NONLINEAR POLYMER RHEOLOGY

MACROSCOPIC PHENOMENOLOGY AND MOLECULAR FOUNDATION

SHI-QING WANG





Nonlinear Polymer Rheology

Nonlinear Polymer Rheology

Macroscopic Phenomenology and Molecular Foundation

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Preface

Nonlinear Polymer Rheology explores the rich phenomenology of the mechanical behavior of polymer melts and concentrated polymer solutions. My main purpose is to expose the reader to the latest knowledge and understanding of the subject, developed in the past decade. This book explores and establishes a microscopic foundation that provides a coherent molecular-level interpretation for various nonlinear rheological behaviors. In absence of such a foundation, the book would not and could not have been written.

Covering nearly every aspect of the nonlinear rheological responses of entangled polymers, this book may be used as a textbook to introduce essential phenomenological information. The reader does not need to be an experienced researcher in the field of rheology. The book presents the subject in a self-contained manner, although familiarity with the literature on nonlinear polymer rheology would allow the reader to contrast different standpoints.

My approach to nonlinear polymer rheology places a great emphasis on understanding transient viscoelastic responses. While steady-flow behavior is also of interest, *Nonlinear Polymer Rheology* differs from other works in that it treats nonlinear responses as primary and linear responses as secondary. We aim to collect sufficient first-hand phenomenology before proposing theoretical concepts, although key concepts including yielding and disentanglement are utilized in as early as Chapters 6 and 7 without elaborative discussion. Since fresh viewpoints are required, the reader will recognize sharp contrasts with conventional knowledge and methodology.

Many excellent books have treated the subject of polymer rheology in a traditional way. The most classical literature is cited and discussed in books including those by Ferry,¹ Doi and Edwards,² Bird et al.,³ Dealy and Larson,⁴ Graessley,⁵ and Phillies.⁶ In general, these books do not have a sufficient discussion of nonlinear rheology that is based on a coherent gathering of key phenomenology. Limited by the available space, the present book omits discussion of the older literature before 2000 and only includes a few pertinent references since 2000.

Scientific inquiries develop in three stages: A. "Empirical," where we find out what happens; B. "Phenomenological," where we learn how it happens; C. "Theoretical," where we explain why it happens. For a complicated subject such as polymer rheology, it is not feasible to formulate a theory without first having sufficient and coherent phenomenological knowledge. *Nonlinear Polymer Rheology* acknowledges this logical sequence and strives to collect and establish the phenomenology before developing any theoretical treatment and formulation. However, these three types of research can and do often proceed interactively and interchangeably. For example, a particular theoretical idea or picture can prompt one to organize phenomenological information in a more coherent manner and to design additional experiments using hypothetical and unproven concepts.

The responses of polymeric liquids to large and rapid external deformations are challenging to depict and understand in molecular terms. The task is difficult because molecular behavior

on nanometer scales dictates rheological properties characterized on macroscopic (millimeter) scales: There exists a gap of six orders of magnitude in length scales. Thus, we should begin by "listening to" what the experiments tell us, and first build a sound phenomenological base. Until we have a sense of the full picture, which could stem from an adequate analysis of the available phenomenology, it is challenging and risky to make theoretical simplifications, for example, in modeling such complex behavior as the response of polymer entanglement to sudden, fast, large external deformations.

Our goal is to arrive at a realistic physical picture for nonlinear polymer rheology. Having collected the essential phenomenology, the process of rational thinking must take us beyond empirical knowledge. To illustrate the merit of reason-guided thinking, let us consider, for example, the phenomenon of viscoelasticity. By definition, all viscoelastic materials are mechanically solid-like (elastic) when probed on short time scales. Viscoelastic liquids become completely viscous only on long time (relative to the material relaxation time) scales. Where does the "elasticity" come from in such a liquid? What is the structure of the material that produces the elasticity? How should we think about the microscopic origin of viscoelasticity?

