ENABLING DESIGN WITH RHEOLOGICAL COMPLEXITY: INTUITION AND OPTIMIZATION OF VISCOELASTIC MATERIALS

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THESIS

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ABSTRACT

In this thesis, we seek to outline a methodology to enable engineering design based on rheologically complex materials. Traditionally, engineers choose hard materials or simple fluids for design. Complex materials (soft solids and non-Newtonian fluids) greatly increase the design space. Additionally, these materials add functionality (viscoelasticity, nonlinearity) that can achieve diverse performance objectives (user experience, vibration isolation, etc.). Here, we focus on a specific rheological complexity: viscoelasticity. Viscoelasticity introduces a material time dependence, often referred to as memory. The design process with these materials is presented as a multi-step inverse problem that begins with identifying optimal target rheology to meet specified performance objectives. This target rheology remains material agnostic, to be achieved through the design of the viscoelastic material microstructure. A survey of material structures to achieve viscoelastic timescales is reviewed, outlining several design strategies for viscoelastic target properties.
To my friends and family, for their support these past two years.
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1 INTRODUCTION

Rheology focuses on complex materials whose properties, unlike simple solids or fluids, are function-valued. Unsurprisingly, using these rheologically complex materials in design presents interesting challenges. The utility of these materials is well established—everything from food products [1] to sticky notes to complex biological systems [2, 3, 4, 5, 6].

Historically, the intersection between materials and design has been primarily materials selection, or choosing an appropriate material from some set of pre-existing materials that may or may not be well suited for the desired application [7, 8, 9].

True design with complex materials presents a multi-step inverse problem, as outlined in Fig. (2.1). Traditional materials science moves along the analysis axis (left to right, in this figure). A known material (or material class) is characterized and a use is (hopefully) found. Design with and of complex materials goes through these steps in the reverse order. First, a performance objective is chosen. Next, the complex rheology is optimized to meet this design target without the limitations of a specific material or material class (thus being material agnostic). After this, a material can be designed that meets the rheological property objectives.

This thesis will include two descriptions of this design process. The first will focus on how this idea can relate to a specific type of performance: how the material is perceived with touch (Chapter 2).

The complex, function-valued properties of rheologically complex materials present a challenge in design for user experience and perception. Here we introduce a stress-amplitude Pipkin Space to connect perception to rheology. The stress-controlled paradigm can (i) correlate with human tactile perception of material properties, (ii) simplify the presentation of rheological complexity, and (iii) guide experimental characterization to be within stress amplitudes and timescales relevant to user experience. A case study of physical therapy put-
Figure 1.1: Design with complex materials can be thought of a multi-step inverse problem (right to left). This process includes: (1) identifying target performance, (2) finding the necessary rheological properties to achieve these goals, and (3) choosing or creating materials which have the rheological properties. Four questions guide this method: For a given performance objective, what is the optimal rheology (Chap. 3)? If you feel a material, can you graph its material functions (Chap. 2)? If you see a material function, do you know how a material will feel (Chap. 2)? If you know the target rheology, can you design the necessary material (Chap. 4)?

ties, designed for a range of user experience (extra-soft, soft, medium, medium-firm, firm, extra-firm), shows that linear viscoelastic properties can correlate with human tactile perception. We show that stress-input measures, namely dynamic compliance and fluidity, are lower-dimensional descriptions of these materials compared to dynamic moduli. Although all linear descriptions are inter-related and inter-changeable, we show that we can reduce the complexity of the data with stress-input descriptions and hence achieve a clearer conceptual understanding of the differences of the materials. This understanding leads to improved tactile intuition with viscoelasticity.

The second approach systematically outlines the optimization of a function-valued material property relating to the linear viscoelasticity (relaxation function) of the material to meet a
Specific design objective (Chapter 3).

Rheologically-complex materials are described by function-valued properties with dependence on a timescale (linear viscoelasticity), input amplitude (nonlinear material behavior), or more generally both (nonlinear viscoelasticity). This complexity presents a difficulty when trying to utilize these material systems in engineering designs. Here, we describe a process to mathematically model and optimize design targets for linear viscoelastic systems, encompassing viscoelastic materials as well as one-dimensional spring-dashpot mechanical systems. We show that simple engineering design assumptions can be relaxed from a conventional spring-dashpot topology to a generalized linear viscoelastic relaxation kernel; $K(t)$ for spring-dashpot components, or stress relaxation modulus $G(t)$ for viscoelastic material properties. With the relaxation kernel as the design variable, one can identify optimal viscoelastic properties agnostic to any specific material structure or spring-dashpot topology. This approach expands the design space, connecting the system-level performance with optimal material functions. Simplifying the relaxation kernel by the use of specific parameterizations for $K(t)$ (e.g. Maxwell fluid model, critical gel model), allows for the use of basic optimization techniques. These early-stage design targets allow for broadly creative ideation of possible material solutions, which can then be used for either material-specific selection or later-stage design of novel materials.

Both stories discussed focus on a specific type of rheological complexity—(linear) viscoelasticity. This property relates to the time dependent response of a material to imposed stresses or strains. Some physical origins of this time dependence are discussed in Chapter 4.
2 STRESS-INPUT RHEOLOGY FOR DESIGN INTUITION AND USER EXPERIENCE

2.1 Introduction and Background

Figure 2.1: Analysis of complex materials (L to R) starts by analyzing a microstructure to describe it with relevant material properties. With any luck, a novel use for the material can later be found. Design with/of complex materials (R to L) is an inverse problem that begins with a target performance. Rheological properties are optimized to achieve this and a material is design to suit these needs.

Engineering design with hard materials and fluids is well established. The use of soft materials, those between the bounds of pure solids and fluids, remains limited. The worth of these materials is readily demonstrated in biological systems. There are many barriers preventing the use of complex fluids, such as viscoelastic materials, in engineering design. First, even simple viscoelastic material properties are functions, not single values. Thus, even at a basic level, design with these materials is a high-dimensional problem. Second, while design intuition with solid and fluid materials is well developed, the same intuition with soft solids is lacking.

The development of intuition with complex materials is central to designing with these tools. Currently, most work is done through analysis of existing materials and material classes and fitting those materials into necessary applications, shown from left to right in Fig. 2.1. True design requires starting at the required performance, while remaining material
agnostic, i.e. agnostic to the particular material used to achieve the performance. This methodology is shown from right to left in Fig. 2.1. The process begins by relating the required performance to rheological properties or material functions. A material is then designed (selected, or created), which meets the criteria necessary.

Here, we develop a method to correlate a specific type of material performance, user experience of a material, with simple rheological characterization. The key approach is a stress-input perspective Pipkin space to map out stress amplitudes and time scales relevant to human perception. The use of this Pipkin space guides experimental characterization of materials to be within the range of user experience. We use some commercially available, non-toxic materials (described in 2.3.1) and encourage the reader to procure and experience the materials while reading this work. The stress-input has additional benefits: we demonstrate that using this stress-input paradigm (material functions compliance and fluidity), the complexity of this high-dimensional problem can be greatly reduced. Reducing complexity leads to better intuition of the interrelation between user experience of a material and its rheological characterization.

2.2 The Stress-input Perspective

When discussing tactile perception and how people interact with materials, it seems natural to speak about stress inputs. This contrasts with how rheologically-complex materials are often described in terms of strains and strain-rates being the controlled input (which is convenient for understanding/solving some constitutive models, e.g. ordered fluid expansions where stress is an explicit function of multiple terms involving strain rate).

2.2.1 Stress-Amplitude Pipkin Space

The two-dimensional operational space put forth by Pipkin is useful in mapping out material behavior and testing [10]. Traditionally, the space is presented as a function of two non-dimensional representations of shear input: the Deborah number (De=\(\lambda \omega\)) and the Weissenberg number (Wi=\(\lambda \dot{\gamma}\)). These terms allow for a description of the relevant time
scale and the strength of the deformation. The Pipkin space is limited to material specific
descriptions by its dependence on a characteristic timescale or relaxation time, $\lambda$.

Here, we present a modified Pipkin space to use as a material agnostic, stress-amplitude
operational map, shown in Fig. 2.2. From a human perspective, stress is a more intu-
itive/natural way to think about interacting with a material, thus making it a helpful tool
in describing how a user would experience rheologically complex materials.

In the stress-amplitude Pipkin space of Fig. 2.2, the strength of the flow is described
simply as the stress amplitude in the place of the traditional Weissenberg number. On the
Pipkin space, we map out regions of interest to a particular problem or use. In Fig. 2.2, the
colored regions are those relevant in the context of physical therapy for human hands (human
tactile perception), but a similar methodology could be followed for other user-experience
problems (e.g. mouthfeel, ....). Visual perception, shown in orange in Fig. 2.2, is particularly
important for viscoelastic materials which can appear solid over short times and flow over
long times. Here, the visual perception is bound by ranges of human perception [11] as well
as timescales and stresses relevant for experiencing the material (e.g. $t_{\text{max}} \sim 24$ hours before
getting bored of watching a material). More obviously, the tactile perception, shown in blue
in Fig. 2.2, is extremely relevant to physical therapy applications. This region further limits
the space of relevance for material properties of physical therapy putties. Similar to the
visual perception limits, the boundaries of tactile perception are a combination of limits of
observation and relevant quantities [12, 13, 14, 15, 16].

In addition to regions relevant to user-experience, the Pipkin map allows for the co-
location of simple rheological characterization. Stress-input rheological tests such as creep
(step-stress), oscillatory tests (fixed stress amplitude, or fixed frequency) can be mapped
over the regions of relevance to insure that rheological characterization best corresponds to
how a material will be used.

In Fig. 2.2, the operational map does not include any material-specific limits, such as the
onset of nonlinear behavior at a critical stress, or the longest relaxation time. In that sense,
the current Pipkin space is material agnostic. If a material has already been selected, then
these limits (or normalizations) could be added to further describe the space.
Figure 2.2: Stress-amplitude Pipkin diagram [10]. Stress-amplitude, $\sigma_0$ replaces traditional strain-rate dependence to better correlate with user-experience. Regions relevant to human perception for a given problem (i.e. physical therapy putties—shown here, mouth feel, etc.) guide rheological characterization, shown as locations or trajectories through the Pipkin space.

2.2.2 Stress-input Material Functions

When users experience the squishiness, hardness, etc. of a material they squeeze, push, or otherwise deform it. These actions are likely methods of applied stress, as pushing harder is more intuitive than pushing further (applied strain) or at a faster rate (applied strain rate). Thus, when considering how a user will experience a material, the most logical rheological tests are stress-input material functions.

An obvious choice for stress-input testing, particularly when comparing with human inputs, is a simple step-stress experiment with an input of

$$\sigma(t) = \sigma_0 H(t) \quad (2.1)$$

where $H(t)$ is the Heaviside step function and $\sigma_0$ is the amplitude of the stress applied starting at $t = 0$. The resulting strain, $\gamma(t, \sigma_0)$ is measured and then normalized by the
input stress to give the material function creep compliance:

\[ J(t) = \frac{\dot{\gamma}(t, \sigma_0)}{\sigma_0} = \left[ \frac{1}{Pa} \right] \]  

Material response to a step-stress input can also be described in terms of the strain rate, \( \dot{\gamma} \) as a creep fluidity

\[ \phi(t) = \frac{\dot{\gamma}(t, \sigma_0)}{\sigma_0} = \frac{1}{Pa.s} \]  

Step-stress experiments are useful, but have limitations. Measurements at short time scales can be limited by the inertia of the instrumentation. Furthermore, dissipative and storage effects are combined in a single measure, whereas oscillations can decompose elastic and viscous features separately. If the material properties of interest are within the linear viscoelastic limit, frequency-dependent data can be readily interchanged with time-dependent data to develop a more complete picture of the material [17]. A simple way to further investigate the material is through oscillatory experiments which probe the material in the frequency-space \( (\omega = 1/t) \) instead of the time-space \( (t) \). Because they are done in the frequency space oscillatory experiments allow convenient access to both short time scales (high frequencies) and long time scales (low frequency). Experiments can be performed in both the stress-input and strain-input regimes. Most commonly, strain-input measurements are taken with an sinusoidal strain input[17]:

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

In the linear viscoelastic limit, the periodic stress response is then measured as a superposition of the signals in \( (\sigma') \) and out \( (\sigma'') \) of phase with the input strain:

\[ \sigma(t) = \sigma_0 \sin (\omega t + \delta) = \sigma'_0 \sin \omega t + \sigma''_0 \cos \omega t \]  

The output response is normalized by the input strain amplitude to derive the traditional
viscoelastic moduli:

\[ G'(\omega) = \frac{\sigma'_0}{\gamma_0} \]  
(2.6a)

\[ G''(\omega) = \frac{\sigma''_0}{\gamma_0} \]  
(2.6b)

In terms of strain-rate input, two more material functions are defined, the components of the complex viscosity:

\[ \eta'' = \frac{\sigma'_0}{\gamma_0} \]  
(2.7a)

\[ \eta' = \frac{\sigma''_0}{\gamma_0} \]  
(2.7b)

Similarly, the stress-input material functions are defined with the input signal

\[ \sigma(t) = \sigma_0 \sin \omega t \]  
(2.8)

The stress-input material functions, the viscoelastic compliances \( J' \) and \( J'' \) are derived similarly by normalizing the output strain response by the input stress amplitude[18]:

\[ \gamma(t) = \gamma(\omega, \sigma_0) + \sigma_0 [J'(\omega, \sigma_0) \sin(\omega t) - J''(\omega, \sigma_0) \cos(\omega t)] \]  
(2.9)

Likewise, two more material functions, the components of the complex fluidity can be defined in terms of the strain-rate response of the material such that

\[ \dot{\gamma}(t) = \sigma_0 [\phi''(\omega, \sigma_0) \cos(\omega t) + \phi'(\omega, \sigma_0) \sin(\omega t)] \]  
(2.10)

It is important to note that within the linear viscoelastic limit, all of these material functions—\( G, J, \eta, \phi \)—are equivalent and interchangeable[17], e.g.

\[ J' = \frac{G'}{(G'^2 + G''^2)} \]  
(2.11a)

\[ J'' = \frac{G''}{(G'^2 + G''^2)} \]  
(2.11b)
However, relations with real experimental data can be non-trivial.

