsic measures for shear stress control LAOS: \( c_1(\omega), c_3(\omega), f_1(\omega), f_3(\omega) \).

Chapter 3 reported experimental measurements of the newly defined LAOStrain intrinsic measures on a transiently crosslinked PVA-Borax system. A rheological fingerprint
of this material system is obtained. The intrinsic signatures provide powerful physical interpretation through their frequency dependent signs and magnitudes. The magnitudes of these measures are small and may be difficult to measure. Techniques for accurate extraction of these measures from experimental data are detailed in Section 3.3.1 and the frequency specific extraction process is shown in Figure 3.4

Chapter 4 developed analytical expressions for LAOStrain intrinsic material functions for nonlinear constitutive equations. Nonlinear constitutive models with available analytical solutions under LAOStrain were identified [Giacomin et al. (2011), Table 1] and explicit expressions were obtained for intrinsic material functions in Section 4.2. The models considered were: a third order fluid (retarded motion expansion), single mode corotational Maxwell (CM) Model [Giacomin et al (2011)], Giesekus Model [Gurnon and Wagner(2012)], integral models with generalized strain measures [Wagner et al. (2011.)], a model for rodlike polymers [(Paul et al. (1969)] and simple emulsions [Yu et al. (2002)]. The intrinsic signatures were functions of the frequency (Deborah number) and a nonlinear parameter, if any. New solutions of intrinsic LAOStrain fingerprints were derived for two transient network models; finitely extensible nonlinear elastic (FENE) model and a wormlike chain (WLC) model. The intrinsic nonlinearities for these models showed the same De dependence and shared a common nonlinear front factor \( N \) that directly related to a microstructure defining quantity (Eq. 4.86 and 4.102). A library of analytical intrinsic LAOStrain fingerprints was thus generated. Although the linear viscoelastic signatures were identical (single mode Maxwell), distinct differences were observed in the newly defined low-dimensional material functions. Interesting features such as sign changes were observed and Section 4.3 compared and contrasted constitutive models based on their intrinsic signatures.

Chapter 5 developed a robust numerical scheme for automated and accurate extraction of LAOStrain intrinsic nonlinearities for any nonlinear differential constitutive model. Section 5.1 discussed the numerical algorithm and a flowchart (Figure 5.4) summarized the proposed techniques. A Deborah number dependent alternance state criterion was hypothesized (Eq. 5.2) and its applicability discussed from simulation results from the single mode pompom model and the Giesekus model. Using the numerical algorithm proposed in Section 5.1), intrinsic LAOStrain nonlinearities were extracted for the Giesekus model and the single mode corotational Maxwell model in Section 5.2. The
numerical signatures perfectly matched the analytical signatures and validated the accuracy of the used algorithm. Intrinsic nonlinearities of the single mode pompom model were extracted numerically in Section 5.3 and its signatures compared across nonlinear parameters. The robustness of the developed numerical scheme to arising complexities from modifications to constitutive models is discussed. Suitable changes to the numerical structure are proposed to accommodate for such modifications.

Chapter 6 detailed the process of matching experimental fingerprints of PVA-Borax with analytically obtained fingerprints in Chapter 4. Intrinsic fingerprints for the CM model showed similar shapes as the experimental fingerprints, but the signs were flipped. The FENE model signatures qualitatively matched experimental fingerprints and allowed fitting a single nonlinear parameter $N$ that directly related to the finite extensibility parameter $b$ (Eq. 4.86). From the fits a nonphysical value of $b = 0$ was obtained. However, a fit of the WLC model fingerprints yielded a physically interpretable value for the normalized persistence length $\xi_p / L \approx 0.26$. The microstructure of the PVA-Borax system could thus be interpreted from macroscopic rheological measurements.