Upon external deformation, it is clear from the established phenomenology that an initial elastic response must end, and a transition to flow must begin. In other words, all viscoelastic liquids undergo yielding when subjected to fast deformation. The transition to flow suggests that there exists some kind of a potential barrier on short time scales. The next question is what creates such a potential barrier. As soon as we ask questions like this, we can make progress toward an instructive understanding of viscoelasticity, instead of stopping at the level of phenomenological models including the Maxwell model and the Oldroyd⁷ model.

This idea to associate the "elasticity" with a potential barrier for any viscoelastic materials is useful even for an external deformation rate \mathscr{R} that is lower than the reciprocal of the dominant relaxation time τ , that is, when the Weissenberg number Wi < 1. In other words, a transition from elastic deformation to flow must occur even when the product $Wi = \mathscr{R} \tau$ is below unity. For $Wi \gg 1$, the initial elastic deformation can be rather remarkable, persisting up to many strain units in the case of entangled polymers. The termination of the elastic-dominant response apparently stems from a breakdown of some microscopic structure. It is an essential task of polymer rheology to identify and delineate the nature of potential barriers, in terms of intermolecular interactions, and show how the structural breakdown takes place.

Figuring out the nature of intermolecular interactions in entangled polymeric liquids under large deformation is a daunting task. Historically, the task has challenged the brightest minds in polymer science. An entangled polymer can be regarded as a physical network of Gaussian chains. Its stress response to startup shear reveals a finite cohesive strength of the network junctions. Maxwell was right⁸: Entangled polymer melts yield, just like ductile polymeric solids (e.g., glasses) do, under continuous external deformation. The rate dependence of the yielding response indicates that chain entanglements are dynamic and have finite lifetimes.

In 1979, Maxwell and Nguyen⁹ described the stress overshoot of polystyrene melts upon startup shear by stating "the yielding behavior indicates that, as straining progresses, the structure of the melt is broken down, thereby permitting flow." In the same year, Doi and Edwards published Paper 4, completing their treatment of nonlinear response aspects in the tube model,^{10–13} building on the appealing idea of reptation from de Gennes.¹⁴ The tube model had a very different molecular interpretation of shear stress overshoot. Perhaps the tube model made the Maxwell and Nguyen's idea of yielding unnecessary and obsolete. Ever since 1979, theory, experiment, and interpretation of polymer rheology have developed on the presumption that the Doi–Edwards tube model encompasses the right physical picture and tells us how to understand the nonlinear rheological behavior of entangled polymers. The tube model paradigm provides a huge backdrop, against which this book discusses the same subject, polymer rheology, especially nonlinear rheology of entangled polymers.

It seems that modern scientific inquiries rarely follow the preaching of Karl Popper (1902–1994) concerning the objective of doing science, that is, (i) to develop falsifiable theories and (ii) to falsify existing theories with experiment. On the contrary, we prefer to work within an existing paradigm as described by Kuhn (1922–1996).¹⁵ There is a tendency for one to do anything and everything to validate and defend a given theory instead of performing experiments aimed at falsifying it. The notion of scientific truth is often not established by objective criteria and logical rationalization in the Popperian sense but instead by the consensus of a scientific community. Consequently, for two reasons it may be difficult to carry out unconventional research: (i) We are predisposed to accept textbooks and literature results. (ii) Unconventional ideas can be inharmonious. Transformative knowledge find it hard to gain acceptance by the community, especially by people who are accustomed to the standard knowledge and approach. Fortunately, science is ultimately not an affair of democracy, dictated by popular vote. The state of our knowledge is not defined by the status quo.

Doing science often amounts to sorting out relationships between causes and effects. Depending on the level of description, causality can be confused or even reversed. Something taken as the cause at a coarser level may actually be an effect at a finer, deeper, or higher level. For polymer rheology, it is unnecessary to go to the quantum-mechanical level; but it is unacceptable to stay at the continuum mechanical level as the Maxwell model does when it is feasible to probe molecular origins. A short presentation has been posted at www.youtube.com/watch? v=2HDD51Mxu8U to discuss this matter of causality in *nonlinear polymer rheology*.