2.3 Case Study 1: Viscoelastic Physical Therapy Putties

Figure 2.3: Time-lapse photograph of the long time behavior of the therapy putties. Manufacturer-defined ‘firmness’ increases from left to right: extra-soft, soft, medium, medium-firm, firm, extra-firm.

2.3.1 Materials and Methods

Materials

This study will first describe six different types of therapy putty manufactured by Depco, Incorporated sold under the name Thera-Flex Brand Therapy Putty which were ordered through Isokinetics, Inc. These materials are used for physical therapy; e.g. hand strengthening after an injury. Per manufacturer specification, the putties range from "extra-soft" to "extra-firm". The six putties tested, shown in Fig. 2.3, were extra-soft (tan), soft (yellow), medium-soft (pink), medium (red), firm (green), and extra-firm (blue). Ingredients of each putty are not specified by the manufacturer, but similar materials are known to be made of dimethylsilicone polymer[19, 20]. The viscoelasticity of the putties is therefore likely due to polymer entanglement in addition to transient cross-linking of the silicone polymer with the use of boric oxide[21], two mechanisms described in Chap. 4, Sections 4.5 and 4.7. The selection of the putties was driven by their viscoelastic behavior in combination with their relevance to human touch, which makes them useful for this study.
Rheometry

Measurements for this study were performed on a single-head, combined motor-transducer rotational rheometer [Discovery Series Hybrid Rheometer (DHR), model HR-3, TA Instruments]. The instrument was used with a 20 mm diameter flat plate geometry at an operating gap of 800 µm. The temperature for the tests was set at 25°C and controlled using a Peltier bottom plate. Measurements were made using creep tests and stress controlled oscillatory shear tests. Stress sweep tests were performed to ensure that data collected in the oscillatory shear tests was within the linear regime. For each test, a sample was rolled into a ball and placed onto the bottom plate and the geometry was lowered onto it. Excess sample was trimmed at a gap of 850 µm before the final lowering of the geometry.

Repeat tests were performed to judge experimental uncertainty due to loading and trimming the sample, as well as sample relaxation within the rheometry geometry. To ensure that the samples had relaxed sufficiently prior to testing, each putty was allowed to relax for a specified duration. These tests ensured that the total error due to the loading procedure and subsequent relaxation was less than or equal to five percent.

Multiple gap heights were also tested to check for the presence of slip with the materials. No significant effect was found.

2.3.2 Rheometry Challenges/Experimental issues

The viscoelastic putties are highly elastic and relatively stiff (elastic modulus $O(10^6 Pa)$ when compared with most common shear rheology samples. Hence, they present a set of unique challenges for measuring rheology, particularly when approaching the nonlinear flow regime.

For step-input experiments, the nonlinear region is only accessible for the softest two putties (extra-soft and soft). For all other putties (medium, medium-firm, firm, and extra-firm), the materials are nonlinear at stresses above what is possible within experimental limits due to maximum torque boundaries and non-ideal kinematics at the sample-air interface.

The materials also experienced interesting edge effects while undergoing oscillatory shear experiments. In oscillatory stress-sweeps, at high shear stresses, some samples eject "arms"
of material, as shown in Fig. (2.4). These edge effects have been discussed in the literature [22, 23, 24], particularly in relation to the second normal stress difference generated in shear. Most importantly, any data taken after this has occurred must be neglected. This highlights the importance of careful and watchful experimentation in shear rheological measurements.

![Image](image_url)

Figure 2.4: At high stress amplitudes in oscillatory experiments, experimental issues arise with fracture at the edge of the sample as seen at right. Data collected after these issues have occurred must be discarded.

2.3.3 Results

Step-stress Experiments

Step-stress shear rheometry may closely correlate with the use of the physical therapy putties. In use, a reasonably constant stress is applied for a long period of time (order of magnitude 10 s). The step-stress, or creep, experiment allows the material response to be tracked in the time-space (Figure 2.2, horizontal line trajectory from right-to-left as time passes).

For these experiments, the input stress amplitudes chosen ($\sigma_0 = 100, 1000, 10000 Pa$) is within bounds outlined for perception relevant to the physical therapy putties on the Pipkin space (Fig. 2.2) implying that they may reveal information about how the material feels to the user.

As shown in Fig.2.5, 100 Pa is the only stress for which all six putties remain linear. The linear creep-compliance, $J(t)$, and creep-fluidity, $\phi(t) = \dot{\gamma}/\sigma$ are shown in Fig. 2.6. At
Figure 2.5: Step-stress experiments at increasing input stresses ($\sigma_0 = 10^2, 10^3, 10^4 Pa$) for each putty (top row L-R: extra-soft, soft, medium, bottom row L-R: medium-firm, firm, extra-firm). For the softest putty, only the lowest stress amplitude is in the linear region. Experimental limits prevent some higher amplitudes for the two firmest putties.

long times, all materials show similar flow behaviors. The largest differences are seen in the extra-soft and soft putties. There are only very slight differences among the firmest four putties, particularly when looking at the creep-compliance. Clearly, the step-stress material response is not enough to correlate the perceived differences in the materials to their rheological proprieties.

Only the softest two putties show nonlinear behavior at stresses accessible to the instrument used. For that reason, as well as other experimental issues relating to the stiffness of the putty, no comparative conclusions can be drawn from the nonlinear step-input data.
Figure 2.6: (a) Linear creep-compliance for a step-stress of 100 Pa. (b) Transient creep fluidity data of the same experiments. The curves show significantly more flow at long time for the softest putties. There is very little difference in creep response for the firmest four putties. (Gray area dominated by system inertia effects [25]).

Oscillatory Experiments

Oscillatory experiments can also span the measurement space where frequency corresponds to inverse time. Long times are measured at low frequency and short times are measured at high frequencies. Just as in the step-stress experiments conducted, it is important to choose experimental parameters appropriate and significant for human perception. Guided by the Pipkin space in Fig. 2.2, a stress amplitude of 100 Pa is chosen. This stress happens to be within the linear viscoelastic limit for these materials, thus the viscoelastic moduli and compliances can be used interchangably (Eq. 2.11).

A frequency-sweep with conventional strain-input perspective six therapy putties is shown
Figure 2.7: Viscoelastic moduli for the physical therapy putties. Oscillatory tests were performed with an input stress amplitude of 100 Pa, within the linear viscoelastic regime for all of the putties. Elastic moduli $G'$ are shown as closed symbols and viscous moduli $G''$ are shown as open symbols. Uncertainty bars are associated with multiple trials; repeatability falls within the symbols for all oscillatory tests. The instrument inertia (dotted line) is as defined in Eq. 2.12.

in Fig. 2.7. This figure also shows the instrument inertia limit (dotted line). This criteria indicates where material torque exceeds the torque due to the inertia of the instrument[25], i.e.,

$$G > \frac{IF_r}{F_\gamma} \omega^2$$

where $I,F_r,F_\gamma$ are constants related to the instrument geometry.

The materials show a Maxwell-like frequency response. The moduli, $G'$ and $G''$, give insight into the differences in material response for all six putties. A characteristic time scale, $\lambda$, can be found for each material, e.g. as the inverse of the cross-over frequency for the elastic and viscous moduli. However, the differences between each putty are obscured by the complexity of the rheologically complex functions (e.g. non-monotonic frequency dependence).

The material response is shown in the stress-controlled rheological functions (compliances and fluidities, Eqs. 2.9-2.10) in Fig. 2.8. The elastic response, $J'$, collapses for all putties at high frequency (short time). Thus, the perceived differences between the materials is likely not in its elastic response. The viscous response, $\phi'$, shows a plateau value for each putty at
low frequencies (long times). The long time viscous behavior may be key to the perceived difference in the materials.

The stress-input paradigm correlates more clearly to user experience because the relevant stress range is more clearly identified than the range of strain-rates. The stress-input material functions also show a reduction of the complexity in the presentation of the data. Differences in the therapy putties are more obvious in these measures. Simplified representations can aid in building intuition for the relevance of these rheological measures to perception.

Is there a way to even further simplify the representation of the data? Rheological material descriptions are function-valued by design. In this case study, it becomes clear that there may be lower dimensional descriptions of the rheological response of the therapy putties, e.g. the nearly horizontal lines of \( J' \) and \( \phi' \), Fig. 2.8. Several low-dimensional descriptions can be found to describe the viscous and elastic nature of the materials, as well as a characteristic material timescale.

The viscous description \( \eta_0 \) of the material is found from the low-frequency plateau in \( \phi' \):

\[
\eta_0 = \lim_{\omega \to 0} \frac{1}{\phi'(\omega)}
\]  

(2.13)
The fluidity is used because the plateau in $\phi'(\omega)$ is longer than the $\eta'(\omega)$ plateau.

The elastic description $G_0$, is related to the plateau in $J$.

$$\frac{1}{G_0} = \lim_{\omega \to \infty} J'$$

Again, the $J'(\omega)$ description is used because it has a larger plateau than $G''(\omega)$

The characteristic timescale, $\lambda$, which describes the transition from a fluid-like response to a solid-like response, is defined via the cross-over frequency for the elastic and viscous material functions ($G''(\omega_c) = G''(\omega_c)$):

$$\lambda_c = \frac{1}{\omega_c}$$

Figure 2.9: Low dimensional descriptions for (a) the viscous material response, $\eta_0$, (b) the elastic material response $G'$ plateau, and (c) the characteristic relaxation time of the material, $\lambda_c$ for each of the six physical therapy putties. Error bars show error related to loading error in addition to repeated tests.

The low-dimensional descriptions are shown in Fig. 2.9. In agreement with the full function-valued material response, the viscous low-dimensional description shows a clearer
differentiation between the therapy putties. For example, the elastic measures $G_0 = \frac{1}{\phi_0}$ changes by 41%, whereas the viscous measure $\eta_0 = \frac{1}{\phi_0}$ changes by 693%. There is also separation in the characteristic timescales, but it is important to refer back to the Pipkin space in Fig. 2.2 and see that the time scales for some of the materials are at the edge of human perception (right side boundary, $10^{-1} < \frac{1}{\lambda_c} < 4 \cdot 10^2$) thus these differences may not be relevant to user experience.

These low-dimensional descriptions naturally omit possibly valuable information about the full material response. However, reducing the complexity of material descriptions from function-valued to scalar improves tactile intuition for these materials.

The range of timescales displayed by the therapy putties is notable. It implies that the relaxation mechanism of the material must account for some differences in the microstructures of the six putties and leads to possible insight into what this mechanism might be. For example, if the putties are composed of an entangled polymer system (or some combination of this microstructure with other microstructures—see Chap. 4), increasing molecular weight of the polymer would lead to changes in $\eta_0$ and $\lambda$ (Sec. 4.5) as is seen with the putties.