In short, the impact of the contributions from this thesis are potentially realizable in identifying and down-selecting predictive tensorial constitutive models that best represent a material response to nonlinear oscillatory deformation. Unique behavior of a material system in its intrinsic regime can also develop insight into new constitutive model development. The rheology-structure interpretations drawn from low-dimensional asymptotic nonlinearities can be directly applied to reverse-engineer structured materials.

Going forward, it will be worthwhile considering analytical solutions to other nonlinear models. Analytical solutions of the Johnson-Segalman model [Johnson & Segalman (1976)] is one next step in this direction as it smoothly connects the upper convected Maxwell model, corotational Maxwell and lower convected Maxwell model for different limits of a nonlinear parameter. The differences in intrinsic signatures with changes in molecular parameters are apparent from the fingerprints of the Single mode pompom model. This informs us of the need to study the intrinsic signatures of other constitutive models as a function of their molecular parameters. Also in our radar are models that do not allow for a continuum level representation to calculate the stress tensor, e.g. nonlinear elastic
networks which do not employ closure approximations. The numerical techniques developed in Chapter 5 are expected to be effective for these studies.
References


Dimitriou C.J., R.H. Ewoldt, G.H. McKinley "Describing and prescribing the constitutive response of yield stress fluids using large amplitude oscillatory stress (LAOStress)," J. Rheol., (2013)

Einstein, A., "Berichtigung zu meiner Arbeit: 'Eine neue Bestimmung der Moleküldimensionen'." Annalen der Physik 34: 591 (1911)


Macosko CW. 1994. Rheology principles, measurements, and applications.


Appendix A

A.1. $Q_0$ for the Corotational Maxwell model

The $Q$ coefficient is defined as [Hyun et al. (2007)] through the relative intensity of the third harmonic stress compared to the first harmonic stress

$$Q = \frac{I_{3/1}}{\gamma_0^2} = \frac{1}{\gamma_0^2} \frac{\sigma_3}{\sigma_1}. \quad (A.1)$$

In the limits of small strain amplitudes, it is possible to define

$$Q_0 = \lim_{\gamma_0 \to 0} \frac{1}{\gamma_0^2} \left( \frac{\sigma_3}{\sigma_1} \right) = \frac{\sqrt{|e_3|^2 + |\nu_3|\omega^2}}{\sqrt{G_1^2 + G_1''^2}}, \quad (A.2)$$

which clearly conflates elastic and viscous measures. Using Eqs. 4.8-4.11 for the intrinsic material functions for the corotational Maxwell model in Eq. (A.2), we obtain

$$Q_0 = \frac{9}{4} G^2 \left( \frac{D_e^4(1-D_e^2)}{(1+De^2)(1+4De^2)(1+9De^2)} \right)^2 + \frac{1}{16} \left( G \lambda \right)^2 \alpha^2 \left( \frac{D_e^2(1-11De^2)}{(1+De^2)(1+4De^2)(1+9De^2)} \right)^2 \quad (A.3)$$

which simplifies to

$$Q_0 = \frac{D_e^2}{2(1+4De^2)(1+9De^2)} \sqrt{9D_e^6 + \frac{49}{4} D_e^4 + \frac{7}{2} D_e^2 + \frac{1}{4}} \quad (A.4)$$

It is clear from Eq. (A.4) that $Q_0$ is always positive, unlike intrinsic measures which change signs with $De$.

A.2. Simple Emulsions

For a strain input $\gamma(t) = \gamma_0 \sin (\omega tt^*)$, the stress output is given as
where the coefficients $a_1 - a_4$ and $b_1 - b_4$ are functions of $Ca_0$, $\omega \tau$, $f_1$, $f_2$ where

$$Ca_0 = \gamma_0(\omega \tau) = \gamma_0 De$$

$$f_1 = \frac{40(p + 1)}{(2p + 3)(19p + 16)}$$

$$f_2 = \frac{5}{2p + 3}$$

where $p = \frac{\eta_d}{\eta_m}$ is the viscosity ratio of the Newtonian droplet to the surrounding Newtonian matrix.

$$K = \frac{3f_1}{4f_2^2} \frac{\Gamma}{R} \frac{C(p, \phi) - A(p, \phi)}{B(p, \phi)}$$

$$= \frac{6\Gamma}{5R} \left[ \frac{(p + 1)(2p + 3)\phi}{5(p + 1) - (5p + 2)\phi} \right]$$

where $\Gamma$ is the surface tension, $R$ the drop radius and $\phi$ the volume fraction.

