MODEL SELECTION IN RHEOLOGY: PROVIDING A PRACTICAL FRAMEWORK, SURVEYING THE FIELD, AND ASSESSING THE USES AND LIMITATIONS OF BIC

BY

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THESIS

Submitted in partial fulfillment of the requirements
for the degree of Master of Science in Theoretical and Applied Mechanics
in the Graduate College of the
University of Illinois at Urbana-Champaign, 2019

Urbana, Illinois

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ABSTRACT

The selection of which model or models to use when studying a complex fluid is of constant relevance in rheology, though often too little attention is paid to framing this problem of selection such as to yield consistent, credible, and meaningful results. In this thesis I provide a novel framework for identifying the purpose of rheological models along with background on model selection techniques and criteria, assess the state of and need for model selection in rheological literature, and perform several case studies investigating how model selection techniques may be applied in rheology and note their advantages and limitations. While there remains no single, straightforward technique for selecting a model in all cases, the rheological literature so rarely acknowledges this crucial step in analysis and often fails to sufficiently report methodology relating to model fits, let alone selection, that even preliminary consideration of this problem and the application of simple criteria such as the Bayesian Information Criterion (BIC) may add significant value and validity to these analyses. There remains even greater opportunity in the application of more sophisticated methods such as the calculation of Bayes Factors and the formulation of priors for rheological models. The background, review, case studies, and examples presented in this thesis provide a jumping-off point for an ongoing discussion regarding the place of these theories and techniques in rheology while offering clear examples of their use and conclusions that may be drawn from them.

To the many people who I care for and who I am fortunate to have care for me, for their support and company.

ACKNOWLEDGMENTS

I thank my adviser Randy Ewoldt for his guidance and unwavering support throughout my time working with him, both as an undergrad and as a graduate student. I thank my friends and my family for being immensely generous in the counsel, understanding, and time they have shared with me me during my studies. I thank Arif Nelson, Rebecca Corman, Brendan Blackwell, the rest of the Ewoldt Research Group for their help, their encouragement, and their company.

Additionally, I would like to thank Jonathan Freund, Arne Pearlstein, and the many other wonderful professors who have inspired and motivated me as a student of mechanical sciences. I would like to thank the instructors I had the opportunity to work with and the students I met as a teaching assistant for providing me with with consistently engaging and fulfilling work through the ups and downs of graduate research.

Finally, this thesis is the culmination of much what those mentioned above have taught, provided, and shared with me; but I would like to specifically thank Piyush K. Singh and Scott Rogman, whose work I present and use in the first case study of this thesis; Matthew J. Armstrong, Antony N. Beris, Simon A. Rogers, and Norman J. Wagner, whose work I present and use in the second case study of this thesis; Carolyn N. Darling for her assistance in the process of collecting and organizing JoR articles; and P&G for funding and insight, especially Dr. William H. Hartt.

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CHAPTER 1

INTRODUCTION

1.1 Motivation

The first choice that a rheologist must make when faced with a new complex fluid material is whether or not the Newtonian constitutive model is sufficient to describe its behavior [1]. This choice may often be straightforward to the point of triviality, relegated to an implicit assumption, worth only the barest mention, if any. Despite its simplicity, this choice represents a fundamental decision that exists in virtually all rheological analysis: What model to use?

Rheological phenomena and behaviors are as diverse and numerous as the material functions and constitutive equations which attempt to describe them. Consequently, the choice of which model or models to use when conducting any sort of rheological analysis is often nontrivial. Such a choice *must* be based on the way in which the model for the fluid behavior is intended to be used or else no meaningful criteria for what is "sufficient" can be employed.

Bayesian inference provides a useful framework for approaching this problem in a rigorous way, but has yet to be widely adopted within the rheological community, despite demonstrations of its applicability [2, 3, 4] and successful use in other fields [5].

The goal of this thesis is to present actionable, pragmatic suggestions and examples for applying the tools of Bayesian inference to model selection in rheology. To this end, this thesis uses three broad categories to organize the purposes of models in rheology: description, prediction, and interpretation.

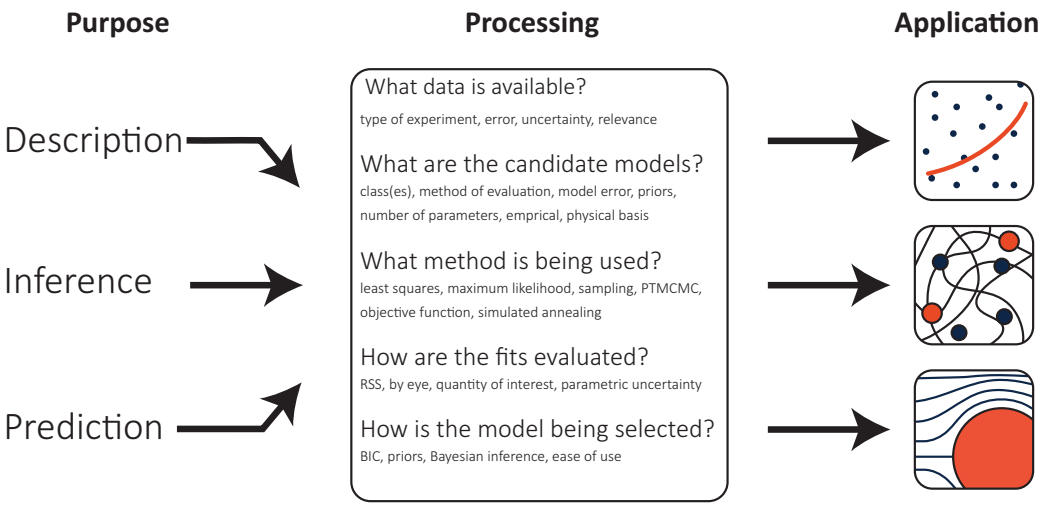


Figure 1.1: A schematic representation of the steps that should go into fitting and selecting a model. Before any fitting or selection is performed, the purpose for the model must be considered. This purpose must then guide the choices which follow: what models to consider, how to perform the fit, what metrics to calculate and report, and ultimately which model(s) to use. Although the categories are presented as distinct for ease of illustration, there will often be overlap between them in how a model is used.

1.1.1 Fitting for Description

Often, one wishes simply to represent data or a material response more concisely than the data itself does. Whether this is for clarity or categorization, what is of most concern in these cases is models or parameter values which describe how one material is different from another. For this reason, rheologists fitting a model for descriptive purposes should concern themselves with the certainty, or lack thereof, of these distinctions.

When estimating parameters for a model based on experimental data, there will inevitably be uncertainty in the parameter values [6, 7]. Depending on the quality of the data and the form of the model, there will be some "error" associated with the estimated parameter values. When the intent is to meaningfully distinguish two or more materials, one must consider how to quantify and report this error. When values and their error estimates overlap, one should exercise caution when reporting apparent differences. Conversely, if values are very close but the associated uncertainty of these values is very low, one may express confidence in the distinction between these materials (on the basis of the selected model, at least).

Most commonly used fitting routines and software will report an estimate of uncertainty made with some assumptions which are not always valid for rheological models. In fact, in many cases estimated error may imply the feasibility of values which one knows to be entirely implausible; for example, symmetrical, gaussian error about a mean may include a negative yield stress. This may make one hesitant to even report these uncertainties, but it should instead motivate careful consideration of what techniques are being employed. Embedding one's knowledge of what values are implausible in a prior will prevent these mathematical aberrations and a thorough sampling routine will allow for an expression of uncertainty that is accurate, meaningful, and experimentally reproducible.

1.1.2 Fitting for Inference

Inferring material structure from rheology has been identified as one of the ultimate aspirations of modern rheology [8]. For a material of interest a rheologist may hypothesize several potential microstructures that would be consistent with their observations. For each theorized microstructure, they may then propose constitutive model which one can attempt to fit to some data.

By fitting the models to the available data, one can begin to quantify and refine their belief in what the microstructure may actually be; examples include deducing fractal dimensions of particle networks [9], relating stimuli responsive chemistry behavior to rheological properties [10], and investigating the mechanism behind time-dependent behavior in a gel system [11]. If the only criterion used in making this determination is the quality of the fit, then more complex models will tend to be favored, regardless of how reasonable they may actually be. In this way, model selection may be used in a manner that is traditionally referred to as "hypothesis testing" [12]. The advantage of doing so in a Bayesian framework is that the use of priors allows for consistent, meaningful statements to be made about the relative plausibility of each model based on the available data. Even in the event that there is no preference for a model expressed in the priors, the priors assigned to the parameters for each model will ensure that each model is properly penalized for its complexity and rewarded for its correspondence to physical reality.

In other circumstances, there may be a material for which the type of microstructure is known, and a corresponding constitutive model is natural or singular in its ability to describe the behavior. If the parameters of the model then correspond to microstructural features of interest, then the interest in using the model may then be to learn about the precise nature of the microstructure. In this case, the inclusion of a prior for the value of this parameter is both useful and necessary for determining and expressing certainty in its possible values; standard least-squares fitting methods may yield uncertainties that are unreasonable and therefore uninformative.

1.1.3 Fitting for Prediction

Most rheological measurements occur in the simple flow situations of simple shear or uniaxial extension, yet it is desirable to use rheological models to predict flow behavior during complex flow situations such as in material processing [8]. The selection of a suitable tensorial model for these predictions may dramatically influence what can be predicted and how accurately; it should be based on both the performance of the model where it is calibrated and also the physical basis of the model which informs how it will perform in other situations.

If there exists significant uncertainty in the preferred parameter values for the model, this uncertainty should be propagated forward to the prediction. Sometimes the uncertainty in the values of the parameters is not well represented by a single, easily propagated statistic; in such a case it may be prudent to sample the parameter space to generate many predictions then report statistics on that population of predictions or simply report them all, as is often done in weather forecasting to account for uncertainty [13]. In cases where there is not a single, strongly preferred model, ensemble modeling may yield the most appropriate prediction; with predictions made by each model are averaged with weights proportionate to their relative plausibility, a technique that has been shown to improve out of sample predictions [14, 15].