Other viscoelastic mechanisms, such as transient cross-linking, have a relaxation time that does not depend on the molecular weight ($\lambda$ depends only on the timescale of cross-linker bonding). This allows for a decoupling of the time scale from the other low-dimensional measures ($\eta_0, G_0$).

2.4 Case Study 2: PVA-Borax

2.4.1 Materials

A polyvinyl alcohol - sodium tetraborate (PVA-Borax) mixture is an ideal model system for linear viscoelastic rheology. The mechanism behind the formation of the system is known as a di-diol complexation reaction where thermoreversible cross-links occur between two diol units of PVA with a single borate ion [26, 27, 28, 29]. PVA-borax is a particularly useful comparison here because, similar to the viscoelastic therapy putties, it shows a single dominant relaxation time.
Data presented here was collected by Ashwin Bharadwaj and samples were prepared according to [30].

2.4.2 Results

Oscillatory linear viscoelastic data is shown in Fig. 2.10 for four concentrations of PVA-borax mixture (6wt%PVA-6wt%Borax, 4wt%PVA-4wt%Borax, 2.75wt%PVA-1wt%Borax, 2.75wt%PVA-0.5wt%Borax). Because the system is dominated by a single relaxation time, the data can be fit with a simple single-mode Maxwell model to find the steady shear viscosity ($\eta$) and the plateau modulus ($G$). A relaxation time can be found from the cross-over frequency of $G'$ and $G''$ such that $\lambda = 1/\omega_c \doteq [s]$.

These values can be directly compared to the low-dimensional descriptions of the viscoelastic therapy putties described in Section 2.3.3.

![Figure 2.10: Linear viscoelastic moduli ($G'$, $G''$) for varying concentrations of PVA-Borax systems demonstrate that the viscous and elastic characteristics of a material can change without drastic changes in relaxation times.](image)

Any two of the three low-dimensional material functions ($\lambda_c$, $\eta_0$, $G_0$) can be chosen to create a two dimensional cross-property plot (Ashby diagram [9]), an example of which is shown in Fig. 2.11 which includes data from the viscoelastic therapy putties, the PVA-Borax system, and a reference material PDMS silicone putty, provided as an instrument calibration standard from TA Instruments.
Ashby diagrams are widely used in design and material selection and allow for comparison of multiple low-dimensional material functions for different materials [9]. The Ashby diagram shown in Fig. 2.11 uses the viscous material description $\eta_0$ and the characteristic time scale $\lambda$, the two descriptions found to be most important to the tactile perception of the physical therapy putties (Sec. 2.3.3). While the putties span a relatively large range of timescales $\lambda_c$ in addition to an order of magnitude of steady shear viscosity $\eta_0$, the timescales for the PVA-borax system vary only from $\lambda = 0.8 – 1.2$ seconds. Thus, the material is a candidate for providing tactile intuition to answer the question: how does it "feel" to keep $\lambda$ constant (and within human perception) but change $\eta_0$ and $G_0$.

Possible explanations for the differences of $\lambda_c$, for all materials in Fig. 2.12 are given in the following section.

2.5 Microstructure and viscoelasticity

Viscoelastic behavior can arise from a variety of microstructural classes (Chap. 4. A selection of these classes is shown in Fig. (2.12). Key relaxation times in these materials are a result
Figure 2.12: Viscoelasticity in materials can be a result of many possible microstructural classes including, but not limited to: (left to right) colloidal networks, dilute polymers, spherical colloidal suspensions, entangled polymers, emulsions, cross-linked polymers, and non-spherical brownian particles, or any combination there-in.

of balancing viscous forces with restoring forces in the structure (e.g. surface tension in emulsion droplets). For some known microstructures, analytical scaling laws for relaxation times are available in the literature, many of which are summarized and discussed in Chap. 4 citelarson1999, derkach2009, tanaka1992, rubinstein2003.

The microstructure of the PVA-Borax system is well characterized in literature [30, 28, 27, 26, 29]. The sodium borate (borax) in the system creates transient cross-links between polyvinyl alcohol (PVA) molecules. The kinetic timescale of these transient cross-links sets the primary relaxation time of the material, thus regardless of cross-linker (borax) or polymer (PVA) concentration, the relaxation timescale stays constant.

On the other hand, the viscoelastic putties are not as well characterized, molecularly or structurally. Based on their similarities to commercially available Silly Putty®, or generically referred to as "Bouncing putty", we can postulate that the putties are likely manufactured by transiently cross-linking dimethyl silicone with a boron compound [19, 31, 20, 32, 33]. The variation in timescales \(0.03ms < \lambda_c < 0.3\) seen in the viscoelastic putties suggests that these transient cross-links, with constant timescale, are not the only contribution to system relaxation. Additional mechanisms can only be speculated, but varying polymer entanglements (i.e. varying molecular weights) seems a likely candidate.
2.6 Conclusions

In this work, we have demonstrated the use of a stress-input perspective Pipkin diagram to guide experimental characterization of physical therapy putties in the stress amplitude and time ranges relevant to the user experience of those materials. This characterization attempts to begin the design process (right-to-left in Fig. 2.1) by connecting macroscopic material behavior with rheological material functions. This method remains material agnostic, as the same material behavior could be achieved using numerous microstructures including colloidal systems, polymer systems, emulsions, etc.

The stress-perspective Pipkin space proposed in this work aids in guiding the characterization and design of materials for which human perception is important. The space shown in Fig. 2.2 is created specifically to be relevant to the tactile perception related to physical therapy putties. It can be further modified for other problems of interest such as food rheology by adjusting relevant regions to processes important to other user experiences (i.e. chewing, spreading, etc.).

Rheological characterization of complex materials is often a high-dimensional question. Using a model system of therapy putties designed for a range of user experiences and a PVA-borax gel, we are able to show that stress-input rheological measures, such as dynamic compliance and fluidity (Fig. 2.8), reduce the complexity of the rheological description when compared to strain-input measures, such as dynamic moduli (Fig. 2.7). We show that in this system, linear viscoelastic rheological properties are appropriate to differentiate between the user experiences of the putties. Complexity was further reduced through the use of several low-dimensional representations of key features of the material (elastic, viscous, viscoelastic time scale). Reducing the complexity of the data allows for a clearer understanding of the differences in the materials which leads to improved tactile intuition with viscoelastic materials.

Reducing the complexity of the data is not without its challenges. Going forward, it will be important to find a systematic way to choose which low-dimensional representations are most useful for a specific design problem. Moreover, the potential role of textit{nonlinear} rheological properties exacerbates this important challenge.
3 DESIGN WITH RHEOLOGICALLY-COMPLEX MATERIALS VIA MATERIAL FUNCTION DESIGN TARGETS

3.1 Introduction

Engineering design is most commonly achieved with the use of hard materials or simple fluids. The advantages of using soft, rheologically-complex materials are demonstrated by many biological systems[2, 3, 4, 5, 6]. A key challenge that inhibits the use of these materials in systematic design is their complexity. The simplest material properties are function-valued, in contrast to the constants necessary to describe simple solids or fluids.

![Diagram](image)

Figure 3.1: The introduction of a viscoelastic connection can change the design space from a discrete arrangement of linear springs and dashpots (left) to a single viscoelastic element with a relaxation kernel, $K(t)$.

Currently, much of the intersection between materials and design includes material selection[7] and material processing optimization[34], but there is increasing interest in designing materials to achieve target functionality to meet a user’s need[35]. As described by Cussler and Moggridge[36], it is the functionality, not the molecule that produces the functionality,

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Corman, R.E., L. Rao, N.A. Bharadwaj, J.T. Allison, R.H. Ewoldt, "Design with rheologically-complex materials via material function design targets," submitted
that is important. Moreover, rather than blindly trying to match existing or discovered materials to possible end use, the design process must begin with intended performance targets. From here, the required material properties are identified to achieve these design targets, agnostic of any particular material. Only once the necessary properties are selected, the required material structure or formulation can be chosen to meet these needs. Thus, the strategy is to be problem-driven rather than solution-driven. Our approach separately connects function/performance of an engineering system to the rheological properties, and subsequently those rheological properties to material design and formulation[37]. This hierarchical structure can be tackled effectively using optimization techniques such as analytical target cascading (ATC) [38, 39] or inductive design exploration methods [40].

By keeping the early stage design material agnostic, fewer restrictions are made on the design space which may help avoid design fixation [41]. In our work, the focus is to allow performance objectives to drive property targets independent of specific chemistry and structure. We take advantage of the fact that rheological complexity, time-dependent viscoelasticity in particular, can enable novel performance[37, 42]. Here, we focus on linear viscoelasticity (a subset of this complexity) for enhanced performance in mechanical systems.

As shown schematically in Fig. 3.1, a complex arrangement of linear springs and dashpots can be replaced by a generalized viscoelastic component whose behavior is governed by a single function-valued parameter $K(t)$ (mathematical details in Section 3.2.1). While the traditional spring-dashpot method is easy to conceptualize, it significantly limits the designer to a finite-dimensional design space. While limited, the designer also must attempt to make systematic choices for both the topology of the connections and the spring/dashpot properties. The introduction of a generalized viscoelastic connection expands the design space to include all possible discrete spring/dashpot arrangements in addition to behaviors that cannot be easily achieved with a typical system, such as power-law behavior which requires an infinite series of springs and dashpots. Topological arrangements of springs and dashpots as well as composite and heterogeneous materials can be designed to achieve target viscoelastic behavior [43, 44]. Even further, viscoelastic materials themselves could potentially achieve the desired viscoelasticity $K(t)$.

Continuing from previous work [45], we develop a methodology to use function-valued
properties, such as \( K(t) \) in Fig. 3.1, as system-level variables while remaining material agnostic (i.e., agnostic to specific molecules or structure of the material). We use optimization methods to solve rheological material property target-setting problems. This methodology will be generalizable to the design of other classes of rheologically-complex materials, where function-valued properties are known as “material functions” [46, 47]. We demonstrate the utility of this method with an example of viscoelastic vibration attenuation.

3.2 Theory and Modeling

3.2.1 General linear viscoelastic element

While previous efforts have addressed viscoelastic material design, some of these efforts have excluded the important feature of frequency-dependent storage and loss properties, resulting in extreme design limitations by ignoring the valuable ability of viscoelastic materials to adjust properties with changes in loading frequency [48]. Other work has accounted for time-dependent behavior, but specifies that the linear viscoelastic relaxation function be described by a superposition of exponentials [49, 50]. While useful, this functional form limits the design space, since the structural form cannot include instantaneous damping (a delta function) and will require large numbers of parameters to describe simple functions such as power-law relaxation.

In its broadest form, the viscoelastic element shown in Fig. 3.1 can include any form of linear or nonlinear viscoelastic behavior in which case the kernel function is input-amplitude dependent. To simplify the scope of design in this work, we consider the limit of linear viscoelasticity. In the linear viscoelastic limit, using Boltzmann superposition [47], the mechanical response of any material or structure is described by an experimentally measurable function that depends only on a timescale, the relaxation kernel, \( K(t) \). The entirety of \( K(t) \) can be optimized without regard to material class, spring-dashpot constitutive model, or ideally, parameterization of \( K(t) \).

Here we consider one-dimensional deformation, and thus are able to represent the force
Table 3.1: Relaxation kernel, $K(t)$, for the generalized viscoelastic component as shown in Fig. 3.1. For 1-D systems, extrinsic component measures can be transformed to intrinsic material measures by a linear mapping depending on component geometry. The relaxation kernel is the design parameter as the dynamic storage and loss moduli are related through the Kramers-Kroenig relations, and thus not fully independent (Eqs.3.8 and 3.8).