The coefficients scale with $\gamma_0$ as

$$a_1 \approx O(\gamma_0) + O(\gamma_0^3),$$

$$a_2 \approx O(\gamma_0) + O(\gamma_0^3),$$

$$a_3 \approx O(\gamma_0^3),$$

$$a_4 \approx O(\gamma_0^3),$$

and
\[ b_0 \approx O(\gamma_0) + O(\gamma_0^2) + O(\gamma_0^4), \]
\[ b_1 \approx O(\gamma_0^2) + O(\gamma_0^4), \]
\[ b_2 \approx O(\gamma_0^2) + O(\gamma_0^4), \]  \hspace{1cm} (A.10)
\[ b_3 \approx O(\gamma_0^4), \]
\[ b_4 \approx O(\gamma_0^4). \]

We now consider how the resulting coefficients in front of \( \sin \omega t, \cos \omega t, \sin 3\omega t \) and \( \cos 3\omega t \) scale, so we can identify which terms can later be neglected.

The coefficient for \( \sin \omega t \) is
\[
\frac{a_1}{b_0 + b_1 \sin 2\omega t + b_2 \cos 2\omega t + b_3 \sin 4\omega t + b_4 \cos 4\omega t}
\] \hspace{1cm} (A.11)
which can alternately be written using Eq. (A.9) and (A.10) as
\[
\frac{O(\gamma_0) + O(\gamma_0^3)}{O(1) + O(\gamma_0^2) + O(\gamma_0^4)}. \] \hspace{1cm} (A.12)

We neglect the \( O(\gamma_0^4) \) term in the denominator, Multiply and divide by the the conjugate and obtain
\[
\frac{O(\gamma_0)O(1) + O(\gamma_0^3)O(1) - O(\gamma_0)O(\gamma_0^2) - O(\gamma_0^3)O(\gamma_0^2)}{O(1)^2 - O(\gamma_0^4)}. \] \hspace{1cm} (A.13)

We must be careful to retain \( O(\gamma_0^2) \) in the denominator but can neglect \( O(\gamma_0^4) \) or \( b_3, b_4 \) to maintain \( O(\gamma_0^3) \) terms overall.

The coefficient of \( \cos \omega t \) results in the same expression as for the coefficient of \( \sin \omega t \).

The coefficient of \( \sin 3\omega t \) is
\[
\frac{a_3}{b_0 + b_1 \sin 2\omega t + b_2 \cos 2\omega t + b_3 \sin 4\omega t + b_4 \cos 4\omega t}
\] \hspace{1cm} (A.14)
which can alternately be written using Eq. (A.9) and (A.10) as
We neglect the $O\left(\gamma_0^4\right)$ term in the denominator, multiply and divide by the conjugate and obtain this coefficient to depend on $O\left(\gamma_0^3\right)$. This means terms $b_1, b_2, b_3, b_4$ can be neglected in the denominator.

The coefficient of $\cos 3\omega t$ is treated similarly and we obtain the same result as that of the coefficient of $\sin 3\omega t$.