Our objective as well as the ultimate goal of Nonlinear Polymer Rheology is to raise and answer the following two questions to the best of our abilities: (i) Under macroscopic deformation, how and why do polymer chains deform in an entangled polymer solution or melt? (ii) When does chain deformation cease to increase and flow begins? In short, for entangled polymers, how does chain entanglement respond to external deformation? Intellectual independence is key to the search for answers. We are going to the places not because they were well lit; we are going to where the truth will be found.

This book (containing ca. 300 data-based figures) was motivated by and based on experiment, written to provide the reader with the comprehensive experimental information and conceptual discussions needed to develop a new, reliable, and realistic understanding of the nonlinear rheology of entangled polymers. As a fundamental step, one must accept that the interchain interactions in an entangled polymer system must be adequately treated to reflect the many-body nature. Intermolecular interactions due to chain uncrossability provide the initial potential barrier for elastic deformation during startup deformation. These interactions are of finite strength and are overcome when intrachain forces grow to a comparable magnitude, leading to force imbalance and yielding of the entanglement network, that is, chain disentanglement. As orientation, we include an introductory chapter to briefly summarize the characteristics of polymer rheology, including its definition and objectives, its history, tradition, culture, philosophy, and emergent new trends.

When I joined the faculty of Macromolecular Science and Engineering at Case Western Reserve University in the fall of 1989, I decided to work on polymer rheology although I was not trained in rheology during my doctoral study and did not know whether or not there would be any remaining important problems. From the early 1990s to 2006, before I developed my own systematic understanding of polymer rheology, I taught graduate courses at Case on polymer rheology based on the books of Ferry,¹ Bird,³ and Macosko.¹⁶ While teaching the subject according to these books, I actually had a lot of trouble in presenting the arguments and the discussions. Viscoelasticity seems rather abstract while shear thinning of polymeric liquids appears obvious. In my formative years, that is, the first 5 years at Case, I was lucky to work on an industrial project concerning extrusion of polyethylenes sponsored by BP Chemicals and thus had a chance to work on the incredibly important problem of polymer wall

slip, into which P. G. de Gennes and F. Brochard had just developed some molecular insights. This research activity truly launched my career to work on polymer rheology. After 11 years at Case, I was recruited in 2000 to the graduate program on Polymer Science and Engineering at the University of Akron. Most of the contents in this book were developed at Akron over the past dozen years.

I have been very lucky to attract many talented students to come to Akron and join my lab. My graduate students (Prashant Tapadia, Pouyan E. Boukany, Sham Ravindranath, Yangyang Wang, Xin Li, Xiangyang Zhu, Shiwang Cheng, Gengxin Liu, Hao Sun, Panpan Lin, Xiaoxiao Li, Mengchen Wang, Jianning Liu, Xianggang Li and Zhichen Zhao) have kept me company. Consequently, I had never been alone on my journey to acquire new knowledge and a new fundamental understanding of polymer rheology. Without their coming to my research group, my scientific world would have been a rather empty place. Without their dedication to carry out all the essential experiments that led to the new worldview on polymer rheology, this book could not have been written. My understanding of nonlinear polymer rheology has changed because of their work. My knowledge about the subject has also increased because of Ed Laughlin who helped us construct many experimental apparatuses including the sliding-plate rheometer.

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I would like to give special thanks to two people who directly helped me with the writing of the book. I am thankful to my current graduate student Jianning Liu who entered all the references for the book using Endnote, replotted several figures based on literature data, and helped me to make the Subject Index. I am infinitely indebted to Professor George Phillies who so kindly offered to copy-edit the book and raise questions about the presentation of various concepts. He made corrections and comments on every single page of the book. Because of George's commitment to good English writing, the book reads much more smoothly.... I cannot thank him enough for his friendly help. At the end, I wonder whether I have coauthored this book with George.