There is never sufficient data to make a perfect prediction (if there were, it wouldn't be called a "prediction") and there may not be a "correct" set of assumptions to use for every problem. For this reason, it is imperative that when making a prediction that any uncertainties are properly propagated

and the assumptions are explicitly acknowledged such that the limitations of the prediction are well-understood. Not only does this make predictions more honest, but it makes them more valuable, as they may be repeated and improved upon as new data is acquired or new assumptions are proposed.

1.2 Model selection criteria

It is desirable to use selection criteria that are both consistent and quantitative, for whatever purpose a model is being selected (summarized in Figure 1.1). Consistent, so that those working from the same assumptions and information towards the same purpose will come to identical conclusions. Quantitative, so that the effect of differing assumptions or information is easily understood. Bayesian methods for inference offer the means to fulfill both of these goals [16], which are briefly summarized below.

1.2.1 Bayes factors

One of the greatest advantages of using Bayesian methods is the ability *and* requirement to encode prior information into the process of inference [16, 12]. A prior must be formulated both for the individual models (usually as single point values) and for the values of each of the model parameters (usually continuous functions). These steps are analogous to the qualitative judgments that are made when models are selected for a given problem and when bounds are set (or not) in standard fitting routines. Bayesian methods simply demand that the rheologist make these choices explicit, while also providing the opportunity to encode more detailed information.

Bayes' theorem

Confidence, or belief, in some model M, after observing some data D, may be calculated using Bayes' theorem

$$P(M|D,I) = \frac{P(D|M,I)}{P(D|I)} P(M|I)\,, \tag{1.1}$$

where $P(D|M,I)$ is the marginal likelihood of the data and $P(M|I)$ is the prior belief in the model. The use of I to represent additional background information or a given state of knowledge is standard practice. The denominator, $P(D|I)$, can be difficult to calculate (or even to meaningfully define in some cases). One can avoid this difficulty by comparing beliefs in models to each other. For example,

$$\begin{aligned} \frac{P(M_1|D,I)}{P(M_2|D,I)} &= \frac{P(D|M_1,I)}{P(D|M_2,I)}\frac{P(D|I)}{P(D|I)}\frac{P(M_1|I)}{P(M_2|I)} \\ &= \frac{P(D|M_1,I)}{P(D|M_2,I)}\frac{P(M_1|I)}{P(M_2|I)}\,, \end{aligned} \tag{1.2}$$

where M_1 and M_2 represent different proposed models. The first factor after the equals sign, the ratio of the marginal likelihoods of the data, is "modifying" the ratio of the the prior belief in each model. This factor, which represents the way the data should influence one's relative confidence in the models, is called the *Bayes Factor*,

$$B_F = \frac{P(D|M_1,I)}{P(D|M_2,I)}\,. \tag{1.3}$$

Marginal Likelihood calculation

Obtaining the *Bayes factors* requires several steps of integration. The first will be to "marginalize out" the unobtainable "true" data $\hat{D}$,

$$P(D|M,I) = \int P(D|\hat{D},M,I)P(\hat{D}|M,I)d\hat{D}\,. \tag{1.4}$$

The expressions for the factors of the integrand are obtained by specifying the form of the experimental and model errors. Taking the errors for each of N points to be independent and normally distributed yields the product of Gaussian functions,

$$\begin{aligned} P(D|\hat{D},M,I) &= P(D|\hat{D},I) \\ &= \frac{1}{(2\pi)^N\prod\sigma_{E,i}}\exp\left[-\sum\frac{(D_i-\hat{D}_i)^2}{2\sigma_{E,i}^2}\right], \end{aligned} \tag{1.5}$$

$$P(\hat{D}|M,I) = \frac{1}{(2\pi)^N\prod\sigma_{M,i}}\exp\left[-\sum\frac{(y(x_i,\theta)-\hat{D}_i)^2}{2\sigma_{M,i}^2}\right], \tag{1.6}$$

where $y(x_i, \theta)$, $\sigma_{E,i}$, $\sigma_{M,i}$ represent the model prediction, experimental error, and model-form error at each point, respectively.

Next, dependence on the choices of specific parameter values must be integrated out. Until now, it has served to refer to a model of interest simply as "M", but now the model form, m, and particular values the parameters might take (including model error), θ, must be distinguished. Taking $M = \{m, \theta\}$ leads to

$$P(D|m, I) = \int P(D|m, \theta, I) P(\theta|m, I) d\theta \,. \tag{1.7}$$

To summarize, there are two marginalization steps. The first is to integrate out any dependence on the unobservable, "true" data. One is able to do this only after formally expressing beliefs about the experimental and model errors as probabilities. The second step is to integrate out the dependence on particular parameter values, which allows a stronger statement to be made about the model itself. This step requires the expression of prior beliefs for the values the parameters are expected to take and then uses beliefs to weigh the model's performance at every possible parameter value. A consequence, and feature, of this weighting is to "penalize" models for having many parameters and to mitigate this penalty when the priors for the parameters are narrow; narrow priors on the parameters likely result from them being physically meaningful.

Ultimately, the determination of a Bayes Factor requires the evaluation of the integrals

$$P(D|m, I) = \int \left[\int P(D|\hat{D}, I) P(\hat{D}|m, \theta, I) d\hat{D} \right] P(\theta|m, I) d\theta \,. \tag{1.8}$$

This integration is frequently difficult, as it is high-dimensional (# of model parameters + 1) and not analytically integrable for most problems of interest. Sampling methods have proved effective for estimating its value, but remain difficult to implement.

1.2.2 Quality criteria

Since calculating *Bayes factors* is frequently difficult or expensive, many alternatives have been proposed which aim to estimate the Bayes Factor

or otherwise balance the descriptive capability of a fit model against its complexity. Two such alternatives are the Bayesian Information Criterion and Adjusted R^2.

Bayesian Information Criterion

The Bayesian Information Criterion (BIC), first proposed by Schwarz [17], serves as an estimate of the Bayes Factor under certain conditions and may be calculated as,

$$BIC = N \ln\left(\frac{RSS}{N}\right) + K \ln(N) \ , \tag{1.9}$$

where N is the number of observed data points used in the fit and K is the number of free parameters in the fit model [18]. RSS is the Residual Sum of Squares

$$RSS = \sum \frac{(D_i - y(x_i, \theta))^2}{2w_i^2} \, . \tag{1.10}$$

Lower BIC values indicate a more credible model. With this in mind, the first term may be viewed as "rewarding" the model for its ability to closely reproduce the data while the second term "penalizes" the model for its number of parameters.

In addition to Schwarz's original derivation, others have offered derivations from a frequentist approach [6] as well as showing that the estimate should hold more generally than under the specific assumptions Schwarz used [19]. Other information criteria have also been proposed, such as AIC [20] and WAIC [21], although only BIC is considered here.

Some have criticized that BIC *cannot* be used as an approximation to a Bayes Factor due to its restrictive and potentially improper formulation of priors [22]. Complete Bayesian formulations of problems, with thoughtful priors and thorough reporting of a posterior distributions, will always provide more meaningful and valuable insight into the performance of models than any estimation or single point criterion for selection.

I believe that BIC has a place in rheological model selection despite these criticisms. The use of a consistent, quantitative method for balancing model complexity and goodness of fit, even a heuristic one, will improve the development and use of models by making the consideration itself explicit.

Adjusted R^2

The Coefficient of Determination, or R^2 value, is commonly used as a goodness-of-fit metric [23, 24, 25, 26, 27] and is often one of the metrics reported by fitting software packages [28, 29]. It can be understood as a normalization of the RSS value for a fit by the Total Sum of Squares (TSS):

$$TSS = \sum \left(D_i - \bar{D}\right)^2 , \tag{1.11}$$

$$R^2 = 1 - \frac{RSS}{TSS} , \tag{1.12}$$

where $\bar{D}$ is the mean of the observed data [30]. The primary benefit of this metric is that it can be easily interpreted, with values closer to unity indicating that the inadequacy of the model in describing the data is small when compared to the total variability of the data.

This metric has been further extended to account for model complexity in the form of Adjusted R^2,

$$R^2_{adj} = 1 - \frac{RSS/df_{Error}}{TSS/df_{Total}} , \tag{1.13}$$

where $df_{Total} = N - 1$ and $df_{Error} = N - K$ [30]. This criterion penalizes models for their number of parameters k, similar to the way BIC does, so that the value only improves (increases towards unity) if the improvement in the fit overcomes this penalty.

Of primary importance to a rheologist is the use of *any* metric which considers this balance between reproducing the data and limiting the number of fit parameters. With that in mind, BIC can still be recommended over R^2_{adj} on the basis that it can be used along with prior confidence in the models being compared and therefore encourages a Bayesian approach to selecting a model, even if the priors are determined to be uninformative. It may therefore be tempting to think of the R^2_{adj} as providing a more "objective" interpretation of the quality of a fit, but it and other metrics which neglect to acknowledge priors, are merely less explicit about which subjective choices have been made. One must be careful not to equate apparent objectivity with validity; although there is room for improvement in both of these standards within the rheological literature.

CHAPTER 2

ASSESSING MODEL FITTING IN RHEOLOGY

To determine the ways in which model selection techniques could be best employed in the field of rheology, an assessment of the use of models in the *Journal of Rheology* (*JoR*) was performed. For each of the 302 articles in the journal spanning the years 2016 to 2018, several questions were asked: Was a model fit to rheological data? What was the purpose of the model used? Is the method used to fit the model(s) reported? Were metrics related to the fit reported? Was the model used selected among several?

2.1 Classifying Rheological Models and Their Uses

For the purposes of determining whether or not a model was fit in a given paper, the presence of parameter estimation was used as the primary criteria. Thus a "model fit" is defined as use of an equation with parameters not determined *a priori*, whose values are then estimated to calibrate the model's ability to describe some data. In some cases a model is calibrated as part of a signal processing step [31, 32], where the data is not necessarily from a rheological measurement; these cases are still counted, as they represent an assumption about the structure of data relevant to to the measurements being made. Additionally, while "modeling" does not strictly necessitate the estimation of parameters [33, 34], attention was limited to cases where it was present as they represent the most straightforward opportunities for improvement in and expansion of methodology.