We now expand the expression for the interfacial stress as

$$\sigma_{12}^x = \frac{a_1 \sin \omega t + a_2 \cos \omega t + a_3 \sin 3\omega t + a_4 \cos 3\omega t}{b_0 + b_1 \sin 2\omega t + b_2 \cos 2\omega t + O\left(\gamma_0^4\right)} = \frac{[\text{Num}]}{[\text{Den}]}, \quad (A.15)$$

$$\sigma_{12}^y = \frac{[\text{Num}]}{b_0 + b_1 \sin 2\omega t + b_2 \cos 2\omega t} \left(\frac{b_0 - b_1 \sin 2\omega t - b_2 \cos 2\omega t}{b_0 - b_1 \sin 2\omega t - b_2 \cos 2\omega t}\right) + O\left(\gamma_0^5\right), \quad (A.16)$$

The second term in the denominator is of $O\left(\gamma_0^4\right)$ and can be neglected resulting in

$$\sigma_{12}^y = \frac{[\text{Num}](b_0 - b_1 \sin 2\omega t - b_2 \cos 2\omega t)}{b_0^2 - (b_1 \sin 2\omega t + b_2 \cos 2\omega t)^2} + O\left(\gamma_0^5\right). \quad (A.17)$$

We now consider each trigonometric term separately, keeping only up to $O\left(\gamma_0^3\right)$ terms, and expecting to generate $\sin \omega t, \sin 3\omega t, \cos \omega t, \cos 3\omega t$ from each term. In the end, we will combine all coefficients in front of each $\sin(n\omega t)$ and $\cos(n\omega t)$ to identify $G', G^*, [e_1], [v_1], [e_3], [v_3]$.

We will use the Fourier moduli representation

$$\sigma = \gamma_0 \sum G'_n \sin(n\omega t) + G^*_n \cos(n\omega t), \quad (A.18)$$

And then convert to Chebyshev notation where $e_1 = G', v_1 \omega = G^*, e_3 = -G'_3, v_3 \omega = G^*_3$
We start by writing the term ahead of $\sin \omega t$ in the numerator as

$$\frac{a_1}{b_0} \left[ b_0 - b_1 \sin 2\omega t - b_2 \cos 2\omega t \right] \sin \omega t + O\left(\gamma_0^5\right),$$

(A.19)

use trigonometric identities and obtain

$$\left[ \left( \frac{a_1}{b_0} + \frac{a_1 b_2}{2 b_0^2} \right) \sin \omega t - \left( \frac{a_1 b_2}{2 b_0^2} \right) \cos \omega t \right]$$

$$+ \left( \frac{-a_1 b_2}{2 b_0^2} \right) \sin 3\omega t + \left( \frac{a_1 b_2}{2 b_0^2} \right) \cos 3\omega t + O\left(\gamma_0^5\right)$$

(A.20)

Similarly the terms ahead of $\cos \omega t$, $\sin 3\omega t$, $\cos 3\omega t$ are respectively written as

$$\left\{ \left( \frac{-a_1 b_2}{2 b_0^2} \right) \sin \omega t - \left( \frac{a_1 b_2}{2 b_0^2} \right) \cos \omega t \right\}$$

$$+ \left( \frac{-a_1 b_2}{2 b_0^2} \right) \sin 3\omega t + \left( \frac{-a_1 b_2}{2 b_0^2} \right) \cos 3\omega t + O\left(\gamma_0^5\right)$$

$$\frac{a_3}{b_0} \sin 3\omega t + O\left(\gamma_0^5\right),$$

(A.21)

$$\frac{a_4}{b_0} \cos 3\omega t + O\left(\gamma_0^5\right),$$

where terms greater than $O\left(\gamma_0^3\right)$ are neglected. The combined terms are then written in the Chebyshev framework as

$$\gamma_0 e_1 = \gamma_0 G'_1 = \frac{a_1 \left( 2b_0 + b_2 \right) - a_1 b_1}{2 b_0^2} + O\left(\gamma_0^5\right),$$

$$\gamma_0 v_{1,0} = \gamma_0 G'_2 = \frac{-a_1 b_2 + a_2 \left( 2b_0 - b_2 \right)}{2 b_0^2} + O\left(\gamma_0^5\right),$$

$$\gamma_0 e_3 = -\gamma_0 G'_3 = \frac{a_2 b_2 + a_2 b_1 - 2a_1 b_0}{2 b_0^2} + O\left(\gamma_0^5\right),$$

$$\gamma_0 v_{3,0} = \gamma_0 G'_4 = \frac{a_1 b_1 - a_2 b_2 + 2a_1 b_0}{2 b_0^2} + O\left(\gamma_0^5\right).$$