Finally, I would like to dedicate this book to my wife Ruth for her love and support. I gave up doing most house chores including cooking in the past 3 years (I used to do a little and always enjoy cooking) and lived like a parasite while writing this book. Over the past decade, I was able to work long hours toward the goal to figure out what is going on in nonlinear polymer rheology because Ruth selflessly supported this endeavor.

Introduction

In materials science and engineering, rheology is an important subject with a long and rich history. The first professional society on rheology and the first journal devoted to rheology both appeared in the United States of America in 1929. A comprehensive discourse of the history of rheology can be found in Tanner and Walters.¹ The specific subject of this book, nonlinear polymer rheology, also has an extensive history, and a brief description of its early history can be found in Chapter 1 of Rohn.² Polymer rheology can be regarded as one of the three major topics in polymer physics; the other two subjects concern with physics of polymers in crystalline and glassy states, respectively. In general, rheology is founded on the basis of macroscopic measurements. Challenges arise when we desire to figure out what microscopic physics is responsible for rheological behavior on macroscopic scales. Somehow polymer chains, with dimensions on the order of 10 nm, act either alone (dilute solutions) or collectively (concentrated solutions and melts) to produce many remarkable macroscopic phenomena. In this chapter, we will provide a brief summary of polymer rheology by highlighting its main ingredients and characteristics. We emphasize at the outset that identification of the molecular origin of mechanical stress during and after deformation is a leading task for polymer rheology. In the following discussions, some technical terms are inevitably used without a complete explanation, and some ideas are brought up without a complete background. The reader can use the Subject Index to obtain more rigorous elaborations in subsequent chapters.

1. Rheology: The Definition

Rheology is a study of how materials undergo deformation. This is a most common description of the task for rheology. By definition, solids have a finite limit of elastic deformability. Within the limit, that is, below a threshold of external deformation, a solid can return to its original state when the load (i.e., force) is removed. In other words, elastic deformation is essentially recoverable. Continuous external strain will ultimately cause a ductile solid to deform plastically without fracturing. When plastic deformation occurs, the sample cannot return its original shape or dimensions. Such irrecoverable or irreversible deformation is also known as flow.

In this book, we avoid using the two phrases deformation and flow interchangeably. While the meaning of flow is unambiguous, by "deformation" we imply strain that is not necessarily flow. In other words, "deformation" is clearly not synonymous with "flow". In fact, E.C. Bingham (1878–1945) also distinguished deformation from flow by stating "Rheology is the study of <u>deformation</u> and <u>flow</u> of matter".³ We are discussing the careful usage of these two most frequently used words at this very beginning because there has been considerable confusion about the difference between the two. Often, flow is a heavily misused word in the rheology literature. Flow actually means something really explicit: irreversible deformation. Startup deformation of viscoelastic materials never starts with flow. Thus, we should not use the phrase "flow" to categorically refer to, for example, startup deformation as startup flow. This essential point will

become clearer, hopefully, by the end of this introduction. Our more detailed evidence and reasoning will be presented later throughout the rest of the book.

Polymeric liquids are fluids of chain-like macromolecules that are not cross-linked to each other so that they may flow at long times by having their chains slide past one another. Experimental characterization indicates that polymeric liquids may respond like a solid when subject to sudden external deformation. At short times, they may be quite incapable of flowing. This simple observation turns out to provide some essential insights leading to a proper understanding of rheological behavior in viscoelastic liquids, particularly the entangled polymer solutions and melts that are the main objects of study in this book. It may be noteworthy that entangled polymeric liquids are uniquely capable of undergoing large elastic deformation in contrast to many other viscoelastic materials such as polymer glasses and colloidal dispersions.