<table>
<thead>
<tr>
<th>Proportionality</th>
<th>Force connection</th>
<th>Material (extension)</th>
<th>Material (shear)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relaxation Kernel</td>
<td>$K(t)$</td>
<td>$E(t)$</td>
<td>$G(t)$</td>
</tr>
<tr>
<td>Dynamic Storage</td>
<td>$K'(\omega)$</td>
<td>$E'(\omega)$</td>
<td>$G'(\omega)$</td>
</tr>
<tr>
<td>Dynamic Loss</td>
<td>$K''(\omega)$</td>
<td>$E''(\omega)$</td>
<td>$G''(\omega)$</td>
</tr>
</tbody>
</table>

through the viscoelastic connection with a single scalar equation,

$$F_{ve}(t) = \int_{-\infty}^{t} K(t-t')\dot{X}(t')dt'$$  \hspace{1cm} (3.1)

where $F_{ve}$ is the force due to a viscoelastic element, $\dot{X}$ is the deformation velocity experienced by the element (dimensions $\dot{X} \equiv [LT^{-1}]$) and the force relaxation kernel $K(t-t') \equiv [FL^{-1}]$. With a change of variable $s = t - t'$ this convolution integral becomes

$$F_{ve}(t) = \int_{0}^{\infty} K(s)\dot{X}(t - s)ds.$$

If the viscoelastic properties arise from a continuum of material, we can make an analogy from extensive properties (force, velocity, stiffness) to intensive material properties (stress, strain, modulus), and therefore complex strain fields within the isotropic linear viscoelastic regime (see Table 3.1). The relaxation kernel $K(t)$ that relates the extrinsic measures of force and displacement is transformed to its analogous material measures $E(t)$ (in extension) or
G(t) (in shear) which relate the intrinsic measures of stress and strain through a linear mapping of area divided by length (dimensions [L]) based on geometry. A simple example of the relationship between the extrinsic and intrinsic measures is shown in one-dimensional tension where the intrinsic measures stress and strain are related through material connection function E (Table 3.1) by \( \sigma = E \epsilon \). Converting these measures to their extrinsic equivalents requires the geometrical relations \( \sigma = F/A \) and \( \epsilon = x/L \). Combining these relations leads to the extrinsic form of Hooke’s law, \( F = (EA/L) x \). Where the extrinsic force connection kernel \( K \) can be written as \( K = EA/L \equiv [F/L] \).

In the isotropic, incompressible, linear viscoelastic regime, the descriptive kernel function, the stress relaxation modulus, is the measured stress response to a step change in strain, which can be used generally in Boltzmann superposition [37, 47]. The modulus is equivalent to a predictive constitutive model parameter, and can be used to compute any three-dimensional deformation history. By analogy to Eqn. (3.1), the 3-D expression for the Boltzmann superposition integral uses the relaxation modulus \( G(t) \), in tensorial form:

\[
\sigma(t) = \int_{-\infty}^{t} G(t - t') \dot{\gamma}(t') dt',
\]

(3.3)

where \( \sigma(t) \) is the Cauchy stress tensor, and the strain-rate tensor is

\[
\dot{\gamma} = \nabla \mathbf{v} + (\nabla \mathbf{v})^T,
\]

(3.4)

where \( \mathbf{v} \) is the velocity field and we define the velocity gradient as \( (\nabla \mathbf{v})_{ij} = \partial v_j / \partial x_i \). Equation (3.3) is limited to small deformation in the linear viscoelastic regime for incompressible materials, but applies for any class of linear viscoelastic material (elastomer, composite, polymeric liquid, colloid, gel, etc.) falling within the framework of a continuum description.

The convolution integral of Eqn. (3.2) (or its material analogy Eqn. (3.3)) presents a significant challenge when optimizing the functional form of \( K(t) \) (or \( G(t) \) in Eqn. (3.3)). In particular, governing equations such as conservation of momentum cannot be written as instantaneous functions of state variables, but instead must involve an integral over all past time.
The relaxation kernel $K(t)$ is treated here as an independent design variable. Alternative viscoelastic material functions, such as the creep compliance $J(t)$, can also be used to define a relation similar to Eqn. (3.3) with the displacement field as the output of the integral. This may be mathematically convenient for load-control inputs. However, in the linear viscoelastic limit, all of the the material functions are interrelated\[17\], and therefore only one single-valued function can be specified in the design.

Linear viscoelastic materials are commonly described in the frequency-domain, such as the dynamic storage and loss moduli are shown in Table 3.1. For a viscoelastic fluid (with stress relaxing to zero at infinite time) the dynamic storage and loss moduli are directly related to $K(t)$ as

$$K'(\omega) = \omega \int_0^\infty K(s) \sin(\omega s) ds$$

$$K''(\omega) = \omega \int_0^\infty K(s) \cos(\omega s) ds.$$  

(3.5)  

(3.6)

Additionally, the dynamic storage and loss moduli are combined to create a complex modulus of the form $K^* = K' + iK''$ where $i$ is the imaginary unit.

Since each function is related to $K(t)$, the two functions are clearly not independent. As shown in Table 3.1, this holds true in the analogous material measures in extension ($E(t)$, $E'(\omega)$, $E''(\omega)$) and shear ($G(t)$, $G'(\omega)$, $G''(\omega)$). The interrelations are given by the Kramers-Kronig relations, shown here in terms of the dynamic moduli\[47\]

$$G'(\omega) - G'(\infty) = \frac{2}{\pi} \int_0^\infty \frac{x G''(x)}{\omega^2 - x^2} dx$$

$$G''(\omega) = \frac{2\omega}{\pi} \int_0^\infty \frac{G'(x)}{x^2 - \omega^2} dx$$

(3.7)  

(3.8)

where we define

$$G'(\infty) = \lim_{\omega \to \infty} G'(\omega)$$

(3.9)

Any in-phase and out-of-phase dynamic material functions must also satisfy these relations. With simple shear properties, this includes moduli $G'$ and $G''$, viscosities $\eta'$ and $\eta''$, compliances $J'$ and $J''$, and fluidities $\phi'$ and $\phi''$ \[46, 47\]. The Kramers-Kronig relations also
restrict the independent specification of frequency-dependent magnitude and phase angle.

The independent function $K(t)$ (or equivalently $G(t)$ or $E(t)$) is therefore treated as the function-valued design variable for linear viscoelasticity.

### 3.2.2 Parameterizations of $K(t)$

In general, the relaxation kernel, $K(t)$, can be treated as a function of arbitrary structure. Passive materials or systems impose the restriction that the function be monotonically decreasing [51, 52], however, this restriction on complexity could be lifted through the use of actively controlled systems. Complete freedom in the shape of the relaxation kernel presents difficulties for numerical optimization. For this initial exploration of $K(t)$ optimization, we consider several parameterizations of $K(t)$ with a finite number of design parameters as shown in Fig. 3.2: parameterization as a dashpot, a single and multi-mode Maxwell, and power law relaxation (analogous to a critical gel material) [53, 54].

For a standard, linear dashpot, the form of the relaxation kernel can be represented as

$$K(t) = c \cdot \delta(t)$$  \hspace{1cm} (3.10)

where $c = [F/(L/T)]$ The dynamic coefficients for a linear dashpot are given by

$$K'(\omega) = 0$$ \hspace{1cm} (3.11)

$$K''(\omega) = c \cdot \omega$$ \hspace{1cm} (3.12)

By analogy, a Newtonian fluid has $G(t) = \eta_0 \delta(t)$, $G' = 0$, and $G'' = \eta_0 \omega$. A Maxwell element is a linear spring and dashpot connected in series. It is the simplest model of a viscoelastic fluid. The model can be generalized to a multi-mode Maxwell model that includes $M$ Maxwell elements connected in parallel. The relaxation kernel, also known as a Prony series, is defined by

$$K(t) = \sum_{m=1}^{M} K_m e^{-t/\lambda_m}.$$ \hspace{1cm} (3.13)

where $K_m$ are the Maxwell spring constants ($K_m = [F/L]$), and $\lambda_m$ are the relaxation times
(\lambda_m \equiv [T])$. The Maxwell dashpot coefficient is $\eta_m = K_m \lambda_m$. Here we will consider the cases of $M = 1$ and $M = 3$ in order to limit the number of parameters ($2M$ parameters for an $M$-mode Maxwell model). For this form, the dynamic coefficients of a force component connection are

$$K'(\omega) = \sum_{m=1}^{M} K_m \frac{(\lambda_m \omega)^2}{1 + (\lambda_m \omega)^2}$$

$$K''(\omega) = \sum_{m=1}^{M} K_m \frac{\lambda_m \omega}{1 + (\lambda_m \omega)^2}.$$  

These are analogous to intrinsic material properties $G'(\omega)$, $G''(\omega)$ [see Table 3.1]. To achieve some functional forms of $K(t)$ such as power law behavior, a Maxwell model would require a large number of parameters. In order to include this broader design space, but with a small number of parameters, we will consider the critical gel power law model. Power-law rheology is an important signature, seen in materials near a gel point [54, 55], food systems such as egg yolk [56], and active biological materials such as cells [57]. Present literature describes this behavior in terms of intrinsic material characteristics $G(t)$, $G'(\omega)$, $G''(\omega)$ [54, 53] which we use to generate their force connection analogs. In component design, these measures are related to $K(t)$, $K'(\omega)$, and $K''(\omega)$ by geometric factors. The critical gel behavior is described by the power-law equation

$$K(t) = S_k t^{-n}$$

where $S_k$, dimensions $[\frac{F}{L} \cdot T^n]$, is the gel strength parameter and $n$ is the power-law coefficient. The exponent is generally restricted to the range $0 < n < 1$, though is $n \approx 1/2$ for stoichiometrically balanced gels [53]. The dynamic moduli for the critical gel can be generalized to an extrinsic force connection as [54, 55, 53]

$$K'(\omega) = \frac{K''(\omega)}{\tan \left( \frac{n\pi}{2} \right)} = \Gamma(1 - n) \cos \left( \frac{n\pi}{2} \right) S_k \omega^n$$

where $\Gamma(\cdot)$ is the Gamma function. The first equality of Eqn. (3.17) links stiffness and
damping, further constraining viscoelastic properties differently than assumed in the previous section. Note that $K''(\omega)$ and $K'(\omega)$ have equal slope for a given $n$ (i.e., the modulus lines are parallel). Importantly, there is no simple mechanical analog with springs and dashpots for the critical gel (it requires an infinite set of parallel Maxwell elements). Yet, this behavior is accessible with real materials, if not (overly simplified) spring and dashpot models.

Figure 3.2: Parameterizations of the relaxation kernel, $K(t)$, for a general linear viscoelastic fluid model (Fig. 3.3b) into numerous linear viscoelastic models to reduce the complexity of the design space. The viscoelastic models used to parameterize the relaxation modulus of the added viscoelastic component are: (i) a linear dashpot (solid), (ii) a Maxwell element (linear spring and dashpot connected in series) single mode (dash-dot), (iii) Multi-mode Maxwell element, (short dash-dot), and (iv) a critical gel model, mechanical spring-dashpot analog is not applicable (dash). Inset plot is double-log plot of the same curves with the Maxwell model characteristic timescale $\lambda$ (as in Eqn. (3.13)) and the critical gel exponent $n$ (as in Eqn. (3.16)) labeled for reference.

While some parameterizations (i.e. Maxwell model) imply the use of a specified topology of linear springs and dashpots, this is not generally necessary for a viscoelastic connection. One could also parameterize $K(t)$ as a spline, or a discrete vector of independent points. This would be the ideal approach, with maximum design freedom. A key difficulty is solving convolution integrals with high degree of freedom parameterizations. This challenge is beyond the scope of the work here which is to simply demonstrate $K(t)$ as a design variable, considering more than just Prony Series parameterizations.

In the most general case, the optimization problem considered here seeks to minimize an objective function that describes the performance of the overall system and depends on
the choice of \( K(t) \). Since the optimization is performed with respect to \( K(t) \), which is a function-valued design variable, this problem would fall under the class of optimal control problems[58]. While there are well-established methods to solve these types of problems[59, 60], the structure arising from the problem is complex due to the characteristic convolution integrals and is not yet well understood. Thus, for the purpose of this paper, we demonstrate certain parameterization of \( K(t) \) and utilize optimization algorithms in MATLAB™ for finite dimensional nonlinear programs.

3.3 Case study

![Diagram](image)

Figure 3.3: Design of optimal viscoelastic vibration isolation for a 1-dimensional spring-mass system(a); (b) the typical approach of an arrangement of springs and dashpots, and (c) a generalized viscoelastic element with relaxation kernel, \( K(t) \). The latter approach increases design freedom and identifies more optimal targets.

In general the linear viscoelastic element of Sec. 3.2.1 could be used to connect any two pieces in a system. As a case study, we consider a simple vibration isolator, shown in Fig. 3.3. In the initial case (Fig. 3.3.a), a mass \( m \) is connected by a spring to a base that is moving with a prescribed displacement of \( y(t) \). The objective is to isolate the top mass from the base displacement. A simple improvement is the addition of a linear dashpot (Fig. 3.3). We will generalize the linear dashpot to be a parallel viscoelastic connection with relaxation kernel \( K(t) \), described in Sec. 3.2.1. We will demonstrate the added performance from a viscoelastic connection, and optimize \( K(t) \) based on the parameterizations described in Sec. 3.2.2.
3.3.1 Governing Equations

Given an initial condition $F_{ve}(t = 0) = 0$, Eqn. (3.2) has limits of integration from 0 to $t$. In general, the expression requires convolution of the kernel function $K(t)$ with the entire time-history of the velocity experienced by the element, $\dot{x}(t)$.