(A.22)

We decompose the coefficients in the stress expression to a convenient form,
where the first term in the subscript denotes the coefficient and the second term denotes the strain amplitude exponents. We then substitute these terms in Eq. (A.22) and obtain expressions for intrinsic measures. Under this representation, the first harmonic elastic Chebyshev coefficient in Eq. (A.22) can be written as

$$\gamma_0 e_1 = \frac{\left( a_{11} \gamma_0 + a_{13} \gamma_0^3 \right) \left( 2b_{00} + 2b_{02} \gamma_0^2 + b_{22} \gamma_0^2 \right) - \left( a_{21} b_{12} \gamma_0^3 + a_{23} b_{12} \gamma_0^3 \right)}{2 \left( b_{00} + b_{02} \gamma_0^2 \right)^2} + O(\gamma_0^3),$$

(A.23)

and

$$\gamma_0 e_1 = \frac{\gamma_0 \left[ 2b_{00} a_{11} + \gamma_0^3 \left[ 2b_{00} a_{13} + 2b_{02} a_{11} \right] \right]}{2 \left( b_{00} + b_{02} \gamma_0^2 \right)^2} \frac{\left( b_{00}^2 - 2b_{00} b_{02} \gamma_0^2 \right)}{\left( b_{00}^2 - 2b_{00} b_{02} \gamma_0^2 \right)} \frac{\left( b_{00}^2 - 2b_{00} b_{02} \gamma_0^2 \right)}{\left( b_{00}^2 - 2b_{00} b_{02} \gamma_0^2 \right)}$$

(A.24)

and

$$\gamma_0 e_1 = \frac{\gamma_0 \left[ 2a_{11} b_{00} \right]}{2 \left( b_{00} + O\left( \gamma_0^4 \right) \right)} + O(\gamma_0^5)$$

$$\gamma_0 e_1 = \gamma_0 \left[ \frac{a_{11}}{b_{00}} \right] + O\left( \gamma_0^3 \right) \left[ \frac{a_{13}}{b_{00}} + \frac{b_{02} a_{11}}{b_{00}^2} + \frac{a_{11} b_{22}}{2b_{00}^2} - \frac{a_{21} b_{12}}{2b_{00}^2} - \frac{2a_{11} b_{02}}{b_{00}^2} \right] + O(\gamma_0^5)$$

(A.25)

giving the linear viscoelastic elastic modulus

$$G' = \frac{a_{11}}{b_{00}} = \frac{2}{3} K f_2^2 f_1^2 \frac{\left( \omega \lambda_0 \right)^2}{f_1^2 \left( 1 + \left( \omega \lambda_0 \right)^2 \right)}$$

$$G' = \frac{2}{3} K f_2^2 \left( \frac{D e^2}{1 + D e^2} \right)$$
where $\lambda_b = \frac{\tau}{b_1}$ is the relaxation time and $De = \omega \lambda_b$ is the Deborah No. The first harmonic intrinsic nonlinearity

$$[e_1] = \left[ \frac{a_{11}}{b_{00}} + \frac{b_{00} a_{11}}{b_{00}^2} + \frac{a_{12} b_{12}}{2b_{00}} - \frac{a_{13} b_{13}}{2b_{00}^2} - \frac{2a_{11} b_{12}}{b_{00}^2} \right],$$

$$[e_1] = -\frac{1}{18} K(\omega \tau)^4 f_2^4 \left[ \frac{f_1^2 + 3(\omega \tau)^2}{(f_1^2 + (\omega \tau)^2)^3} - \frac{5f_1^2 + 8(\omega \tau)^2}{(f_1^2 + (\omega \tau)^2)^3 (f_1^2 + 4(\omega \tau)^2)} \right],$$