In the past, the emphasis of experiment and theory was often placed on delineating the constitutive behavior in steady state. Shear thinning is one such characteristic, relating the steady shear stress to the shear rate. Moreover, rheometric measurements are frequently simplified to assume that the deformation field can be experimentally prescribed *a priori*. In this tradition, students of rheology rarely realize that the task of rheology is to separately and independently determine both the deformation field and the corresponding stress state.

2. Molecular Approach of Tube Model and Continuum-Mechanical Constitutive Modeling Versus a Phenomenology-Based Treatment

Polymeric materials are a unique class of matter in the sense that many of their physical properties depend explicitly on the chain length, which in the case of linear polymer chains is proportional to the total molecular weight M. Dynamic and rheological properties are particularly sensitive to M. Such experimental facts motivated scientists to build molecular models. Molecular modeling began as early as the 1940s, climaxing in the celebrated bead-spring theories of Rouse⁴ and Zimm⁵. The long-awaited groundbreaking explanation of the scaling law $\eta_0 \sim M^3$ for melt viscosity came much later in 1971,⁶ where we note that experimental data usually indicate a notably higher exponent than three. Doi and Edwards⁷ took some significant steps to advance de Gennes' model of reptation. They asserted with sound reasoning that in an entangled polymer melt or solution, the emergent stress during either external shear or extension can be evaluated in terms of the intrachain retraction forces of a coarse-grained (test) chain confined to a fictitious tube. This Doi-Edwards (DE) model satisfactorily describes linear viscoelasticity of entangled polymer melts and solutions.⁸⁻¹⁰ It also claims to describe and explain nonlinear rheological properties.¹¹ The subsequent three decades witnessed extensive efforts to improve the original de Gennes-Doi-Edwards model.¹²⁻²⁰ Experiments, too many to cite them here, seem to support the theoretical description.¹ However, it is actually not

¹ The validation of the tube model usually adopts the following logic: Since the constitutive continuum description, extracted from the tube model, can describe such instabilities as shear banding, non-quiescent relaxation and necking instability in uniaxial extension it must have captured the correct molecular physics. Such reasoning overlooks the model degeneracy in science: Different models can produce similar data. A recent continuum-mechanics-level theoretical study on extensional necking most strikingly revealed such a degeneracy when Hoyle and Fielding showed in J. Rheol. 2016;60(6):1347-1375 that uniaxial extension is unstable against necking in several constitutive models, including a variant of the tube model and models that have no microscopic basis for chain entanglement. Thus, to declare that it could describe the macroscopic world of nonlinear polymer rheology, the tube model needs not incorporate the molecular physics that has to answer the question of whether an entangled polymer liquid should be treated as a junction-forming entanglement network and whether fast external deformation could weaken or destroy the network. This book suggests that we must move behind such a modest goal, collect more phenomenology, and search for a more useful and predictive theoretical framework by identifying the molecular origins for the key emergent phenomena including various macroscopic instabilities.

obvious that interchain interactions can be treated in such a smoothed-out manner. Moreover, admittedly, the tube model is inherently self-inconsistent.²¹

Treatments based on the tube description include the slip-link models.^{22,23} These models aim to relate macroscopic rheological phenomena to molecular dynamics on nanometer scales, contrasting sharply with the constitutive continuum approach that preceded the tube model. James Clerk Maxwell (1831–1879) and Ludwig Boltzmann (1844–1906) explored phenomenological linear viscoelasticity at the continuum level. James Gardner Oldroyd²⁴ (1921–1982), among others, made well-known contributions to the field of constitutive modeling for nonlinear continuum behavior of viscoelastic fluids. Many textbooks present various constitutive descriptions without sufficient molecular ingredients.^{25–31} According to these books, constitutive models contain physical parameters that may be determined from linear viscoelastic measurements. These parameters, such as the shear viscosity, are usually assumed to be constant, that is, fixed everywhere in space and time. The validity of assumptions of spatial and temporal uniformity has not been tested adequately in the past.