For the particular system in Fig. 3.3, with a generalized viscoelastic element and the initial condition $F_{ve}(t = 0) = 0$, the governing equation for conservation of linear momentum is most generally written as

$$-k(x - y) - \int_{0}^{t} K(s) [\dot{x}(t - s) - \dot{y}(t - s)] \, ds = m\ddot{x}(t)$$  

(3.18)

where $s = t - t'$ and $\dot{x} - \dot{y} = \dot{X}$, or the velocity of deformation, as defined in Eqn. (3.2).

The convolution integral structure has two important consequences. First, the equations cannot be written in matrix form. Second, the numerical simulation of this model requires increased computation at each time step, since each time derivative function evaluation requires an integration of the entire prior time-history of velocities. This is an important challenge to be addressed for general design of $K(t)$ (or $G(t)$), and is the subject of ongoing work. Here, we simplify the analysis by considering time-periodic solutions, for which the convolution integral simplifies. Consider a time-periodic prescribed base excitation, $y(t) = Y \sin(\omega t)$. For a linear system, the steady-state displacement response of $x(t)$ will be time-periodic at the forcing frequency[61]. The known structure of this harmonic solution will simplify the convolution integral terms, to an extent that we can write the governing equations as a function of instantaneous state variables. Thus, integral calculations of $K(t)$ terms are not required at each time step.

Using complex notation, the displacement of the mass has the form

$$x(t) = \text{Im} \{ x^* e^{i\omega t} \}$$  

(3.19)

where $\text{Im}\{\}$ takes the imaginary portion of the complex quantity. The coefficients are

$$x^* = X_R + iX_i$$  

(3.20)
By substituting Eqns. (3.19) and (3.20) into Eqn. (3.18), a linear system of two equations and two unknowns will result. The system of equations takes the form

$$Mx = B. \quad (3.21)$$

The unknowns are

$$x = [X_R, X_i]^T \quad (3.22)$$

The nonhomogeneous portion is

$$B = [-Y(\omega S + k), -Y\omega C] \quad (3.23)$$

and the 2 by 2 matrix is given by

$$M = \begin{bmatrix} (m\omega^2 - \omega S - k) & (\omega C) \\ (-\omega C) & (m\omega^2 - \omega S - k) \end{bmatrix} \quad (3.24)$$

The scalar coefficients $C$ and $S$ require integral calculations that depend on the kernel function $K(t)$,

$$C(\omega) = \int_0^\infty K(s) \cos(\omega s) ds \quad (3.25)$$

$$S(\omega) = \int_0^\infty K(s) \sin(\omega s) ds. \quad (3.26)$$

Comparing this result to Eqn. (3.5) and Eqn. (3.6) shows that these integrals are related to the dynamic material functions as

$$C = K''(\omega)/\omega \quad (3.27)$$

$$S = K'(\omega)/\omega. \quad (3.28)$$

The primary design variable is still $K(s)$, since it gives the rheological signature of both dynamic moduli, and the dynamic moduli are not independent parameters due to the Kramers-Kronig relations in Eqns. (3.8)–(3.8).
The solutions to the governing equations give $|x|$, the displacement amplitude of the mass, as a function of frequency. Normalizing this result by the input displacement amplitude, $Y$, leads to the non-dimensionalized amplitude

$$|\tilde{x}| = \frac{|x|}{Y}$$  \hspace{1cm} (3.29)

From the displacement, the acceleration amplitude of the mass is defined to be

$$|\ddot{x}| = \omega^2 |x|$$  \hspace{1cm} (3.30)

Equivalently, it can be non-dimensionalized by the problem inputs of displacement ($Y \equiv [\text{length}]$), mass ($m \equiv [\text{mass}]$), and spring constant ($k \equiv [\text{mass} \cdot \text{time}^{-2}]$) as

$$|\ddot{x}| = \frac{|\ddot{x}|}{Y \left( \frac{k}{m} \right)}$$  \hspace{1cm} (3.31)

In general $K(t)$ can take any form, but here $K(t)$ is parameterized using the methods described in Section 3.2.2. The response $|\ddot{x}|$ is optimized by minimizing the peak value with respect to a finite set of design variables that parameterize $K(t)$. These parameters can themselves be non-dimensionalized as follows. For the linear dashpot, $\tilde{c} = c/\sqrt{km}$; for the Maxwell model, $\tilde{\lambda} = \lambda/\sqrt{m/k}$ and $\tilde{\eta} = \eta/\sqrt{km}$; and for the critical gel, $\tilde{S} = S/k^{\frac{4}{m \cdot n \cdot \gamma}}$ (note that the critical gel exponent, $n$, is dimensionless).

The objective function $f$ for the design optimization problem here is the maximum non-dimensionalized acceleration amplitude,

$$f(x) = \max |\ddot{x}|$$  \hspace{1cm} (3.32)

3.3.2 Results

The typical approach for vibration isolation is to combine a linear spring and dashpot in parallel, as in Fig. 3.3b. The addition of the dashpot is equivalent to the parameterization for the relaxation kernel given in Eqn. (3.10). In this parameterization, the design space has
Figure 3.4: Design trade-off from added dashpot in Fig.3.3.b vibration isolator, displacement amplitude ($|x|$) and acceleration amplitude ($|\ddot{x}|$) responses. Decreasing peak amplitude at a resonant frequency lends to worse signal attenuation at higher frequencies. Damping coefficients ($\zeta = c/2m\omega_n$) of $\zeta = 0.1, 0.5, 0.9$ are shown. Response of the mass is plotted with respect to $\omega_{\text{shifted}}$, a frequency normalized by the resonant frequency.

only one dimension, the dimensionless damping coefficient defined as

$$\zeta = c/2m\omega_n$$  \hspace{1cm} (3.33)

The effect of varying this parameter is shown in the displacement and acceleration amplitude response in Fig. 3.4, where a non-dimensional displacement amplitude ($|\tilde{x}| = |x|/Y$) and the non-dimensional acceleration amplitude are plotted against a frequency normalized by the resonant frequency of the initial system, $\tilde{\omega} = \omega/\sqrt{k/m}$. The resonant frequency is influenced by the elasticity in $K(t)$.

This presents the clearest design trade-off in optimization. As the dissipation increases, it
attenuates the resonant response in both the displacement and acceleration at the natural frequency of the system \( (\omega_n = \sqrt{k/m}) \). Any finite dissipation, however, changes the high-frequency displacement response of the system from a scaling \( |x| \sim \omega^{-2} \) to \( |x| \sim \omega^{-1} \). This leads to a penalty at high frequency, most clearly demonstrated with the acceleration \( |\ddot{x}| \sim \omega^2 x \) of the mass. A finite amount of damping changes the slope of the high frequency acceleration behavior from \( |\ddot{x}| \sim \omega^0 \) to \( |\ddot{x}| \sim \omega^1 \). While damping can decrease the peak acceleration at the resonant frequency, it comes at the cost of ever increasing acceleration at large \( \omega \) (Fig. 3.4b).

Figure 3.5: Design involving a generalized viscoelastic element with relaxation kernel \( K(t) \) can eliminate high frequency acceleration. Here shown with Maxwell element (dash-dot), and critical gel (short dashed) compared to dashpot (solid), or no additional component (dashed).

Relaxing the design space to include even simple parameterizations of viscoelastic flu-
ids can change the behavior of the vibration isolator, as demonstrated in Fig. 3.5. While parametrization does not provide infinite design freedom, it is valuable for this initial treatment, as it allows a visualization of the extended design space. A Maxwell model allows for the introduction of an additional timescale, $\lambda$ from Eqn. (3.13); for characteristic deformation timescales longer than $\lambda$ where the connection (or material) behavior transitions from spring-like (elastic) to dashpot-like (viscous). The high-frequency (short timescale) elastic behavior is a key feature. Properly designed, this allows for an attenuation of the peak acceleration at a resonant frequency without the penalty of ever-increasing acceleration at large $\omega$. This is illustrated in Fig. 3.5. Note $\tilde{\omega} = \omega/\omega_{res}$, where $\omega_{res}$ depends on the Maxwell parameters. Other parameterizations likewise allow for reduction of the resonant acceleration with reduced penalty at high frequencies.

![Figure 3.6:](image)

Figure 3.6: The design space for (a) the single mode Maxwell element and (b) the critical gel to isolate vibrations in a single mass-spring system (given by Eqns. (3.13) and (3.16)). Each model increases the design space to two dimensions, compared to the single dimension of a simple linear dashpot. More saturated colors correlate with lower peak accelerations under simple sinusoidal displacement forcing. The white circle identifies a global minimum of peak acceleration.

Both the critical gel and single mode Maxwell model expand the design space from the conventional linear dashpot solution. A portion of the expanded design space for these parameterizations is shown in Fig. 3.6.

We optimized the different forms of the kernel function to minimize the peak acceleration of the mass $m$. Optimization was performed using the MATLAB™ optimization toolbox with the functions ‘ga’ and ‘fmincon’. The results for the optimal viscoelastic kernel functions are presented in Table 3.2. The optimal values for a single mode Maxwell model and a critical gel model are shown as the white dot in Fig. 3.6.
Table 3.2: Optimized peak acceleration and corresponding viscoelastic design for a simple vibration isolator. Accelerations and parameters are non-dimensionalized according to Section 3.3.1.

| VE Model                | Peak Acceleration $|\ddot{x}|$ | VE Parameters                  |
|-------------------------|------------------|-------------------------------|
| Dashpot                 | 309.67 ± 0.000   | $\ddot{c} = 0.00155 ± 0.00000$ |
| Maxwell Element         | 3.001 ± 0.004    | $\tilde{\eta} = 0.553 ± 0.011$ ; $\lambda = 0.277 ± 0.005$ |
| Multi-mode Maxwell $(m = 3)$ | 3.000 ± 0.000 | see text                      |
| Critical Gel            | 10.755 ± 0.026   | $\tilde{S} = 0.046 ± 0.037$ ; $n = 0.259 ± 0.008$ |

In the case of a multi-mode Maxwell model, the optimized viscoelastic parameters are not listed in Table 3.2, since there was too much variation in the individual values. However, all values for $\eta$ and $\lambda$ produced similar $K(t)$ curves (in addition to being similar to the single mode Maxwell model). This shows that the shape of the curve is the key factor in optimization, not its exact parametrization.

The peak amplitude can occur either as a local maximum near resonance (e.g., Fig. 3.5, critical gel), or at the highest frequency considered (e.g., Fig. 3.5, dashpot). Therefore, some solutions depend on the frequency range of interest. Shapes of all optimized $K(t)$ curves are shown in Fig. 3.7. For both the dashpot and critical gel, the acceleration amplitude increases without bound at higher frequency, thus increasing the upper-bound of the frequency range will increase the acceleration amplitude at that value, possibly above the local peak value at the resonant frequency. For real applications a finite range of frequency is reasonable, e.g., excitation amplitudes decrease and may be negligible above a critical frequency.

Introducing a linear viscoelastic connection decreases the peak acceleration beyond that of a simple linear dashpot. With the introduction of a characteristic timescale, a Maxwell model provided the most improvement compared to the conventional method. A critical gel element also provides a marked improvement. Surprisingly, in this simplified problem, additional design freedom in the form of additional viscoelastic parameters (i.e. a multi-mode
Maxwell model) does not provide further improvement over a single mode Maxwell model. This is likely due to the fact that this toy problem has only one characteristic frequency, thus only one additional time scale is necessary for optimal performance.

These results suggest that a critical gel model and multi-mode Maxwell model may further improve performance for more complex problems involving a more complicated forcing function. Critical gel performance may prove beneficial in situations such as a power-law roll-off in forcing amplitude with frequency (such as that found in wind driven waves \[62, 63\]). Likewise, more degrees of freedom and additional characteristic timescales may prove beneficial in excitations that superpose multiple frequencies, or structures with multiple vibration modes.