$$[e_1] = \frac{Kf_2^4}{9} (\omega \tau)^4 \left[ \frac{f_1^4 - f_1^2 (\omega \tau)^2 - 6(\omega \tau)^4}{(f_1^2 + (\omega \tau)^2)^3 (f_1^2 + 4(\omega \tau)^2)} \right],$$

$$[e_1] = \frac{Kf_2^4}{9} De^4 \left[ \frac{1 - De^2 - 6De^4}{(1 + De^2)^3 (1 + 4De^2)} \right].$$

The above expression for $[e_1]$ is then normalized by the plateau modulus $G = \frac{2}{3} Kf_2^2$ from Eq. (A.25)

$$\frac{[e_1]}{G_0} = \frac{f_2^4}{6} De^4 \left[ \frac{1 - De^2 - 6De^4}{(1 + De^2)^3 (1 + 4De^2)} \right].$$

The first harmonic viscous Chebyshev coefficients can be written as
\[
\gamma_0 v_1 \omega = \frac{-\left(a_{13} \gamma_0 + a_{13} \gamma_0^3\right) \left(b_{12} \gamma_0^2\right) + \left(a_{21} \gamma_0 + a_{23} \gamma_0^3\right) \left(2b_{00} + 2b_{02} \gamma_0^2\right)}{2\left(b_{00} + b_{02} \gamma_0^2\right)^2} + O\left(\gamma_0^5\right),
\]
\[
\gamma_0 v_1 \omega = \frac{\gamma_0 \left[2b_{00} a_{21}\right] + \gamma_0^3 \left[2b_{00} a_{23} + 2b_{02} a_{21}\right]}{2\left(b_{00} + b_{02} \gamma_0^2\right)^2} + 2\left(b_{00} + b_{02} \gamma_0^2\right) \left(b_{00} - 2b_{00} b_{02} \gamma_0^2\right) + O\left(\gamma_0^5\right),
\]
\[
\gamma_0 v_1 \omega = \frac{\gamma_0 \left[2b_{00} a_{23} + 2b_{02} a_{21}\right] - 2b_{00} a_{12} b_{02} a_{21} - a_{21} b_{22} b_{00}^2 \gamma_0^3}{2\left(b_{00} + b_{02} \gamma_0^2\right)^2} + O\left(\gamma_0^5\right).
\]
Retaining \(O\left(\gamma_0^3\right)\) terms in the numerator and neglecting \(O\left(\gamma_0^4\right)\) terms in the denominator, we have
\[
\gamma_0 v_1 \omega = \gamma_0 \left[\frac{\frac{a_{21}}{b_{00}} + \frac{b_{02} a_{21}}{b_{00}^2} - \frac{a_{12} b_{22}}{b_{00}^2} - 2\frac{a_{21} b_{02}^2}{b_{00}^2}}{2\left(b_{00} + b_{02} \gamma_0^2\right)^2} + O\left(\gamma_0^5\right),
\]
where the linear viscoelastic viscous loss modulus is given as
\[
G_{LVE}^\sigma = \frac{a_{21}}{b_{00}} + \frac{b_{02} a_{21}}{b_{00}^2} - \frac{a_{12} b_{22}}{b_{00}^2} - 2\frac{a_{21} b_{02}^2}{b_{00}^2} + \frac{2}{3} \frac{K_f f_1^2}{f_1^2 + \left(\omega \tau\right)^2},
\]
\[
G_{LVE}^\sigma = \frac{2}{3} \frac{K_f f_1^2}{1 + De^2},
\]
and the corresponding first harmonic viscous nonlinearity is given by
\[
[v_1] \omega = \frac{a_{21}}{b_{00}} + \frac{b_{02} a_{21}}{b_{00}^2} - \frac{a_{12} b_{22}}{2b_{00}^2} - \frac{a_{21} b_{02}^2}{2b_{00}^2} - 2\frac{a_{21} b_{02}^2}{b_{00}^2}.
\]
which can alternately be written as
\[
[v_1] \omega = \frac{1}{b_{00}^2} \left[-a_{21} \left(b_{22} \frac{2}{2} + b_{02}\right) + a_{23} b_{00}^2 - a_{11} b_{12}^2 \right],
\]
that in turn reduces to
The above expression for $[v_1]$ is then normalized by the steady shear viscosity $\eta = G\lambda_b$,