Separate from the continuum description and tube model for polymer rheology, there was a period of several decades in which the transient network models (TNMs) were the standard description, developed by Green and Tobolsky,³² Lodge,³³ and Yamamoto.³⁴ To make the transient network models quantitative, for example, to describe shear thinning, the network junctions were assumed in an *ad hoc* manner to have a stress- or rate-dependent lifetime. Although both the tube model and the transient network model are phenomenological, there was an impression that the tube model is anything but *ad hoc* and thus far superior to the transient network model. In fact the tube model is also *ad hoc*.

There are two ways to explore what happens in experiment. In the first way, experiments are carried out because of an existing theory. For example, in the past decades, countless experimental studies have been made to vindicate the tube theory. Here the theory dictates how the phenomenology should be collected. The danger is that such an approach could be highly biased and lack basic objectivity. For example, up to 2004, nearly all rheological experiments had been analyzed on the basis of shear homogeneity because none of the extant theoretical approaches insisted *a priori* that the deformation field should be determined independently. In the second way, phenomenology is established without theoretical prejudice or favoritism. In this approach, the rheological behavior of entangled polymers is investigated in experiment without any presumptions about how the polymeric liquids should respond to various modes of external deformation. Instead of assuming homogeneous shear in rheometric measurements, experiments are performed to determine the state of deformation and stress field simultaneously and independently in real time. Such objective phenomenology must be collected first. Any reliable theoretical description of nonlinear rheology of entangled polymers only comes after the phenomenology. In this work, we follow the second approach. Neither the tube model nor the latest formulation of nonlinear rheology (presented in this book) has received explicit molecular-level confirmation. Thus, it would be unreasonable to only say that there is not yet any molecular-level substantiation of the new picture discussed in this book. The future molecular dynamics simulation and small angle neutron scattering measurements will tell which one is more realistic and useful.

3. Linear Versus Nonlinear Responses: Characterization Tool Versus Science of Rheology

The linear responses of viscoelastic liquids, such as entangled polymer solutions and melts, reflect and manifest the microstructure, which remains nearly intact during small external deformations. Through adequate molecular modeling, linear rheology thus becomes a characterization tool. Linear responses form one aspect of the subject. However, the core objective of polymer rheology has to do with something else, namely, studying nonlinear responses of entangled polymers to large fast deformation of different types. This book is devoted to exploring the physics behind the nonlinear rheological behavior of entangled polymeric liquids.

4. Shear Thinning, Stress Plateau, and Yielding

Nonassociating polymers, for example, most of the commodity polymers, including polyethylenes, polypropylenes, polystyrene, polybutadiene, and polyisoprene, with a global production rate of several hundred billion pounds per year, exhibit shear thinning as shown in Fig. 1(a). If steady shear can be reached, then the shear viscosity is found to decrease with increasing shear rate y. For monodisperse linear polymers, the shear thinning is steep: the shear viscosity η scales nearly reciprocally with the rate, that is, $\dot{\gamma}^{n-1}$ with $n \ll 1$. When we represent this steady-state behavior in terms of the shear rate as a function of the shear stress, we see a transition at a threshold stress level σ_c as shown in Fig. 1(b), where the nominal shear rate sharply rises. Beyond the terminal flow regime (where σ is linearly proportional to $\dot{\gamma}$), the stress level saturates with respect to increasing shear rate, a phenomenon that is known as stress plateau behavior. This stress plateau character is reminiscent of the yield-stress in materials such as ketchup, toothpaste, and yogurt that exhibit much higher fluidity only when a critical level of shear stress is exerted. The plateau width can span many orders of magnitude in the shear rate for well-entangled polymers and other yield-stress materials. Equivalently, the shear viscosity of these materials can drop by many decades within a narrow range of stress. Thus, the state of matter at low shear rates, in the terminal flow regime, must be rather different from the state of matter after yielding around σ_c . In other words, when the quasi-solid (i.e., the liquid with an enormous viscosity due to chain entanglement) turns into an inviscous state, the structure has undergone significant alternation. The change in viscosity must reflect a massive loss of entanglement.