The purpose of a model being used in a paper was classified into three broad categories: *description*, *prediction*, and *inference*. *Description* is the simplest and most common use for a model, where its main advantage is that it can represent data or a phenomenon in a compact manner, useful for ordering or categorization of complex materials. *Prediction* is using a model

to try to anticipate a behavior or outcome outside of an experiment ("out of sample" prediction). The word "prediction" is employed frequently in papers which fit models to refer to the value of a model equation evaluated as a particular experimental point, compared to the values measured at the same point; this is not, for present purposes, considered a *prediction*. *Inference* is using a model, frequently through the interpretation of some physically relevant parameter(s), to understand physical features of the material, such as its structure. It should be noted that these categories are not mutually exclusive, although each paper was categorized into only one based on what appeared to be the predominant use of a model. *Description* is frequently present among other uses, and a paper given this label does not necessarily lack *prediction* or *inference*.

Determining methodology and reported metrics were based purely on what was explicitly provided or referenced in a paper and its supplementary material (where present). The level of detail given in reported methodology varied, from identifying what software was used [35, 36, 37, 38, 39, 40, 41] to providing an objective function and optimization method were used [42, 43, 44].

There are several degrees of model selection present in *JoR*, implicit and otherwise. Some models are presented almost without comment and are simply assumed to be relevant and meaningful as they are used. More often, the model used receives some sort of justification, either on a basis of physical understanding or experience that leads to an expectation that the model will be helpful. Additionally, a paper may list or provide examples of alternative models which are not employed, perhaps with a brief comment as to why. Finally, there are instances of explicit selection, where multiple models are employed and their usefulness is compared; the criteria used and the depth of the comparison varies. One common example, to be discussed later, is the selection of the number of modes for use in a multimode Maxwell model, in which a number is selected as "sufficient" without details given as to what criteria are being used.

While an attempt has been made to categorize the papers as accurately and consistently as possible, there is an inherent subjectivity involved in doing so. Additionally, there is a practical limitation to the level of nuanced understanding one can achieve of every paper assessed in a short period of time. With these caveats in mind, I believe that meaningful conclusions may be drawn from the trends observed in the application of these categories.

Furthermore, it is my hope that any disagreement over a categorization I have made prompts thoughtful discussion on the topic of how rheological models are employed.

2.2 Summary of Fitting in Journal of Rheology 2016-2018

Based on these criteria, it was determined that in the three years 2016, 2017, and 2018, of the 302 articles published in the *Journal of Rheology*, 215 (71%) employed some sort of model fit involving parameter estimation. This is taken as clear evidence that this practice holds substantial value within rheological research. It is for this reason that the further details of the assessment may be considered troubling.

Of those 215 papers which fit a model, 155 (72%) did not indicate what methodology they used to do so. Of the 60 that did, 23 were incomplete or vague in such a way as to make their fit difficult to reproduce, if not impossible. For any article in which a conclusion is drawn from the results of a fit, this omission should be viewed—at the very least—as a failure to adhere to the principle of reproducibility in research. Depending on the purpose to which the model is put, this lack of methodological detail may call into question the validity of the conclusions themselves.

From the same set of articles in which a model was fit, 175 neglected to make any sort of quantitative report of the quality of the fit or of uncertainty in the values of estimated parameters. A failure to report these values does not necessarily mean that the authors are misrepresenting their results; in fact in many cases it may be a missed opportunity to *strengthen* the quality of the conclusions drawn.

Not every use of a model necessitates or benefits as much from maximally careful and thorough application of model fitting and selection techniques, so it is important to contextualize the above observations with commentary on what use the models in these articles were put to. A summary of the categorization and inclusion of details relating to model fit and selection is presented in Figure 2.1.

A large majority of the articles with fits (73%) in *JoR* use models in a way that I classify as *descriptive*; this means the model is used primarily as

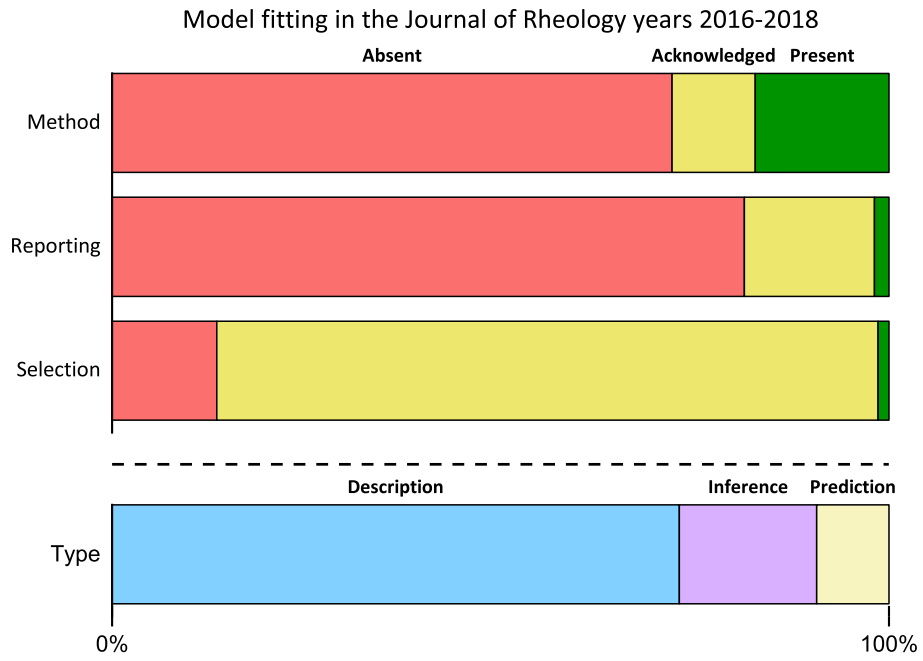


Figure 2.1: Summary of the 215 of the 302 articles appearing in *JoR* 2016-18, in which a fit was identified. The presence of stated methodology, reporting of fit results, and model selection are each labeled as either *Absent*, *Acknowledged*, or *Present*. *Absent* indicates that a method was not mentioned, no quantitative measure of fit quality was provided, or no reference was made to the process of selecting a model. *Acknowledged* indicates that a method or procedure was named or described, ether a measure of fit quality or parameter error was provided, or the process of selecting a model was mentioned but no comparisons were made. *Present* indicates that a method was described in sufficient detail to reproduce, both fit quality and error estimates were reported, or an explicit comparison is made between the performance of two or more candidate models. Additionally, the breakdown into which of the three purposes each model was identified as fitting into best is shown. See Table 2.1 (below) for numerical data used to make this figure.

a lower-dimensional description of the data, a sort of "data compression". In these cases it is permissible—if not ideal—to leave out much of the detail of the model fit and selection process. But if *any* additional conclusions are drawn or comparisons made from the results of these fits, such as an ordering of materials by some quantity of interest, then leaving out how the parameters and their uncertainties were estimated means that these descriptions, and any conclusions drawn from them, are incomplete.

Is a model fit?	Yes	215
	No	77
	Unsure	10
Purpose	Description	155
	Inference	39
	Prediction	21
Methodology	Method	38
	Vague	12
	Procedure	22
	None	154
Reporting	Both	4
	Error	28
	Quality	9
	None	174
Selection	Selection	4
	Justified	136
	Alternatives	47
	None	28

Table 2.1: Summary of the data used to generate the plot in Fig. 2.1 (above). See the caption of Fig. 2.1 for a description of each label.

The second-most common use for models in JoR that I identified was *inference* (18%); instances where the results of a model fit are used primarily to infer something unobserved, usually molecular features or material composition [11, 9, 10]. In these cases it should be considered absolutely imperative to—at the very least—justify the choice in model with some theoretical argument or understanding of what the model and its parameters represent. If there are multiple models considered that each represent a different hypothesis regarding the structure of the material then it becomes incumbent on the rheologist to do as much detailed model selection as is feasible or else risk the results of their work being rightfully regarded as meaningless. In instances where it is the value or values of a number of parameters which lead to the inference, then reporting how the value was estimated and the error associated with it should be considered necessary.

Lastly, the least common use to which models were put in *JoR* was *prediction* (9%); the use of a model to predict behavior in a circumstance other than that created in the experiment. Although this is frequently stated as a goal for the development of a model, their use in this way does not appear often. This is understood to be a product of the current focus of the journal

on rheological complexity rather than flow prediction as opposed to an indication that prediction is not of interest in rheology, as its significance has been described elsewhere [8].

2.3 Noteworthy Cases

Categorization and summary are often at odds with nuanced understanding; in order to gain additional insight from this survey of *JoR* several articles and their use of models will be discussed in greater detail. By examining these articles more closely, examples of both good practices and opportunities for improvement will be highlighted.

2.3.1 Multimode Maxwell Model

Fitting a multimode Maxwell model to data was among the most common uses of model fitting and was the primary illustrative example used by Freund and Ewoldt in their 2015 article demonstrating the application of quantitative model selection in the same journal [4]. Wang et al. follow in the same spirit, citing Winter and coworkers [45, 46], in their use of criteria to "best fit the data with the minimum number of modes" or "converge to a 'parsimonious spectrum'" [47]. In doing so, they provide the objective function used for optimization and reference to the code that was used but neglect to provide quantitative results for the value of a selection criterion or uncertainty. As the purpose of the models in this work was determined to be largely *descriptive*, relating the behavior of hydrogen-bonded polymer complexes to observed structure parameters, this level of detail is appropriate.