$$\frac{[v_1]}{\eta} = -\frac{f_2}{2} \left[ \frac{1 + 4\text{De}^2 + 3\text{De}^4}{(1 + \text{De}^2)^3 (1 + 4\text{De}^2)} \right].$$

(A.34)

The third harmonic elastic Chebyshev coefficient can be written as

$$\gamma_0 e_3 = \frac{\left\{ \left( a_{11}\gamma_0 + a_{13}\gamma_3^3 \right) (b_{22}\gamma_0^2) + \left( a_{21}\gamma_0 + a_{23}\gamma_0^3 \right) (b_{12}\gamma_0^3) \right\}}{2 \left( b_{00} + b_{02}\gamma_0^2 \right)^2} + O\left(\gamma_0^5\right),$$

$$\gamma_0 e_3 = \frac{\gamma_0^3 \left[ a_{11}b_{22} + a_{21}b_{12} - 2a_{33}b_{00} \right] + O\left(\gamma_0^5\right) \left( b_{00}^2 - 2b_{00}b_{02}\gamma_0^2 \right)}{2 \left( b_{00}^2 + 2b_{00}b_{02}\gamma_0^2 \right) \left( b_{00}^2 - 2b_{00}b_{02}\gamma_0^2 \right)}$$

(A.35)

$$\gamma_0 e_3 = \frac{\gamma_0^3 \left[ a_{11}b_{22} + a_{21}b_{12} - 2a_{33}b_{00} \right] + O\left(\gamma_0^5\right)}{2 \left( b_{00}^2 - O\left(\gamma_0^4\right) \right)}$$

Retaining $O\left(\gamma_0^3\right)$ terms in the numerator and neglecting $O\left(\gamma_0^4\right)$ terms in the denominator compared to $b_{00}^2$, we have

$$\gamma_0 e_3 = \gamma_0^3 \left[ \frac{a_{11}b_{22}}{2b_{00}} + \frac{a_{21}b_{12}}{2b_{00}} - \frac{a_{33}b_{00}}{b_{00}} \right] + O\left(\gamma_0^5\right)$$

(A.36)

The third harmonic elastic intrinsic nonlinearity is then given by
\[ [e_3] = \frac{a_1 b_{22} + a_{21} b_{12} - a_{33}}{2 b_{00}^2} \]

which can be rewritten as

\[ [e_3] = \frac{2 K f_a^4}{9} \left( \frac{2 f_1^4 + (\omega \tau)^2 f_1^2 - (\omega \tau)^4}{(f_1^2 + (\omega \tau)^2)^3} \right) \]

\[ [e_3] = \frac{2 K f_a^4}{9} D e^4 \left( \frac{2 + D e^2 - D e^4}{(1 + D e^2)^3 (1 + 4 D e^2)} \right) \]

(A.38)

The normalized expression for \([e_3]\) is

\[ \frac{[e_3]}{G} = \frac{f_2^2}{3} D e^4 \left( \frac{2 + D e^2 - D e^4}{(1 + D e^2)^3 (1 + 4 D e^2)} \right) \]

(A.38)