![Figure 3.7: Optimized performance (acceleration amplitude), left, and the corresponding optimal viscoelastic design (kernel function), right. The viscoelastic models used to parameterize the relaxation kernel of the added viscoelastic component (shown in Fig. 3.3c) are: (i) a linear dashpot, solid, (ii) a single mode Maxwell element, dash-dot, (iii) Three-mode Maxwell element, short dash-dot, (iv) a critical gel model, short dashed, and (v) no additional component, dashed. A multi-mode Maxwell model only uses its additional degrees of freedom to achieve the same relaxation kernel and performance as a single mode, which therefore overlap as the most optimal of these parameterizations.](image)

### 3.3.3 Case Study Extension

As an extension to the above results and in order to get a better intuition for more practical systems, the dynamic vibration isolator was further generalized to consider a range of non-dimensional natural frequencies $\tilde{\omega}^*$ for which a single viscoelastic element is used. This
natural frequency is normalized by some reference spring-mass system \((k_0, m_0)\) such that

\[
\tilde{\omega}^* = \frac{\omega^*}{\omega_0} \tag{3.34}
\]

where \(\omega_0\) is the natural frequency of the reference system \(\omega_0 = \sqrt{k_0/m_0}\).

This is analogous to a “one size fits all” damper where the primary mass and spring may vary by application (Fig. 3.8). As shown before, use and optimization of a generalized viscoelastic element for a fixed natural frequency (i.e. \(\tilde{\omega}^* = 1\)), significantly improves the system response. However, the benefit of the optimized viscoelastic element is diluted for a system whose natural frequency is different from that for which the system is optimized.

In practice, it is unlikely that a system will be as idealized as the simple spring-mass isolator system proposed in the previous case study. A simple example can be thought of as a vehicle suspension system, where the vehicle is expected to perform over a wide range of additional mass. By extending the original example to include a range of natural frequencies, we allow for the possibility of added mass or a range of system stiffness.

![Figure 3.8](image)

Figure 3.8: The simple vibration isolator problem is extended to optimize the performance for a range of natural frequencies of the system, but a fixed \(K(t)\). Increasing the natural frequency of the system \((\omega_1 = \sqrt{k/m})\) can be conceptualized by increasing the spring constant \(k\) and/or decreasing the system mass, \(m\), shown in (a)-(c).

For the previous studies with a fixed \(\tilde{\omega}^* = 1\), the objective function was chosen to be the maximum of the acceleration curve. Now, with a range of natural frequencies, selecting the absolute maximum would result in a a discontinuous and non-smooth objective function. To avoid problems associated with discontinuities, the following (similar) objective function
was used instead:

\[ f(x) = \left[ \sum_{\omega_{1i}}^{m} \max(\ddot{X}_i) \omega_{1i}^n \right]^{1/n} \] (3.35)

where the non-dimensional frequency increases and decreases by an order or magnitude, i.e. \( \tilde{\omega}^* \in \{0.1, 1, 10\} \) and \( \ddot{X}_i \) refers to the corresponding acceleration versus frequency curve for each \( \tilde{\omega}^* \).

Equation (3.35) is the \( n \)th norm of the acceleration peaks over a range of natural frequencies. It becomes essential to assign a reasonable value for \( n \) so that the objective function adequately weighs the cost of a high peak in acceleration. Here \( n \) is chosen to be 4. The results from this optimization formulation are discussed below.

The Maxwell model and critical gel model were both used within this new optimization scheme. The dashed lines in Fig. 3.9 show the system design (right) and performance (left) over a range \( \tilde{\omega}^* \) optimized for a reference natural frequency \( \tilde{\omega}^* = 1 \). While the response of the \( \tilde{\omega}^* = 1 \) system is obviously optimized, the system as a whole is problematic. In the case of the Maxwell element, the time scale optimized for this natural frequency (shown as the dotted vertical line in Fig. 3.9a) matches the resonance peak with the high-frequency plateau behavior. However, this characteristic timescale is too long (i.e., the frequency is too low) to prevent an increased high-frequency plateau should the system have a lower natural frequency. Likewise, the timescale is too short to effectively attenuate the resonance peak for a system of a higher natural frequency. The extended optimization problem takes these trade-offs into account and is able to effectively match the most significant high frequency component \( \tilde{\omega}^* = 0.1 \text{ rad/s} \) with the most significant resonance acceleration \( \tilde{\omega}^* = 10 \text{ rad/s} \), leading to a design that is optimized in a more balanced manner, reducing the objective function by 32%.

Likewise, the critical gel model optimized for the reference natural frequency \( \tilde{\omega}^* = 1 \) leads to problems with high frequency behavior for lower natural frequencies and resonance attenuation for higher natural frequencies. Optimizing for the entire range of natural frequencies allows for improved overall results for the system, as shown in the solid lines of Fig. 3.9. The objective function is decreased by 51%.

In both viscoelastic parameterizations, overall optimization of the system comes at a cost
of higher maximum accelerations for some natural frequencies, shown as the circles along the non-dimensional acceleration axes in Fig. 3.9. Values of nondimensionalized acceleration are shown in Table 3.3.

For the extension of the original case study, the maximum acceleration amplitude was reduced for both the single element Maxwell and critical gel models. As in the previous case study, the additional degrees of design freedom in the multi-mode Maxwell model provided no further improvement over a single mode. The full results of this extension are presented in Table 3.3.

The new optimization scheme dramatically affects the optimized kernel function shape, $K(t)$. The kernel functions optimized for a fixed natural frequency and a range of natural frequency are shown in Fig. 3.9. The expanded range pushes the optimal characteristic timescale, $\lambda$, lower to improve the high-frequency behavior of the system. The range of frequencies decreases the magnitude of $n$, the critical gel exponent, effectively making the system more solid-like, again improving the high-frequency behavior of the system.

Table 3.3: Optimized peak acceleration magnitudes and optimized viscoelastic parameters for the extended vibration isolator problem. Bolded values indicate the objective function for the optimizer.

<table>
<thead>
<tr>
<th>Opt. For</th>
<th>Maximum Acceleration</th>
<th>Fourth Norm</th>
<th>V.E. Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maxwell</td>
<td>$\tilde{\omega}^* = 1$</td>
<td>21.0</td>
<td>22.5</td>
</tr>
<tr>
<td></td>
<td>$\tilde{\omega}^* = 10$</td>
<td>25.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\tilde{\omega}^* = 0$</td>
<td>21.0</td>
<td>22.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Range of $\tilde{\omega}^*$</td>
<td>15.4</td>
<td>15.5</td>
</tr>
<tr>
<td>Critical Gel</td>
<td>$\tilde{\omega}^* = 1$</td>
<td>99.9</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td>Range of $\tilde{\omega}^*$</td>
<td>33.1</td>
<td>42.5</td>
</tr>
</tbody>
</table>

An important note to make is that these results, even more so than the original problem,
Figure 3.9: The performance (left) and viscoelastic design (right) for a Maxwell element and critical gel element in the extended vibration isolation problem. Multi-mode and single mode system response was identical, thus only a single mode is shown. The system performance is measured by the acceleration response while the viscoelastic design corresponds to the kernel function, $K(t)$, of the viscoelastic element. Dashed lines represent optimization for a reference non-dimensional natural frequency $\tilde{\omega}^* = 1$, where $\tilde{\omega}^*$ is as described in Eq.3.34; solid lines represent the results optimized for the range of $\tilde{\omega}^*$. In the left panels (performance), the values of the objective function (fourth order norm of the maximum accelerations of each curve), optimized for a reference $\tilde{\omega}^* = 1$ (dashed) and a range of $\tilde{\omega}^*$ values are shown as horizontal black lines. The optimizer works to minimize this objective function. (See online for color)

are dependent on the range of input frequency ($\tilde{\omega}$) chosen. The ever-increasing acceleration at high frequency for a liquid-like system as well as a critical gel model drives the optimized results.

Passive vibration isolators find use in a variety of practical applications. In their use as air isolators in large industrial equipment, the typical natural frequency range is 1.5-3 Hz. In the case of base isolators used in buildings and large structures, the natural frequency varies over a low seismic range. Their usage in vehicles and aviation pertains to a frequency range
of 10-20 Hz. The key takeaway here is that real world vibration isolation occurs over not just one but a range of resonant frequencies, for which viscoelastic responses can be optimized.

3.4 Conclusions

In this work, we have outlined a generalized mathematical framework for the design of linear viscoelastic materials and structures. Driven by performance objectives, the paradigm identifies optimal targets for a properly-posed function-valued kernel function (equivalent to a stress-relaxation modulus $G(t)$ describing a viscoelastic material). The target function is agnostic to the underlying material structure or spring-dashpot arrangement. This improves achievable performance of mechanical systems by expanding the design space.

A case study of a simple vibration isolator demonstrated the utility of parameterizations—Maxwell and critical gel models, specifically—of a generalized linear viscoelastic connection to improve performance of the system compared to the best performance available through linear dashpots. In this case, a single-mode Maxwell model proved effective for a structure and loading scenario with a single timescale. Other models, such as the critical gel and multi-mode Maxwell, may show even further performance improvement for more complex forcing scenarios or structures with a broad spectrum of inherent time scales.

An additional case study involved a system subject to a range of possible natural frequencies, but with an unchanging viscoelastic connection to isolate vibrations. Again, a single-mode Maxwell model showed the largest improvement over the conventional linear dashpot system.

This work primarily lies along the first step of the design hierarchy relating performance (in this case, the effectiveness of a vibration isolation system) to material properties (the generalized viscoelastic kernel function, $K(t)$). The next step in the process is the design of viscoelastic materials to achieve the target $K(t)$ of the system. While difficult, this is known to some extent, as the characteristic relaxation time for various viscoelastic materials (i.e. emulsions, polymer solutions and melts, colloidal suspensions and gels) follow known scaling laws [64, 65, 66]. However, should the exact design target not be precisely achievable, it is not known how sensitive the performance of a system will be to the shape of the kernel.
function. This sensitivity analysis stands as important future work. An alternative approach is to identify an appropriate material class based on the optimal target $K(t)$ functions, and reformulate the system optimization problem with additional constraints due to material-specific assumptions. This would result in an optimal solution that is informed by the early-stage material design results, and is closer to a physically realizable material specification.

The methodology outlined in this work can be further generalized to eliminate the need to specify a functional form and parameterization of the linear viscoelastic kernel. This will bring the challenge of optimizing a high dimensional object, but would allow for a greater expansion of the design space, while only using a single time-dependent material function as a system-level variable. This type of study is particularly relevant to early-stage design investigations before many design decisions are finalized and activities are more exploratory in nature. The results here serve as a foundation for design with rheological complexity, including efforts to expand beyond linear viscoelasticity to fully nonlinear viscoelastic behavior and complex fluids which may provide a wide range of novel functionality yet to be discovered.
Beyond taking advantage of viscoelasticity, it is important to understand its physical origins. The work of Chapters 2 and 3 is done on the right-hand side of Fig. (2.1) and remains completely material agnostic, but to complete the design paradigm, material structures must be chosen and understood.

Figure 4.1: Many sources organize their discussion of microstructural origins of viscoelasticity by describing multiple rheological properties of a single microstructure or material class [64, 66]. Here, we choose just one rheological property (relaxation time, $\lambda$) and describe how it can relate to many microstructures and material classes.

Reference texts and peer reviewed publications discuss many rheological properties that arise from different microstructures or material classes [64, 66, 67, 65]). Generally, these
texts are organized around specific material systems discussing the many complex rheological properties that arise from each structure (see left of Fig. (4.1)).

In our design scheme, we choose material agnostic rheological properties based on a target functionality. Thus, we are left with a specific property (e.g. relaxation time, $\lambda$, or relaxation kernel, $K(t)$) for which we want to explore possible microstructural design concepts (see right of Fig. (4.1)).

The key feature of viscoelasticity is stress relaxation. Fundamentally, the timescale of this relaxation is set by a balancing of elastic restoring forces and viscous dissipation.

Dimensionally, this relaxation time can be thought of as a ratio of a viscosity $\eta$ and an effective elastic modulus $G_{eff}$, such that the relaxation time $\lambda$

$$\lambda = \frac{\eta}{G_{eff}} \simeq [time]$$

(4.1)

After flow has deformed the material, the tendency to return to an equilibrium state governs this $G_{eff}$. For some simple material classes, the scaling of this relaxation time $\lambda$ with the important system parameters can be analytically derived. What follows is a survey of different material structures that have viscoelastic relaxation and their known scaling relations to determine $\lambda$. Many follow the form of Eq. (4.1), as will be seen.