When models are being used to *infer* structural parameters from rheological data, the standard for the level of detail provided is much higher. Du et al. observe a "large deviation" from a single Maxwell mode in their work and theorize that this is due to the coexistence of both *trans*- and *cis*-form of a model polymer in solution [10]. They attempt to confirm this by a fitting a generalized Maxwell model with two modes and conclude that their hypothesis is correct because the two mode model fits "much better" and is consistent with the presence of two isomers [10]. They fail to describe their fitting methodology in any detail, to report any quantitative measure of the

quality of the fits, or even comment on the fact that a model with more modes will always better reproduce the data. The absence of these features in their work dramatically limits the strength of the conclusion drawn from the data and fit versus what could be argued if they offered a quantitative statistic like BIC.

Similarly lax treatment of the selection of a number of modes is seen in the work of Dessi et al. who use a multimode Maxwell model in their finite element analysis to "perform a parametric study of the effects of the aspect ratio in the cross-sectional stress distribution and the linear viscoelastic torsional response [of industrial rubbers]" [48]. To this end, they do not appear to require a model that relates to a particular material structure, just one that captures the material response under the conditions of interest. A process of fitting the model with progressively more modes until "sufficient accuracy" is described [48]. While a more detailed description of the methodology would be preferable and lend itself better to reproducibility, it does not appear to have significant bearing on the results. If a model is being employed in this way, than this treatment of selection may be considered adequate, if not ideal.

2.3.2 Other Examples

An exceptional level of detail in describing fitting methodology is found in the work of Horner, Armstrong, Wagner, and Beris; who formulate, fit, and compare to others a thixotropic and viscoelastic model to dynamic rheological data of human blood [44]. To this end they use a multiparameter global optimization method based on that which was proposed in the earlier work of Armstrong et al. [49]. The objective function used in the optimization is provided and the method for determining error in the parameter estimation is explained. First and foremost, this paper should be lauded as an example of the level of detail and thought to give to the process of fitting rheological models. With that in mind, there are several ways in which it could be improved.

Within this thesis the models presented are being evaluated primarily on their ability to reproduce data, and thus I have counted this article as being primarily concerned with *description*. The authors also discuss the opportu-

nity that may exist to use rheological characterization of blood as a method of identifying medical conditions [44], which is *descriptive* in the sense that it categorizes behavior. For the purpose of comparing models' ability to reproduce data, reporting a quality of fit metric would have strengthened these comparisons by quantifying the improvement; which could also be weighed against increasing number of parameters in the proposed model (perhaps with a metric that penalizes them, such as BIC [17]). The authors also give attention to the value of the error in the parameter estimates and how they may be interpreted. The conclusions that may be drawn from the error values are limited by the fact that they are based on single point value estimate for the parameters; a more complete view of the uncertainty in these values may be obtained by looking at their full, calculated or sampled distribution [50, 22]. Although some reframing of the problem with priors may be necessary to obtain the proper distribution, it is possible that the more difficult numerical work can be achieved through some modification to the optimization algorithm [49], which already employs many of the techniques to have been found useful for sampling posterior distributions and evaluating Eqn. 1.8 [5].

The difficulty of implementing these methods having been remarked upon, it is worth considering what improvements can still be made when using them is not deemed practical or worthwhile. Lang uses model fits to *infer* molecular mass distributions (MMD) in polymer melts; they report that they used the Levenberg–Marquardt algorithm and compare error in their calculated MMD to that determined by other methods [51]. By evaluating a model's performance in precisely the way it is proposed to be used, Lang avoids the use of more abstract methods of comparison. Still, more details such as the objective function used in the fitting process and some measure of the quality of the fit would aid other rheologists who wish to reproduce or reapply this work.

Evaluation of the performance of a model does not always eliminate the need for thoughtful comparison; sometimes the differences in performance need further contextualization. Varchanis et al. [52] compare two tube-theory based constitutive models in their ability to describe and *predict* simple and complex flows of entangled linear polymeric liquids, stating that "An ideal model... should be able to predict the actual properties of such materials, have the minimum possible number of material parameters, and be computa-

tionally manageable in complex flows". Despite this statement and a direct comparison of the models' abilities to predict flow with experiments, no direct treatment is given to the problem of limiting the number of material parameters; modes are added to the models until some nebulous sufficiency criterion is achieved.

Even in the cases of *inference*, where standards should be higher, small additions can be a significant improvement. In the work of Zhang et al., compatible bilayer systems are investigated in a manner typical throughout the paper surveyed; a variety of rheological experiments are performed on a model material system and models to describe the observed behavior are proposed [53]. This particular example has been categorized as *inference* due to its reported ability to determine an unobserved property of the system, the tube diameter. This value was determined by fitting a model to data with a "finite difference Levenberg-Marquardt routine"; a correlation coefficient was reported and plots of the model curve and the data shown; alternative models for describing this data were also discussed, particularly that they were inadequate for describing "certain experimental observations" [53]. The model proposed in this work is therefore presented as improved both in its ability to better describe certain observations and also its capacity to estimate a physical quantity of interest. Providing even rudimentary estimates of parameter uncertainty and its impact on the inference of physical values would provide a basis for comparison against other methods, more firmly establishing its value in rheological analysis of materials and their composition.

2.4 Best Practices

Having evaluated several particular articles, identified their strengths and areas of potential improvement, these comments and suggestions can be generalized into a set of best practices to apply when fitting models to rheological data. There is no one-size-fits-all recipe for model fitting and selection, but by following some general guidelines one can achieve a standard of clarity, reproducibility, and significance that meets or surpasses the current state of the rheological literature.

1. Identify purpose

The first step should always be to consider for what purpose a model is being used. The categories laid out in this thesis are not the only—or likely even the best—way to frame this question, but they serve as a practical place to start. What can be said, made clearer, or achieved only after a model is calibrated to the data? The answer to this question is precisely that which the rheologist must strive to express with the utmost clarity.

2. Determine what features to report

Perhaps the simplest way to add clarity, and one that many papers published in the *Journal of Rheology* still fail to achieve, is to report what method was used to estimate the model parameters. Regardless of what method was chosen and how, reporting it in sufficient detail to reproduce the estimates (algorithm, objective function, priors, code, etc.) will always make one's results clearer. Even in cases where a "fit by eye" was performed, where the parameter values were manually adjusted until the fit "looks good", one should report so and comment on what qualitative criteria were considered when deciding that the fit was sufficient. This will highlight what features in the data were considered significant to the work and communicate the relative unimportance of precise values.

In cases where precision is a matter of greater importance it follows that one should quantitatively report the quality of any fits performed and uncertainty in estimated values. Quality of fit metrics, such as residual sum of squares and coefficient of determination, are important when one's primary interest is in how closely a model can describe data; especially when comparing models. No matter how a model was fit or how closely it reproduces the data, parameters and other quantities of interest estimated from a fit will have some error or uncertainty associated with them. Some software and fitting packages will yield an estimate of parameter uncertainty; which should be remarked upon when it is the only value available. Further consideration of sources of experimental error, simplifying assumptions, and inherent model inaccuracy in a particular analysis can lead to an improved estimate of uncertainty; as the assumptions used in fitting software are not universally applicable.

3. Consider basis for selection

It is because all models are—to some degree—inaccurate that the choice of a model cannot be based entirely on which can fit the data the most closely. Selection of models based solely on this criterion will inevitably favor models with more parameters, but not necessarily those which are most useful. It is therefore necessary to apply additional consideration to determine which model(s) to use. As above, a rheologist is left to decide exactly what methodology and criteria to apply to make this determination. It is the position of this thesis, and others [16, 12, 5, 4], that Bayesian inference methods are a consistent, practical, and flexible approach to this end. Yet the implementation of these methods remains intimidating, and beyond the scope of many works, so a case study examining and comparing this approach with others will follow.

CHAPTER 3

USING MODEL SELECTION IN RHEOLOGY

Having performed an assessment of the state of model selection in rheology and outlined a general set of best practices, two case studies demonstrating methodology for fitting and selecting a rheological model shall be presented. Rather than explore the numerous potential applications for rheological models that require fits, which each require their own specialized considerations as discussed above, simple illustrative examples using easily calculated fit statistics will be performed. Two classes of models are considered: one which describes steady shear and one which describes thixotropy and steady shear, each calibrated to a corresponding model material. In order to compare the performance and credibility of the models within each class, RSS and BIC are calculated and their uses and limitations are discussed. In doing so, these practices that are relevant and accessible to the widest number of rheologists are demonstrated and discussed.

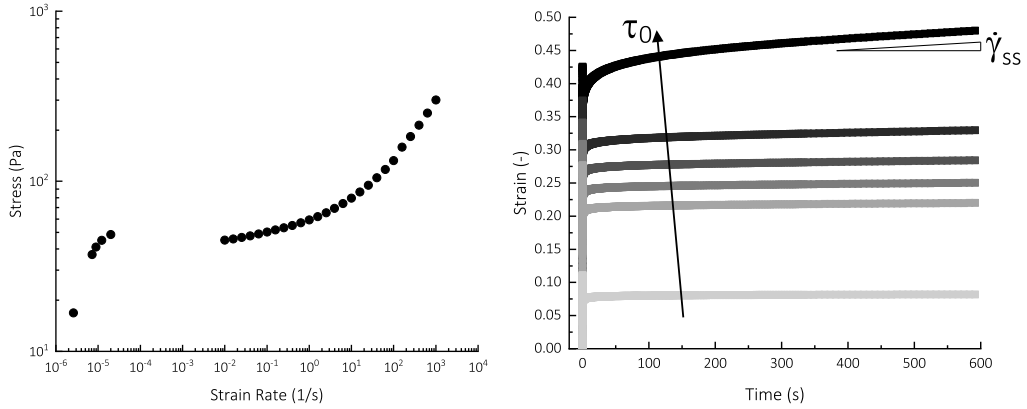
3.1 Materials and Methods

3.1.1 Shear-thinning material: Carbopol

Carbopol is a commonly used model complex fluid, known to exhibit a yield stress at sufficiently high concentrations [54]. It is an aqueous suspension of microgel particles which swell in the water environment, capable of forming a jammed system which creates the aforementioned yield stress. An aqueous solution of 0.2 wt.% Carbopol 940 was both prepared in the manner of Blackwell et al. [55] and characterized as described below by Piyush Singh and Scott Rogman.