The third harmonic viscous Chebyshev coefficient can be written as

\[ \gamma_{v3}^\omega = \frac{\left( a_1 \gamma_0 + a_{13} \gamma_0^3 \right) (b_{12} \gamma_0^2) - \left( a_{21} \gamma_0 + a_{23} \gamma_0^3 \right) (b_{22} \gamma_0^2) + 2 a_{43} \gamma_0^3 (b_{00} + b_{02} \gamma_0^2)}{2 \left( b_{00}^2 + b_{02} \gamma_0^2 \right)^2} + O(\gamma_0^5) \]

(A.38)

\[ \gamma_{v3}^\omega = \frac{\gamma_0^3 \left[ a_1 b_{12} - a_{21} b_{22} + 2 a_{43} b_{00} \right] + O(\gamma_0^5) \left( b_{00}^2 - 2 b_{00} b_{02} \gamma_0^2 \right)}{2 \left( b_{00}^2 + b_{02} \gamma_0^2 \right)^2} \]

(A.38)

Retaining \(O(\gamma_0^3)\) terms in the numerator and neglecting \(O(\gamma_0^4)\) terms in the denominator compared to \(b_{00}^2\), we have

\[ \gamma_{v3}^\omega = \gamma_0^3 \left[ \frac{a_1 b_{22} - a_{21} b_{12} + a_{33}}{2 b_{00}^2} \right] + O(\gamma_0^5) \]

(A.39)

The third harmonic viscous intrinsic nonlinearity is then given by
\[ [v_3] \omega = \left[ \frac{a_{11} b_{12}}{2 b_{00}^2} - \frac{a_{21} b_{22}}{2 b_{00}^2} + a_{33} \right] \]  
\[ (A.40) \]

\[ [v_3] \omega = \frac{K f^4}{18} (\omega \tau)^3 \left( \frac{-2 f_i^4 + 7 (\omega \tau)^2 f_i^2 + 6 (\omega \tau)^4}{(f_i^2 + (\omega \tau)^2)^3 \left(f_i^2 + 4 (\omega \tau)^2\right)^4} \right), \]  
\[ (A.41) \]

\[ [v_3] = \frac{K \lambda f^4}{18} De^2 \left( \frac{-2 + 7 De^2 + 6 De^4}{(1 + De^2)^3 (1 + 4 De^2)} \right). \]  
\[ (A.42) \]

The normalized expression for \([v_3]\) is

\[ \frac{[v_3]}{\eta_0} = \frac{f_j^2}{12} De^2 \left( \frac{-2 + 7 De^2 + 6 De^4}{(1 + De^2)^3 (1 + 4 De^2)} \right). \]  
\[ (A.43) \]

**A.3. Rodlike Polymers**

For the simple case of a dumbbell type molecule, the summation terms become (see [Kirkwood and Plock (1956), Eq. 11])

\[ S_1 = \sum_{l=-n}^{n} l \psi_1(\lambda_0) = \frac{1}{2(1 - \lambda_0)}, \]  
\[ (A.44) \]

\[ S_2 = \sum_{l=-n}^{n} l \psi_1(2 \lambda_0) = \frac{1}{2(1 - 2 \lambda_0)} \]

and for the case where \(n\) is large

\[ S_1 = \sum_{l=-n}^{n} l \psi_1(\lambda_0) = \frac{n^3}{3 \lambda_0 \log(L/b)}, \]  
\[ (A.45) \]

\[ S_2 = \sum_{l=-n}^{n} l \psi_1(2 \lambda_0) = \frac{n^3}{3(2 \lambda_0) \log(L/b)}, \]
where \( \lambda_0 = \zeta / 8 \pi \eta_0 b \). In the limits of large (for a single large dumbbell type molecule) we can assume \( \lambda_0 \ll 1 \) which leads to 

\[
S_1 = \sum_{l=-n}^{n} h\psi_l(\lambda_0) \approx \frac{1}{2} \quad \text{and} \quad S_2 = \sum_{l=-n}^{n} h\psi_l(2\lambda_0) \approx \frac{1}{2} .
\]

These values directly feed into Eqs. 4.29-4.32.