4.1 General Brownian/Thermal Particles (non-spherical)

When a dilute suspension of non-spherical thermal particles is placed under flow, the particles tend to align along extensional flow directions; in shear they rotate (Jeffreys orbits, [68]) and on average have an alignment due to a non-constant rotational velocity that depends on particle orientation. Thus, the average particle orientation becomes anisotropic, as shown schematically in Fig. 4.2. The elasticity in these materials is caused by the restoration of particles to a random and isotropic equilibrium. Here, the key restoring parameter is the rotational diffusivity of the particle, $D_r \doteq [rad^2/s]$. Thus, the time scale is set by the ratio of a diffusion ‘distance’ to the diffusivity, thus, $\lambda \propto \theta^2/D_r$, where $\theta$ is the angle diffused For a
Figure 4.2: Non-spherical brownian particles have an overall anisotropic alignment when placed in simple shear flow (bottom). The particles return to equilibrium through rotational diffusion back to an isotropic state (top).

simple case of a high aspect ratio cylinders, this gives a relaxation time scaling of

$$\lambda \propto \frac{\eta_s}{kT/L^3}$$  \(4.2\)

where $\eta_s$ is the solvent viscosity, $k$ is the Boltzmann constant, $T$ is the system temperature and $L$ is the length of a cylinder \[64\]

For more general shapes (e.g. prolate and oblate spheroids), the relaxation time is governed by a more complex equation \[68\], but the general scaling of Eq.(4.2) still tends to hold, albeit with multiple length scales in $L^3$.

4.2 Hard spherical Brownian/Thermal Particles

Under flow, spherical particles cannot themselves have an orientation (in contrast to non-spherical particles, Section 4.1). Rather, the spatial distribution of the particles is the initial deviation from equilibrium. For example, particles tending to form rows or planes. This deviation can be quantified with a pair-distribution function (the probably of finding neighboring particles in a particular direction from a reference particle). The return to equilibrium is governed by translational diffusion (random motion) which drives the particles back to an isotropic equilibrium state.
4.3 Dilute emulsions

In the dilute limit of emulsions the distortion of flow due to one droplet does not influence other droplets. When such an emulsion is placed under flow, the droplets become stretched due to the fluid. The elasticity in these systems is due to the tendency of the droplets to regain their shape. This, of course, is driven by surface tension and minimizing the surface
area of the droplet. Thus, the relaxation time scales as

\[ \lambda \propto \frac{\eta_s}{\Gamma/a}, \]  

where \( \Gamma \) is the surface tension and \( a \) is the droplet radius [64, 67].

4.4 Dilute polymer solutions

Figure 4.5: In equilibrium, polymer chains cluster into a random walk conformation (top). When sheared, these clusters deform with a mean alignment with the flow (bottom). Brownian motion (diffusion) returns the polymers to their original state.

In a dilute solution of polymers, the chains are coiled in a random walk and do not
interact with other chains. When placed under flow, the polymer coils elongate. There are multiple chain relaxation models that give predictions for important system relaxation times (shortest/monomer relaxation time, longest relaxation time, distribution of relaxation times) such as the Rouse and Zimm models.

Here we will discuss the longest relaxation time as it relates to the elasticity of polymer solutions. Like hard thermal particles, the elasticity in a dilute polymer system is caused by the polymers returning to an isotropic, coiled equilibrium state through Brownian motion. Here, the characteristic length scale for diffusion rate is the radius of gyration, $R_g$. Thus the relaxation time scales as

$$\lambda \propto \frac{\eta_s}{kT/R_g^3}$$

(4.6)

### 4.5 Entangled polymer solutions

![Figure 4.6: For entangled polymers, a single polymer must slide through or reptate around other polymers in order to relax. This motion is related to the diffusion of the polymer chain.](image)

In polymer solutions of high enough molecular weight and concentration, the individual chains become entangled in one another. To relax, the individual chains must slide (often referred to as reptate) through one another. The model proposed by deGennes is that an entangled chain diffuses through a tube formed by surrounding polymers [69].

In these systems, the relaxation time is analogous to this reptation time, $\lambda_{\text{reptation}}$. Analogous to the previous examples, the reptation time is set by diffusion of the entangled polymer. However, because the polymer is restricted to motion in one direction (along the backbone of the polymer chain), the diffusivity is set by $D \propto \frac{kT}{\zeta M}$, where $\zeta$ is a friction set by polymer-polymer interactions and $M$ is the molecular weight of the polymer chain, an
analogous measure to the chain length. This model predicts a reptation time scaling of

\[ \lambda \propto \frac{\zeta M^3}{kT} \]  \hspace{1cm} (4.7)

Empirically, the relaxation time for these types of materials is found to scale with the molecular weight (a proxy for the length of the polymer chain) such that

\[ \lambda \propto M^{3.4} \]  \hspace{1cm} (4.8)

4.6 Particulate gel

Figure 4.7: Colloidal networks are formed by attractions between the Brownian particles. The relaxation of this microstructure is set by how strong these attractions are as compared with the thermal diffusion of the individual particles.

If colloidal particles are attractive, they will form networks known as particulate gels. In these systems, there are two characteristic timescales that contribute to the overall relaxation of the gel. The first, of course, is the timescale of diffusion of individual particles, as described in Sec. 4.2. The other contribution is set by the "stickiness" of the interaction between the particles (i.e. how difficult it is to "un-stick" two particles after they have attached). Overall, this leads to a relaxation time of

\[ \lambda = 6\pi \frac{\eta_s}{kT/6\pi a^3} \exp \left( -\frac{a W_{\text{min}}}{kT} \right) \]  \hspace{1cm} (4.9)

where \( \eta_s \) is the solvent viscosity, \( k \) is Boltzmann's constant, \( T \) is the temperature, \( a \) is the radius of the colloidal particles, and \( W_{\text{min}} \) is the potential well required to unstick two particles ([64], Equation 7-23).
4.7 Cross-linked polymers

Figure 4.8: Cross-linked polymers (covalent and transient) are long chains attached by small molecules or other interactions. Covalently bonded cross links will not fully relax. The relaxation in transiently cross-linked systems is set by the reaction time of the cross-linking bonds.

Polymers can be cross-linked by other molecule or other induced interactions. This can occur through covalent bonding or through a transient chemical reaction. Polymers transiently cross-linked do have a characteristic relaxation timescale. This timescale is set by the duration of the cross-linking bond. Thus the characteristic relaxation is defined to be

\[ \lambda = \frac{1}{\omega_0} \exp \left( \frac{W}{kT} \right) \]  

(4.10)

where \( \omega_0 \) is the natural frequency of thermal vibrations and \( W \) is the potential barrier for the bond [65].

A permanent, covalent bond can be thought of as a transient bond at the limit of \( W \to \infty \). In this limit, the relaxation time becomes

\[ \lambda = \infty \]  

(4.11)

4.8 Conclusions

The limited selection of microstructures discussed are summarized in Table 4.1. For all microstructures excluding for dilute emulsions, the relaxation time is dependent on \( kT \). In all of these cases, the thermal energy is the main driving factor back toward equilibrium. These relaxation times all also have a strong dependence \( (L^3) \) on the characteristic length
scale of the microstructure. This is only not true of entangled polymers, where the empirically found length scale dependence is actually \( L^{3.4} \), due to relaxation mechanisms that are not well described by these stronger, basic physical arguments.

Table 4.1: Viscoelastic timescales across material classes

<table>
<thead>
<tr>
<th>Material</th>
<th>( \lambda \propto )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-spherical Brownian particles</td>
<td>( \frac{\eta_s}{kT/L^3} )</td>
</tr>
<tr>
<td>Hard, spherical Brownian particles</td>
<td>( \frac{\eta_s}{kT/\pi a^3} )</td>
</tr>
<tr>
<td>Dilute emulsions</td>
<td>( \frac{\eta_s}{\Gamma/a} )</td>
</tr>
<tr>
<td>Dilute polymer solutions</td>
<td>( \frac{\eta_s}{kT/R^3} )</td>
</tr>
<tr>
<td>Entangled polymer solutions</td>
<td>( M^{3.4} )</td>
</tr>
<tr>
<td>Particulate gel</td>
<td>( \frac{\eta_a}{kT/\omega_0 a^3} \exp\left(-\frac{\alpha W_{\text{min}}}{kT}\right) )</td>
</tr>
<tr>
<td>Transiently cross-linked polymers</td>
<td>( \frac{1}{\omega_0} \exp\left(\frac{W}{kT}\right) )</td>
</tr>
<tr>
<td>Covalently cross-linked polymers</td>
<td>( \infty )</td>
</tr>
</tbody>
</table>

It is important to note that none of the time scales listed above have a concentration dependence. These scalings depend only on the simple physics that govern systems that are dilute, or with minimal interactions. These represent only a small number of the possible microstructures that can lead to viscoelastic behavior. Naturally, the next extension of these scalings is to consider the behavior of semi-dilute and concentrated systems. In concentrated systems, other relaxation mechanisms such as caging are at play [70]. There are also other microstructural classes that may be of interest. One such system is micellar solutions, such as entangled worm-like micelles [71, 72]. These are governed by two time scales: reptation and a breaking-reforming time scale. There are also liquid crystalline systems which may be useful in different design applications. There are also a whole variety of active systems such as biological or artificial swimmers. These active suspensions open up an entirely different range of timescales than any passive systems.

In addition, any of these single microstructures can be combined with a number of other microstructures leading to an entire distribution of time scales. Combinations of these basic microstructural classes leads to an almost infinitely large design space when creating viscoelastic materials. As such, it may be possible to create a wide range of viscoelastic timescales \( \lambda \) and relaxation functions \( G(t) \) to achieve a diverse range of design objectives. A
specific target function must first be identified, the process for which is considered in Chap. 3.
5 CONCLUSIONS AND OUTLOOK

In this thesis, we have discussed incorporating rheologically complex materials into design. Effectively using these materials is difficult because material properties are complex and function valued. When we talk about design with complex materials, it is helpful to break the discussion into multiple steps of an inverse problem, as shown in Fig. 2.1. The process starts by identifying a target performance. Then, the material properties needed to achieve this target are found—either by optimization or other means. Importantly, this step does not specify the actual material or material type used, just some material-agnostic material function. The next, and final step is to create a real material to achieve these targeted material functions. Much of the work presented here focuses on relating these material functions to a desired material performance, or the first half of the design inverse problem.

The last step of the process requires the formulation of real materials. This presents its own difficulties. Finding or creating materials that can meet the desired objectives can be done through a variety of methods. Of course, if a known material fits the criteria, it is an obvious choice. For some material classes and some material properties, there are handbooks that compile experimentally gathered descriptions of many materials. The material properties for some material classes can also be computationally predicted, allowing for the virtual creation of these optimized materials. Even so, it is unlikely that materials can be created that have properties exactly equal to the desired properties. To alleviate this concern, a next step in this work is to assess the sensitivity of the end performance to the targeted material function. It will be helpful to know if small deviations in material function values will lead to small changes in performance or drastic changes in performance. In other words, we need to know: How close is close enough?

Here, we have specifically considered linear viscoelasticity and its associated material functions ($G(t)$, $G'(\omega)$, $J(t)$, etc.) as our rheological complexity. While this incorporates
potentially useful material behavior, it also limits the design space to a more manageable size. This reduction allowed us to systematically approach design with complex materials. To help with the last step in the design process when designing systematically with linear viscoelasticity, it will be useful to create a database of linear viscoelastic properties of different material types. These properties could be displayed in Ashby diagram-like [7, 8, 9] cross-property plots, as in Fig. 2.11. Even this is not a completely straightforward task. First and foremost, the information is inherently high-dimensional—material properties are not only a function of time (i.e. viscoelastic), but also of the specific material chemistry. To reduce some of the complexity, it may be possible to distill function-valued properties into single important scalar values (as in the penultimate figure Chap.2). Even then, we must decide what language (i.e. material properties) is best used to effectively describe these materials in a way that is useful for design.

A natural extension of this current work is to bring the same results and methodology to nonlinear rheology. Nonlinear rheology allows for even more interesting behavior. It is also extremely critical when discussing how to connect complex rheology to tactile perception. It is likely that much of how people interact (touching, poking, stretching, squeezing, chewing, swallowing) with complex materials is in the nonlinear regime. To truly characterize how people experience the materials, we must include these nonlinear viscoelastic properties. This will require developing new, systematic ways to describe a variety of materials in the nonlinear regime.
APPENDIX: HIGH FREQUENCY SCALING OF DISPLACEMENT AMPLITUDE

In Figs. 3.4–3.5, high-frequency power law scaling is indicated. This appendix provides derivations of these frequency-dependent scalings of the displacement amplitude, for multiple assumed constitutive models, used as reference slopes in Figs. 3.4–3.5.