Rheological characterization was performed on a TA Instruments AR-G2 rotational rheometer using a parallel-plate geometry held at 25 degrees Cel-

sius. Experimental protocols included a steady flow sweep from 0.01 to 1000 s^{-1} and creep tests performed to probe low stress behavior. A solvent trap was utilized to prevent evaporation during the creep tests, which spanned a longer period of time. Corrections were applied to apparent shear stress to account for the non-uniform strain rate present in parallel plate geometry [1] for both the steady flow and creep data; the corrected data is plotted in Figure 3.1.



(a) Steady flow experiments (b) Creep experiments

Figure 3.1: Data collected for carbopol 940. Steady shear data is shown in (a), the 6 lowest strain-rate points were determined form creep tests shown in (b) by estimating a constant shear rate at long times.

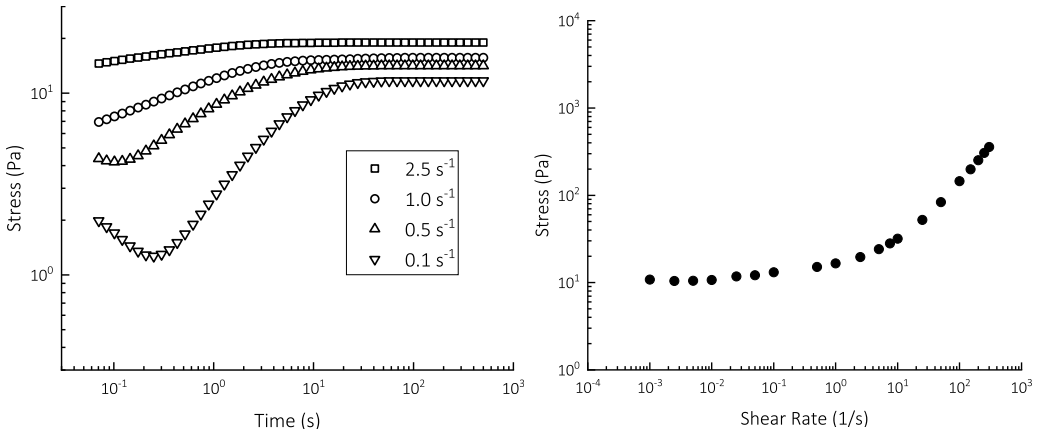
Ten empirical constitutive models developed for describing shear-thinning and yield stress behavior were fit and considered for selection. Five of the models are traditional yield stress models frequently employed in rheological literature [56, 57, 58, 59, 60]. These models all exhibit diverging viscosity at low shear rates, a feature that poses potential difficulty in numerical simulations using these models and which has received criticism on theoretical grounds [1]. Models have been proposed which avoid this problem either through the regularization of the viscosity function or new model forms altogether; three such models are also fit to the data [61, 62, 63]. Additionally, two novel model forms are introduced to further illustrate considerations that go into model fitting and selection. These "naive expansion models" are formed simply by adding additional terms to the 1-D forms of existing models as,

$$\tau = \tau_m[\dot{\gamma};\theta] + \sum A_n \dot{\gamma}^{1/2^N} \,. \tag{3.1}$$

The coefficient of each additional term is treated as a free parameter to be estimated along with the others in the model and it is known *a priori* that each additional term will either improve or not affect the ability of the model to describe the data. All of the models fit in this section are summarized in Table 3.1.

3.1.2 Thixotropic material: Fumed Silica Suspension

A dispersion of fumed silica particles (2.9 vol.%) in a mixture of paraffin oil (69 wt.%) and poly(isobutylene) (PIB) (31 wt.%) was developed by Dullaret and Mewis as a model thixotropic material [64]. The material exhibits (a tunable) thixotropy due to the build-up and break-down of flocs of colloidal particles as well as an apparent yield stress [64]. This material was reformulated and characterized for the purpose of testing constitutive models by Armstrong et al.; steady shear data and transient step-down data are taken from the supplementary material of that work and used to fit candidate models models [65].



(a) Step down experiments

(b) Steady flow experiments

Figure 3.2: Thixotropic data for fumed silica suspension from supplementary material of Armstrong et al. [65]. (a) shows step down tests from 5.0 s^{-1} to values indicated in legend. b) shows steady shear flow.

Three thixotropic constitutive models are fit to this data; all of the "structural kinetics" variety as described by Mewis and Wagner [66]. They share a common rate equation which describes the evolution of a structure parameter $\lambda(t)$ and are summarized in Table 3.2. [67, 68, 69]. These models were

Models		
Name	**Equation**	**# Parameters**
Yield stress models		
Bingham (1916)	$\tau = \tau_y + \eta_\infty \dot{\gamma}$	2
Herschel-Bulkley (1926)	$\tau = \tau_y + k\dot{\gamma}^n = \tau_y(1 + (\dot{\gamma}/\dot{\gamma}^*)^n)$	3
Casson (1959)	$\tau = (\sqrt{\tau_y} + \sqrt{\eta_p \dot{\gamma}})^2$	2
Generalized Casson (1975)	$\tau = (\sqrt{\tau_y} + k\dot{\gamma}^n)^{(1/n)}$	3
Shulman (1978)	$\tau = (\tau_y^{1/n} + (\eta_p \dot{\gamma})^{1/n})^n$	3
Regularized Models		
Cross (1965)	$\tau = \dot{\gamma}(\frac{\eta_0 - \eta_\infty}{1+(k\dot{\gamma})^{1-n}} + \eta_\infty)$	4
Carreau-Yasuda (1972)	$\tau = \dot{\gamma}((\eta_0 - \eta_\infty)(1 + (k\dot{\gamma})^a)^{\frac{n-1}{a}} + \eta_\infty)$	5
Papanastasiou's Regularization of Herschel-Bulkley (1987)	$\tau = \tau_0(1 - e^{-m\dot{\gamma}}) + k\dot{\gamma}^n$	4
Naive Expansion Models		
NBingham	$\tau = \tau_y + A_0\dot{\gamma} + A_1\dot{\gamma}^{1/2} + A_2\dot{\gamma}^{1/4} + ... + A_N\dot{\gamma}^{1/2^N}$	N+2
NPHB	$\tau = \tau_0(1 - e^{-m\dot{\gamma}}) + k\dot{\gamma}^n + A_0\dot{\gamma} + A_1\dot{\gamma}^{1/2} + ... + A_N\dot{\gamma}^{1/2^N}$	N+4

Table 3.1: Shear-thinning models fit in this thesis. Three categories of model are considered, yield stress models, regularized models, and naive expansion model constructed to investigate behavior of fit statistics. The number of parameters in the standard models range from 2 to 5; the expanded models are fit with up to 11 parameters.

chosen for their relative simplicity, commonality, and use as bases for the development for more complex models.

Model	Form	Yield stress?	# Parameters
Rate equation: $\frac{d\lambda}{dt} = -k_1(\lambda)\dot{\gamma} + k_2(1-\lambda)$			
Moore (1959)	$\tau = \eta_0\dot{\gamma} + \eta_\lambda(\lambda)\dot{\gamma}$	None	4
Worrall (1964)	$\tau = \eta_0\dot{\gamma} + \eta_\lambda(\lambda)\dot{\gamma} + \tau_y$	Constant	5
Toorman (1997)	$\tau = \eta_0\dot{\gamma} + \eta_\lambda(\lambda)\dot{\gamma} + \tau_y(\lambda)$	Structural	5

Table 3.2: Structural kinetics thixotropic models fit in this thesis. Each model uses the same rate equation, but vary in inclusion of yield stress.

3.1.3 Fitting and Selection

The candidate constitutive models were fit to the data using the `lmfit` package for Python [29]. The Levenberg-Marquardt method is used by the software to minimize the objective functions (defined below). The minimization was performed repeatedly from many different initial parameter values ($N = 10000$) generated from Latin Hypercube Sampling (LHS) to verify that a global minimum was found. This method for finding the global minimum is relatively unsophisticated, but the results did not indicate the presence of many local minima in the objective function over a wide range of parameter initializations and were thus interpreted as sufficient.

Additional consideration was necessary to fit models to the thixotropy data (Sec. 3.1.2) due the inclusion of data taken from multiple experiments of different types and under different experimental conditions; each requiring the evaluation of a different form of the candidate constitutive equation. Most standard fitting packages do not support fitting a single model to multiple sets of data with these requirements and it is common practice within rheological literature to fit differing model forms to subsets of the data in order to estimate the model parameters *sequentially*. The parameter estimates in this thesis are obtained by fitting the model to all of the available data *simultaneously*; a method that is more consistent with the statistical assumptions presented below and which is more permissive of sampling as discussed in Appendix A.

The objective function used in the minimization is defined as

$$RSS = \sum_{i=1}^{N} \frac{(\tau_m[\dot{\gamma}_i, t_i; \theta] - \tau_i)^2}{\tau_i^2}, \tag{3.2}$$

where τ_i is the measured stress value and τ_m is the model evaluation; this

is the residual sum of squares with the value of the data point chosen as the weighting. This weighting function is frequently employed in rheology to avoid artificially weighting data with greater absolute value in experiments where the numerical measurements for a given observed quantity range over one or more orders of magnitude [70, 71].