Initial Case (Spring only)
With an input base displacement of

\[ y(t) = Y_0 \sin(\omega t) \]  \hspace{1cm} (A.1)

we consider assumed solution form

\[ x(t) = X_0 \sin(\omega t + \phi) \]  \hspace{1cm} (A.2)

For this scaling analysis, we consider the order \( \mathcal{O}(\cdot) \) of front factors, dropping all trigonometric terms, as they are \( \mathcal{O}(1) \). Inserting these assumptions into the equation of motion for the initial case (Eqn. (3.18) with \( K(s) = 0 \)), we find the relation between force amplitude and acceleration amplitude

\[ -k(X_0 - Y_0) \sim mX_0\omega^2 \]  \hspace{1cm} (A.3)

This gives a nondimensional amplitude (normalized by the input magnitude) of

\[ \frac{X_0}{Y_0} \sim \frac{1}{1 + \left(\frac{m}{k}\omega^2\right)} \]  \hspace{1cm} (A.4)
Taking the limit of large frequency, where $\omega \gg \sqrt{\frac{k}{m}}$, or $\omega \gg \omega_n$

$$\lim_{\omega \gg \omega_n} \frac{X_0}{Y_0} \propto \frac{1}{\omega^2} \quad (A.5)$$

Spring + Linear Dashpot

Using identical assumptions and methods as in the initial case, the equation of motion for the mass $m$ becomes

$$-k(X_0 - Y_0) - c(X_0\omega - Y_0\omega) \sim -mX_0\omega^2 \quad (A.6)$$

This gives a nondimensional amplitude of

$$\frac{X_0}{Y_0} \sim \frac{k + c\omega}{-m\omega^2 + c\omega + k} \quad (A.7)$$

Taking the limit of large frequency,

$$\lim_{\omega \to \infty} \frac{X_0}{Y_0} \propto \frac{1}{\omega} \quad (A.8)$$

Spring + Generalized Viscoelastic Element

As in Sec. 3.3.1, the equation of motion for mass $m$, attached to a base with a spring and generalized viscoelastic connection becomes:

$$-k(x - y) - \int_0^t K(s) [\dot{x}(t - s) - \dot{y}(t - s)] \, ds = m\ddot{x}(t) \quad (A.9)$$

The resulting motion is assumed to be of the expanded form:

$$x(t) = X_R \sin \omega t + X_i \cos \omega t \quad (A.10)$$
Thus the equation of motion has an assumed form of

\[- k (X_R \sin \omega t - X_i \cos \omega t) + k Y \sin \omega t\]

\[- \int_0^t K(s) [\omega X_R (\cos \omega t \cos \omega s + \sin \omega t \sin \omega s) - \omega X_i (\sin \omega t \cos \omega s - \cos \omega t \sin \omega s)] \, ds\]

\[+ \int_0^t K(s) Y (\cos \omega t \cos \omega s + \sin \omega t \sin \omega s) \, ds\]

\[\sim - m [\omega^2 X_R \sin \omega t + \omega^2 X_i \cos \omega t] \quad (A.11)\]

**Single mode Maxwell model**

For a single mode Maxwell model, the viscoelastic parameterization is:

\[K(s) = K_m \exp \left( - \frac{s}{\lambda} \right) \quad (A.12)\]

Inserting this parameterization into the equation of motion and expanding gives:

\[- k [X_R \sin \omega t + X_i \cos \omega t] + k Y \sin \omega t\]

\[- K_m \omega X_R \cos \omega t \int_0^t \exp \left( - \frac{s}{\lambda} \right) \cos \omega s \, ds\]

\[- K_m \omega X_R \sin \omega t \int_0^t \exp \left( - \frac{s}{\lambda} \right) \sin \omega s \, ds\]

\[+ K_m \omega X_i \sin \omega t \int_0^t \exp \left( - \frac{s}{\lambda} \right) \cos \omega s \, ds\]

\[- K_m \omega X_i \cos \omega t \int_0^t \exp \left( - \frac{s}{\lambda} \right) \sin \omega s \, ds\]

\[+ K_m \omega Y \cos \omega t \int_0^t \exp \left( - \frac{s}{\lambda} \right) \cos \omega s \, ds\]

\[+ K_m \omega Y \sin \omega t \int_0^t \exp \left( - \frac{s}{\lambda} \right) \sin \omega s \, ds\]

\[\sim - m \omega^2 [X_R \sin \omega t + X_i \cos \omega t] \quad (A.13)\]

Evaluating each integral for the steady-state case \(t \to \infty\)
\[-k \left[ X_R \sin \omega t + X_i \cos \omega t \right] + kY \sin \omega t \]

\[-K_m \omega X_R \cos \omega \frac{\left( \frac{1}{\lambda} \right)}{\left( \frac{1}{\lambda} \right)^2 + \omega^2} \]

\[-K_m \omega X_R \sin \omega \frac{\omega}{\left( \frac{1}{\lambda} \right)^2 + \omega^2} \]

\[+ K_m \omega X_i \sin \omega \frac{\left( \frac{1}{\lambda} \right)}{\left( \frac{1}{\lambda} \right)^2 + \omega^2} \]

\[-K_m \omega X_i \cos \omega \frac{\omega}{\left( \frac{1}{\lambda} \right)^2 + \omega^2} \]

\[+ K_m \omega Y \cos \omega \frac{\left( \frac{1}{\lambda} \right)}{\left( \frac{1}{\lambda} \right)^2 + \omega^2} \]

\[-K_m \omega Y \sin \omega \frac{\omega}{\left( \frac{1}{\lambda} \right)^2 + \omega^2} \]

\[\sim -m\omega^2 \left[ X_R \sin \omega t + X_i \cos \omega t \right] \quad (A.14)\]

Grouping sine terms gives the relation

\[X_R = \frac{1}{D} \left[ -kY - K_m Y \frac{\omega^2}{\left( \frac{1}{\lambda} \right)^2 + \omega^2} - K_m \frac{\omega}{\left( \frac{1}{\lambda} \right)^2 + \omega^2} X_i \right] \quad (A.15)\]

Where

\[D = m\omega^2 - k - K_m \frac{\omega^2}{\left( \frac{1}{\lambda} \right)^2 + \omega^2} \quad (A.16)\]

Similarly, grouping cosine terms of the equation of motion gives

\[X_i = \frac{1}{\Delta} \left[ -\frac{1}{D} K_m k Y \frac{\omega}{\left( \frac{1}{\lambda} \right)^2 + \omega^2} - \frac{1}{D} K_m Y \frac{\omega^3}{\left( \frac{1}{\lambda} \right)^2 + \omega^2} - K_m Y \frac{\omega}{\left( \frac{1}{\lambda} \right)^2 + \omega^2} \right] \quad (A.17)\]

Where

\[\Delta = m\omega^2 - k + \frac{1}{D} K_m^2 \frac{\omega}{\left( \frac{1}{\lambda} \right)^2 + \omega^2} - K_m \frac{\omega^2}{\left( \frac{1}{\lambda} \right)^2 + \omega^2} \quad (A.18)\]

Now checking the limit of \( \omega \gg \frac{1}{\lambda} \) (i.e. \( \omega \to \infty \))
\[ D \propto \omega^2 \quad (A.19) \]
\[ \Delta \propto \omega^2 \quad (A.20) \]

Thus plugging these in to the relations for \( X_R \) and \( X_i \) at the limit of \( \omega \to \infty \) gives the high frequency behavior of:

\[ X_i \propto \frac{1}{\omega^3} \quad (A.21) \]
\[ X_R \propto \frac{1}{\omega^2} \quad (A.22) \]

The nondimensional amplitude is defined as

\[ |X| = \left[ X_R^2 + X_i^2 \right]^{\frac{1}{2}} \quad (A.23) \]

And thus the full nondimensional amplitude high frequency behavior is

\[ |X| \propto \frac{1}{\omega^2} \quad (A.24) \]

Critical gel model

For the critical gel model, the viscoelastic parameterization is:

\[ K(s) = S_k s^{-n} \quad (A.25) \]

Inserting this parameterization into the equation of motion and expanding gives:
\(- k [X_R \sin \omega t + X_i \cos \omega t] + kY \sin \omega t \)

\(- S_k \omega X_R \cos \omega t \int_0^t s^{-n} \cos \omega s ds \)
\(- S_k \omega X_R \sin \omega t \int_0^t s^{-n} \sin \omega s ds \)
\(+ S_k \omega X_i \sin \omega t \int_0^t s^{-n} \cos \omega s ds \)
\(- S_k \omega X_i \cos \omega t \int_0^t s^{-n} \sin \omega s ds \)
\(+ S_k \omega Y \cos \omega t \int_0^t s^{-n} \cos \omega s ds \)
\(+ S_k \omega Y \sin \omega t \int_0^t s^{-n} \sin \omega s ds \)

\(\sim -m\omega^2 [X_R \sin \omega t + X_i \cos \omega t] \quad (A.26)\)

Evaluating each integral for the steady-state case \((t \to \infty)\)

\(- k [X_R \sin \omega t + X_i \cos \omega t] + kY \sin \omega t \)

\(- S_k \omega X_R \cos \omega t \left[ \omega^{-1+n} \Gamma(1-n) \sin \left(\frac{n\pi}{2}\right) \right] \)
\(- S_k \omega X_R \sin \omega t \left[ \omega^{-1+n} \Gamma(1-n) \cos \left(\frac{n\pi}{2}\right) \right] \)
\(+ S_k \omega X_i \sin \omega t \left[ \omega^{-1+n} \Gamma(1-n) \sin \left(\frac{n\pi}{2}\right) \right] \)
\(- S_k \omega X_i \cos \omega t \left[ \omega^{-1+n} \Gamma(1-n) \sin \left(\frac{n\pi}{2}\right) \right] \)
\(+ S_k \omega Y \cos \omega t \left[ \omega^{-1+n} \Gamma(1-n) \cos \left(\frac{n\pi}{2}\right) \right] \)
\(+ S_k \omega Y \sin \omega t \left[ \omega^{-1+n} \Gamma(1-n) \sin \left(\frac{n\pi}{2}\right) \right] \)

\(\sim -m\omega^2 [X_R \sin \omega t + X_i \cos \omega t] \quad (A.27)\)

Grouping sine terms gives the relation

\(X_R = \frac{1}{D} \left[ kY - S_k Y \omega^n \Gamma(1-n) \sin \left(\frac{n\pi}{2}\right) - S_k X_i \omega^n \Gamma(1-n) \sin \left(\frac{n\pi}{2}\right) \right] \quad (A.28)\)
Where

\[ D = m\omega^2 - k - S_k\omega^n\Gamma(1 - n)\cos\left(\frac{n\pi}{2}\right) \]  \hspace{1cm} (A.29)

Similarly, grouping cosine terms of the equation of motion gives

\[ X_i = \frac{1}{\Delta} \left[ -\frac{1}{D}\frac{S_k}{k}Y\omega^n\Gamma(1 - n)\sin\left(\frac{n\pi}{2}\right) \right] \]
\[ - \frac{1}{\Delta} \left[ \frac{1}{D} S_k^2 Y^2 \left[ \Gamma(1 - n)\sin\left(\frac{n\pi}{2}\right) \right]^2 \right] \]
\[ - \frac{1}{\Delta} \left[ S_k Y\omega^n\Gamma(1 - n)\cos\left(\frac{n\pi}{2}\right) \right] \]  \hspace{1cm} (A.30)

Where

\[ \Delta = m\omega^2 - k + \frac{1}{D} S_k^2 \left[ \omega^n\Gamma(1 - n)\sin\left(\frac{n\pi}{2}\right) \right]^2 - S_k \omega^n\Gamma(1 - n)\sin\left(\frac{n\pi}{2}\right) \]  \hspace{1cm} (A.31)

Now checking the limit of \( \omega \gg \frac{1}{\lambda} \) (i.e. \( \omega \to \infty \))

\[ D \propto \omega^2 \]  \hspace{1cm} (A.32)
\[ \Delta \propto \omega^2 \]  \hspace{1cm} (A.33)

Thus plugging these in to the relations for \( X_R \) and \( X_i \) at the limit of \( \omega \to \infty \) gives the high frequency behavior of:

\[ X_i \propto \omega^{n-2} \]  \hspace{1cm} (A.34)
\[ X_R \propto \omega^{n-2} \]  \hspace{1cm} (A.35)

The nondimensional amplitude is defined as

\[ |X| = \left[X_R^2 + X_i^2\right]^\frac{1}{2} \]  \hspace{1cm} (A.36)
And thus the full nondimensional amplitude high frequency behavior is

$$|X| \propto \omega^{n-2}$$

(A.37)

In summary, Eqs. A.5, A.8, A.24, A.37 are used as theoretical high-frequency limits of power-law slopes in Figs. 3.4–3.5.
REFERENCES


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