This choice of residual is consistent with the assumption that the experimental error for each data point is independent and Gaussian, the associated uncertainty is constant relative to the scale of the data, and that there is no model error (the model represents the underlying data-generating process, or "truth", exactly). These assumptions may be represented mathematically as

$$\begin{aligned} \tau_i &= \tau_{true,i} + \epsilon_i \,, & (3.3) \\ \tau_{true,i} &= \tau_m[\tau_i, t_i; \theta] \,, & (3.4) \\ \epsilon_i &= \text{NormDist}[0, \tau_i^2] = \mathcal{N}[0, \tau_i^2] \,. & (3.5) \end{aligned}$$

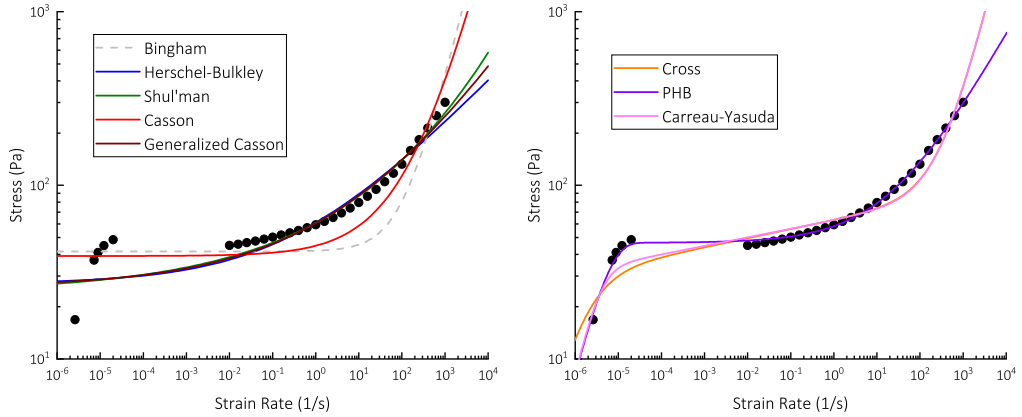
Under the above assumptions, the least-squares problem of minimizing Equation 3.2 and the maximum likelihood estimate (a more purely statistics-based single-point method of parameter estimate, "MLE") are equivalent [6, 71]; both of which may be justified through a Bayesian approach with the additional assumption that the prior for the parameter values is uniform (constant) [12]. This choice is not unique or usually even the best justified; Sing et al. have demonstrated that estimating data uncertainty as in Equation 3.5 is not, in general, valid [71]. Even so, this approach to parameter estimation remains among the most used in rheological studies and is convenient, so it will be used in this study. The results will be examined in light of what has been discussed, their limitations, and possible next steps.

3.2 Results

3.2.1 Shear-thinning models

The standard shear-thinning models evaluated with the parameters from the fitting procedure described above are plotted, along with the data used in the fit, in Figure 3.3. Among the yield stress models, it is not obvious which is the best fit just by looking at the plot. The Bingham and Casson models

perform well at the low shear rate data, but the other models appear to better describe the data at higher shear rates. Among the regularized models, Papanastasiou's regularization of the Herschel-Bulkley (PHB) model clearly adheres to the data far better than the other models. With that exception, it is otherwise difficult to compare the quality of fit of these models "by eye".



(a) Yield Stress Models (b) Regularized Models

Figure 3.3: Comparison of the standard shear-thinning models with best fit values for Carbopol data.

Yield stress models									
Bingham		Herschel-Bulkley		Casson		Generalized Casson		Shulman	
σ_y	41.6 $\pm$3.73	σ_y	27.1 $\pm$3.07	σ_y	39.2 $\pm$2.97	σ_y	25.93 $\pm$3.20	σ_y	24.2 $\pm$3.58
η_∞	0.39 $\pm$0.08	k	33.9 $\pm$5.11	η_p	0.19 $\pm$0.04	K	2.69 $\pm$0.42	η_p	1.3×10^{-4} $\pm 2.9 \times 10^{-4}$
-		n	0.26 $\pm$0.03	-		n	0.20 $\pm$0.03	n	6.46 $\pm$1.11

Table 3.3: Parameter values for yield stress models determined from least-squares fit. Error estimates are the standard error values calculated from the covariance matrix.

The fit statistics (Table 3.5) offer additional clarity and insight. Unsurprisingly, the PHB model has the lowest RSS value, confirming what was easily seen in the plots. In terms of RSS values, Bingham and Casson models were outperformed by the other yield stress models and for this data the regularized models performed better overall. The BIC metric estimates model credibility, penalizing over-parameterization (see Sec. 1.2.2). BIC values

Regularized models					
Cross		Carreau-Yasuda		Papanastasiou	
η_0	2.24×10^7 $\pm 1.11 \times 10^7$	η_0	8.48×10^6 $\pm 1.69 \times 10^6$	σ_0	46.6 ± 0.75
η_∞	0.28 ± 0.04	η_∞	0.28 ± 0.03	m	1.91×10^5 $\pm 8.87 \times 10^3$
k	7.16×10^5 $\pm 4.64 \times 10^7$	k	2.48×10^5 $\pm 6.78 \times 10^4$	k	11.6 ± 0.82
n	0.05 ± 0.01	n	0.5 ± 0.009	n	0.45 ± 0.01

Table 3.4: Parameter values for regularized models determined from least-squares fit. Error estimates are the standard error values calculated from the covariance matrix.

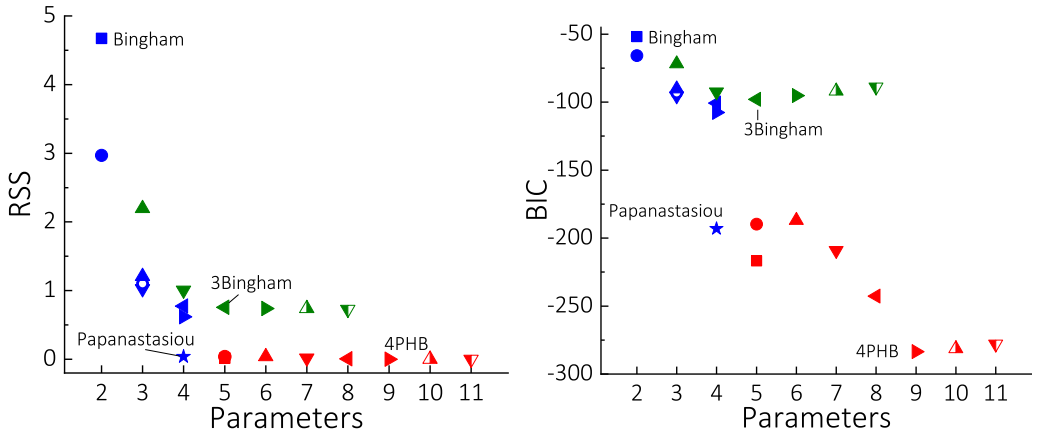
suggest that among these models for this data, an additional parameter is always "worth it"; the penalty incurred by the additional parameter is always outweighed by the improved quality of the fit. That is, the best (lowest) BIC is for the PHB model with 4 parameters.

Fit Statistics			
Model	RSS	BIC	# Parameters
Bingham	4.67	-52	2
Casson	2.97	-66	2
Herschel-Bulkley	1.21	-90	3
Generalized Casson	1.10	-93	3
Shul'man	1.03	-95	3
Cross	0.773	-100	4
Carreau	0.617	-107	4
Papanastasiou	0.0394	-193	4

Table 3.5: Fit statistics for the standard models fit to Carbopol data. Note that BIC decreases (improves) monotonically with decreasing (improving) RSS. By both criteria, Papanastasiou's Regularization of the Herschel-Bulkley model is preferred.

This raises the question: under what set of circumstances will BIC indicate that an additional parameter is *not* justified? This question is what motivated the application of naive expansion models. Additional terms were added to both the Bingham (the simplest) and the PHB (best fitting) models. The results are summarized in Figure 3.4 along with those from the standard models fit.

As additional terms, and therefore parameters, are added to each model, the closeness of the fits achieved are—unsurprisingly—improved. Eventually this improvement saturated as the additional terms offer no improvement to the fit. Once 4 additional terms are added to the Bingham model and 5 terms are added to the PHB model in this way, the penalty imposed by BIC finally overcame the marginal improvement. And thus, it is the PHB model with 5 additional terms (4PHB) that is ultimately suggested by the fit statistics (RSS= 1.22×10^{-3} and BIC= -283) and therefore the best justified according to the criteria used here. Observe the excellent fit of this model compared to the standard PHB in Figure 3.5.



(a) Residual comparison

(b) BIC comparison

Figure 3.4: Graphical comparison of fit statistics for fit models. The standard rheological models fit are represented by blue symbols. The "naive expansions" to the Bingham (NBingham) and Papanastasiou's Regularization of Herschel-Bulkley (NPHB) models are represented by green and red symbols, respectively. Notable models are labeled for convenience.

3.2.2 Thixotropy models

The thixotropy models, fit simultaneously to the step-down and steady shear experiments, are plotted in Figure 3.6. As before, The difference in model performance in difficult to discern visually, but there are several notable features that may be commented on. The fit statistics (Table 3.7) offer more clarity than the graphical representation and suggest that the Worrall model is the best fit *and* most credible.

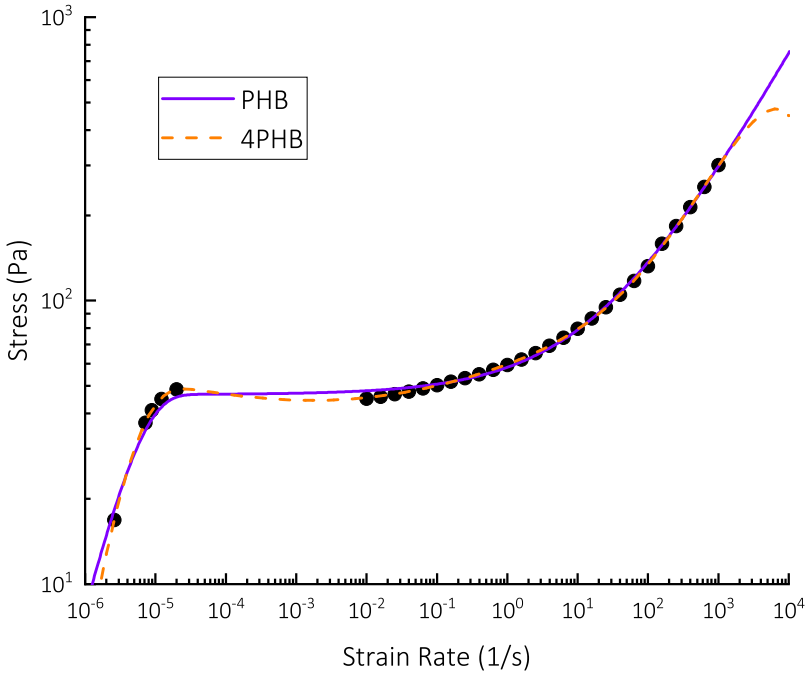
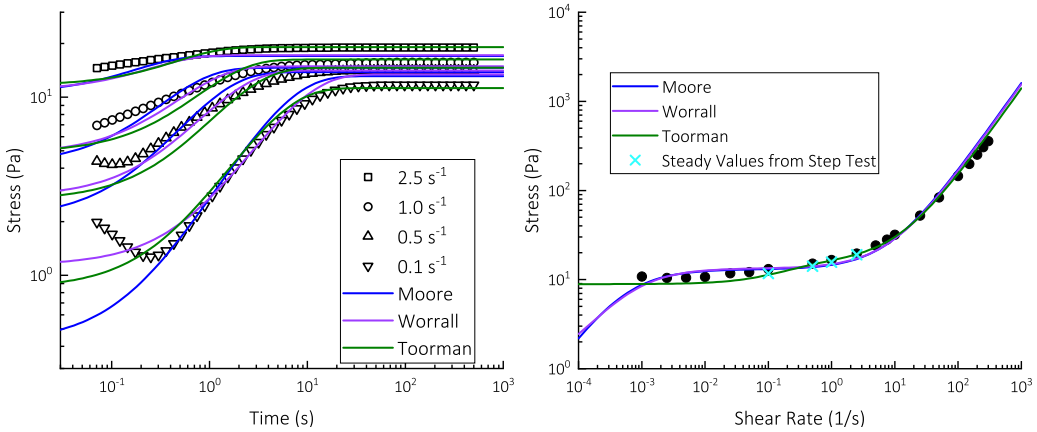


Figure 3.5: Behold the 4PHB; 9 parameters and preferred according to BIC. Nonmonotonic behavior is observed both within the range of available data and at high shear rates.

The Moore and Worrall models predict similar low shear rate behavior, due to the the yield stress value in the Worrall model being estimated as so low as to be unobservable in this range of shear rates; likely due to the simultaneous fit "forcing" the yield stress to be low in order to accommodate the step-down data. While this might be viewed as a drawback of simultaneous fitting, sequential fitting is only an *ad hoc* solution; at best loosely justified by a concept of differing sensitivity to certain parameter values. Some alternatives which follow more consistent reasoning include modified objective functions (which may weight the steady data more, justified through assumptions regarding model or experimental error) and sampling methods (which would reveal a wider range of yield stress values than the much "choosier" single-point maximum likelihood or least-squares estimates, see Appendix A).

At high, steady shear rates, the three models appear to be in close agreement. This can be seen as well in the values estimated for η_0 for each of the models (Table 3.6). Due to the structural similarities of the models, they predict similar, Newtonian-like behavior at high shear rates, when the

structure of the material is completely broken down ($\lambda \to 0$).



(a) Fits to step-down data

(b) Fits to steady data

Figure 3.6: Comparison of thixotropy with best fit values for fumed silica suspension data, determined by a simultaneous fit to all the available data.

Thixotropy models					
Moore		Worrall		Toorman	
η_0	1.59 ± 0.07	η_0	1.54 ± 0.05	η_0	1.38 ± 0.06
η_t	$2.60 \times 10^4 \pm 1.15 \times 10^4$	η_t	$1.97 \times 10^4 \pm 6.16 \times 10^3$	η_t	70.4 ± 6.15
$k1$	1.97 ± 0.09	$k1$	1.36 ± 0.07	$k1$	0.67 ± 0.05
$k2$	$9.88 \times 10^{-4} \pm 4.39 \times 10^{-4}$	$k2$	$8.72 \times 10^{-4} \pm 2.74 \times 10^{-4}$	$k2$	$0.16 \pm 8.67 \times 10^{-3}$
-	- -	τ_y	0.73 ± 0.06	τ_y	8.89 ± 0.32

Table 3.6: Parameter values for thixotropy models determined from least-squares fit. Error estimates are the standard error values calculated from the covariance matrix.

3.3 Case Study Conclusions and Outlook

Despite its excellent agreement with the data, there is little expectation that the 4PHB model is going to see widespread adoption throughout the rheological community, even for purely descriptive purposes. Even though it

Fit Statistics		
Model	RSS	BIC
Moore	4.79	−820
Worrall	2.77	−935
Toorman	2.98	−920

Table 3.7: Fit statistics for the models fit to fumed silica suspension data. By both criteria, the Worrall model is preferred.

appears to be "justified" by the analysis above, little consideration was given to the purpose the model would be used for. Clearly, the 4PHB model offers virtually no *inferential* value, as its parameters are the result of a naively motivated expansion of an already empirical model and offer no special insight into the structure or behavior of the material. It may perform adequately in a *predictive* capacity under certain conditions, as it smoothly passes through much of the data; although the non-monotonicity between the steady shear and creep data and at shear rates above those seen in the experiment should give a would-be simulator pause.

Even as a purely *descriptive* model, which may be considered those with the loosest standards for model selection (See Sec. 1.1.1), the 4PHB model leaves much to be desired. While the BIC value has indicated that the model's 9 parameters are not enough to outweigh its excellent fit, a rheologist wishing to summarize their data may still prefer the standard PHB model, or even the cruder and more compact Bingham model due to its low dimensionality. In many works, what is of primary concern to a rheologist is the yield stress of a material [43, 72] and it is determining and communicating this value that is most important. In such cases, one may not even wish to include the creep data in the fit, as it does not increase accuracy of the fit value of yield stress. This concern could be dealt with more rigorously by including a form for the model error other than what is presented here (ie. yield stress models have large error at low shear rates).

Ultimately, the scope of the thixotropic models considered in the thixotropy case study is too narrow to have revealed much insight into the applicability of these fit statistics. Additional models, both with more parameters and differing forms must be compared in order to begin to see where these single-value statistics may perform well or poorly (consider integral approaches as discussed by Mewis and Wagner [66], stretched exponential methods proposed

by Wei, Soloman, and Larson [73], the Delaware model [74], or Armstrong et al.'s extension of the Delaware model [65]).

The RSS and BIC fit statistics are fundamentally limited in their ability to guide model selection, but this should *not* be taken to mean that they are without value (the analysis Appendix A is consistent with the BIC in the examined instance). These quantitative measures provide a much-needed basis for the comparison of different models and belong in any discussion pertaining to model selection. What they do not provide is a replacement for common sense, experience, and thoughtful consideration of the applications at hand. More complex methods of Bayesian inference allow for the codification of such subjective, yet useful, information into quantitative priors. For example, the knowledge that the naive expansions of PHB predict non-monotonic behavior that is inconsistent with rheologists' experience with similar materials might be expressed in a prior credibility that is 100 times lower than the more traditional model(s); the naive expansion models would then need to perform significantly better in reproducing the data to overcome this preference. Furthermore, a rheologist is unlikely to assign a narrow prior range to the value of the parameters that are added in the naive expansions; these broad priors will lead to a greater penalty in the full Bayesian analysis. There remains great opportunity in applying these methods to rheological model selection.

CHAPTER 4

CONCLUSION

4.1 Is it really worth the trouble?

If anything has been learned through the work of this thesis it is that the problem of model selection in rheology belies a single, prescriptive solution. The formulation and subsequent evaluation of the "full" Bayesian evidence integral of Equation 1.8 may be theoretically sound for the purposes of selecting a model, but it is difficult to recommend—especially within a community that still struggles to frame model selection problems as such. Though, the tone adopted here should not be interpreted as defeatist. In fact, the complexity of this problem may be viewed optimistically; the number of ways in which a rheological study may be improved by the use of even rudimentary model selection techniques are many, one must simply choose to consider them.

In Sec. 1.1, a framework for understanding the purpose of rheological models was presented and in Sec. 2.2 the ways in which modeling for these purposes may be improved or strengthened through thoughtful selection. It is vital to consider the purpose to which a model is being set to when deciding whether or not and what types of selection techniques are warranted. Generally speaking, selection is minimally important for *description*, moderately important for *prediction*, and maximally important for *inference*; but specific cases always need be examined in order to determine what is most helpful.

4.2 Future Work

There exist many opportunities for continuation and expansion of the work that has been presented here. First and foremost, the exploration of the ways in which the evaluation of the integral Eqn. 1.8 may guide and inform model selection. While this method may not be viable for many or even most cases in rheology, it holds an important position as a metric against which to test other, simpler techniques such as BIC; a more thorough case study comparing their performance is certainly warranted. The relatively simple—in form—shear-thinning models studied in Sec. 3.1.1 are ripe for beginning this work, as their evaluation should not pose any significant hurdles to sampling techniques; especially due to the the availability of existing software for this purpose (see Appendix A). The models of thixotropy, such as those in Sec. 3.1.2 and others, on the other hand, may pose a more significant challenge as their evaluation becomes more difficult. Still, the work of Freund and Ewoldt demonstrates that this technique is not limited to models of the simplest form or fewest parameters [4]. Another way to expand on this and the work of Freund and Ewoldt would be to explore the ways in which choices of the form of model error and priors affect selection.

Additionally, the categorization framework presented in Sec. 1.1—or something like it—should be used as the basis for an ongoing discussion among rheologists about the purpose of the models they are fitting. Further review and reflection of the work that has been done in the field should inform the progression of the state of the art. The *Best Practices* of Sec. 2.2 are extremely general, and should be refined into more detailed and instructive guiding principles for specific applications within rheology. Ultimately, it is only through an enhanced understanding of models' purposes *and* the implementation of thoughtful selection techniques that a rheologist will add significant value to their work

APPENDIX A

PTMCMC SAMPLING

To begin to asses the applicability and relative difficulty of evaluating the integral in Equation 1.8, the assumptions of Equations 3.3-3.5 are made for the Bingham ($\mathcal{B}$) and Herschel-Bulkey ($\mathcal{H}$) models fit to the carbopol data presented in Sec. 3.1.1. Additionally, proper, uniform (linear) priors on the parameter values are given by

$$P(\theta|I) = \frac{1}{\theta_M - \theta_m}\,, \tag{A.1}$$

where θ_M and θ_m are upper and lower bounds, respectively, on the values for a given parameter θ. This form of prior is not necessarily most-reflective of a state of ignorance (see references to "Jeffreys Prior" for scale parameters in other works [12, 4]), but it remains consistent with the least-squares estimate assumptions of Sec. 3.1.3 and is therefore used for the sake of comparison. For all the parameters considered in these models, the minimum value given nonzero credibility is 0. The maximum values are summarized in Table A.1.

The software package used for this sampling, `ptemcee` [75] (a fork of the Python package `emcee` [76]), takes as input the natural logarithm of the *likelihood* for a model given the data and the natural logarithm of the *prior* for each of the parameters. They are provided as

$$C = -\frac{N\ln[2\pi]}{2} - \sum_{i=1}^{N} \ln[\tau_i^2]\,, \tag{A.2}$$

$$\ln[P(D|\eta,\tau_y,\mathcal{B},I)] = C - \sum_{i=1}^{N} \frac{(\tau_i - \tau_{\mathcal{B}}(\dot{\gamma}_i;\eta,\tau_y))^2}{2\tau_i^2}\,, \tag{A.3}$$

$$\ln[P(D|k,\tau_y,n,\mathcal{H},I)] = C - \sum_{i=1}^{N} \frac{(\tau_i - \tau_{\mathcal{H}}(\dot{\gamma}_i;k,\tau_y,n))^2}{2\tau_i^2}\,, \tag{A.4}$$

$$\ln[P(\eta,\tau_y|\mathcal{B},I)] = -\ln[\eta_M \tau_{y,M}]\,, \tag{A.5}$$

$$\ln[P(k,\tau_y,n|\mathcal{H},I)] = -\ln[k_M \tau_{y,M} n_M] \tag{A.6}$$

The constant term C (Eqn A.2) is common to both likelihood equations and does not depend on the choice of model or parameter values (under the form of error assumed in Eqns. 3.3-3.5). Equations A.3 and A.5 were used for the Bingham model (τ_B) and Equations A.4 and A.6 were used for the Herschel-Bulkley model (τ_{HB}).

Bingham		Herschel-Bulkley	
η_M	100	k_M	100
$\tau_{y,M}$	100	$\tau_{y,M}$	100
-		n_M	5

Table A.1: Upper bounds on uniform prior for each model, used in Equations A.5 and A.6. The lower bounds used in this case are 0 for each parameter. Values chosen serve as an illustrative example; a more throughoughly investigation into the sensitivity of the results to these values is warranted.

The package `ptemcee` uses a parallel tempered Markov-Chain Monte Carlo (PTMCMC) sampling method described in the work of Earl and Deem [77] and a thermodynamic integration method as presented by Goggans and Chi [78] to estimate the the log value of the evidence integral (Eqn. 1.8). These are the same methods described in *Bayesian Logical Data Analysis for the Physical Sciences* by Gregory [5] and employed by Freund and Ewoldt [4]. Settings used for the sampler are summarized in Table A.2.

From this sampling and estimation method, the following values are obtained from a sampling of $N = 10000$ steps:

Setting	Value
`nwalkers`	20
`ntemps`	40
`Tmax`	1000

Table A.2: Settings used for the sampling method of `ptemcee`. Each setting determines a feature of the temperature ladder; `nwalkers` is the number of MCMC walkers used at each level, `ntemps` is the number of (exponentially-spaced) temperatures in the ladder, and `Tmax` is the maximum temperature used.

$$\ln[P(D|\mathcal{B}, I)] \approx -300.6\,, \tag{A.7}$$

$$\ln[P(D|\mathcal{H}, I)] \approx -297.5\,; \tag{A.8}$$

$$\tag{A.9}$$

from which a Bayes Factor (Equation 1.3) may be calculated as

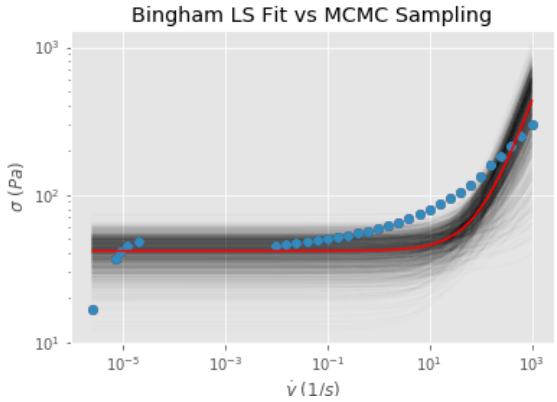
$$\begin{aligned} B_{\mathcal{B},\mathcal{H}} = \frac{P(D|\mathcal{B}, I)}{P(D|\mathcal{H}, I)} &\approx e^{\ln[P(D|\mathcal{B},I)]-\ln[P(D|\mathcal{H},I)]} \\ &\approx 0.045\,. \end{aligned} \tag{A.10}$$

This factor may then be multiplied by the prior odds assigned to these models to determine the posterior odds ratio,

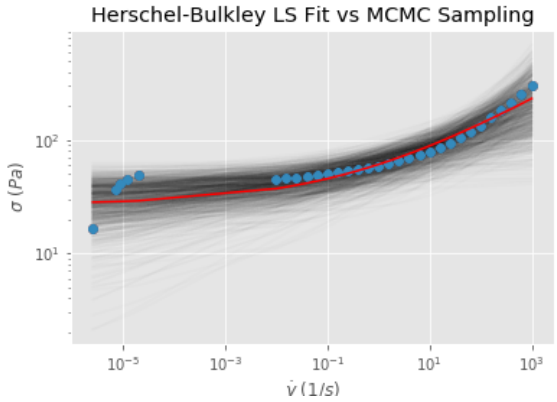
$$\frac{P(\mathcal{B}|D, I)}{P(\mathcal{H}|D, I)} = 0.045\frac{P(\mathcal{B}|I)}{P(\mathcal{H}|I)}\,. \tag{A.11}$$

In other words, if a rheologist were to express *no preference* for either model in their priors (odds ratio of 1:1) then the observation of this data, combined with the aforementioned assumptions, should lead them to update their belief to view the Herschel-Bulkley model as over *twenty times* more credible than the Bingham model (odds ratio of ∼22:1). The additional parameter is justified by the data, just as was indicated by BIC.

Performing the sampling to make these estimates can be costly in terms of computer time. Thankfully, there are additional benefits to be had from the samples themselves, which may be leveraged to gain additional insight into the model's ability to describe the data, described in figures A.1 and A.2.

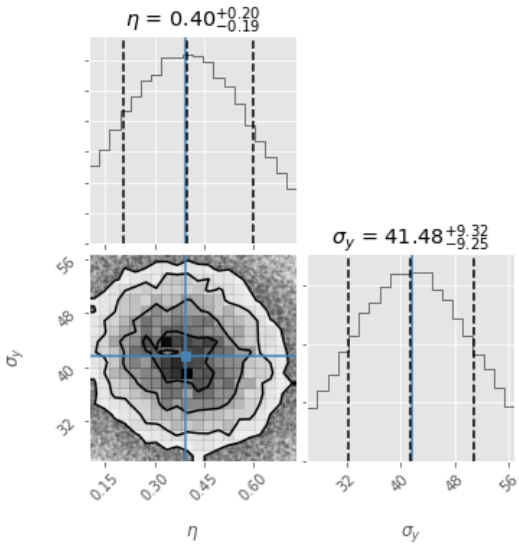


(a) Bingham model

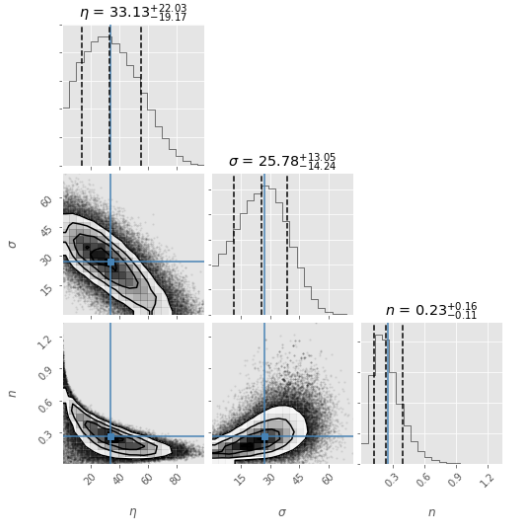


(b) Herschel-Bulkley model

Figure A.1: The steady shear data for Carbopol plotted against the least squares fit (red) and evaluations of the (a) Bingham and (b) Herschel-Bulkley models at sets of parameters ($n = 1000$) values selected randomly from the MCMC sampling ($N = 10000$) of the marginal likelihood distribution such that the relative density of the black lines correspond to the frequency with which models that pass through a given region appear in the marginal distribution. These plots offer much broader insight into the uncertainty in the model fit, as the range feasible fits is visually apparent. The flexibility and limitations of the models can clearly be seen; the Bingham model virtually never going through the data near $10\,\mathrm{s}^{-1}$.



(a) Bingham model sampling



(b) Herschel-Bulkley model sampling

Figure A.2: Histograms depicting the distribution of parameter values in the MCMC sample generated using the Python package `corner`. Along the diagonal are marginal distributions of each of the individual parameter. Below the diagonal are density plots of two parameter values within the sample; each contour level represents an additional "sigma" deviation in the distribution, past the 3-sigma level points are shown as scatter plot. Blue lines and points correspond to values from least-squares estimates. The dashed, vertical lines correspond to the median and 1-sigma deviation values, also shown above each plot. This procedure and visualization offers a more complete and potentially more accurate picture of the uncertainty in the values of the model parameters as it does not rely on the assumption that they are themselves normally distributed.

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