5. Is There Always Homogeneous Deformation?

Let us consider simple shear generated by displacing two parallel plates in opposite directions. This is a standard protocol adopted in most studies of the shear rheology of entangled polymers. We have taken it for granted that homogeneous shear can be produced with such a boundary displacement, as depicted by Fig. 1.1(a), where the plates are taken to be separated by a distance H. The shear deformation is taken to be uniformly the same at all positions along the



Figure 1 (a) Steady shear viscosity as a function of shear rate. (b) Steady shear rate as a function of shear stress σ , showing a stress plateau around σ_c .

gap. This assumption of homogeneous shear is not only out of convenience but also out of necessity. We could not perform any conventional rheometric measurements if a uniform shear field could not be prescribed by the imposition of a velocity V on one plate while holding the other plate stationary. Misleadingly, one could make a seemingly reasonable argument to assert that homogeneous shear should prevail since the steady shear stress should be constant along the gap direction, as discussed in Section 4.1.1. Traditionally, we tend to first think about the steady shear behavior, paying less attention to the fact that strongly viscoelastic liquids including entangled polymers are anything but a liquid when responding to sudden startup deformations. At times much shorter than the reptation time, they are transient solids and may experience solid-like breakup, for example, they undergo strain localization in spite of molecular diffusion. Thus, during any rheometric investigation of rheological behavior of entangled polymers, including startup shear and large stepwise shear, we should make efforts to verify the basic assumption that the shear rate is independent of position. Sound rheological measurements should involve experimental techniques that make *in situ* determination of the shear field.

The era of performing rheological studies based on an untested premise of homogeneous shear has come and gone. Since 2006, numerous studies from Akron^{35–37} and other parts^{38–40} of the world have recommended that the experimenters must determine the deformation field explicitly. In particular, particle-tracking velocimetry (PTV) has been applied in conjunction with commercial rheometric instruments to quantify shear banding during startup shear⁴¹ and nonquiescent relaxation after stepwise shear both for well-entangled polymer solutions^{37,42} and for melts.⁴³ It is found that localized yielding can lead to shear strain localization. Similarly, strain localization is a common feature in startup uniaxial extension of entangled melts. It is important to realize that the concepts of yielding and chain disentanglement remain valid even when there is no shear strain localization. The PTV observations of strain localization nonetheless most evidently demonstrate the nature of nonlinear rheological responses, leading to the new perspective that the entanglement network can yield and break up.

To reiterate, yielding can result in severe strain localization in well-entangled polymer solutions and melts. Thus, there is a breakdown in conventional rheometric analyses that are based on the textbook assumption of homogeneous shear. The demonstration of shear and tensile strain localization spells the end of conventional rheometry. In traditional rheology, the deformation field is chosen by the experimentalist and is assumed to be known *a priori*. In reality, in simple shear rheometry we can only control the speeds (0 and V) at the two parallel surfaces. We cannot dictate whether or not the velocity field is given by v(y) = V(y/H), that is, we cannot assume that the strain field is homogeneous along the velocity gradient direction.

6. Rheology Versus Fluid Mechanics

The mission of rheology is entirely different from that of fluid mechanics. The aim of polymer rheology is to explore and plausibly derive constitutive relations from the principles of microscopic molecular physics. In contrast, fluid mechanics of polymeric liquids describes the state of deformation and field of stress by applying a given set of macroscopic constitutive relationships.

A detailed description of polymer processing requires fluid mechanical calculations based on constitutive equations. Such practice is reliable and realistic only when the constitutive behavior of polymeric liquids has been adequately captured in terms of molecular mechanisms. The subject of fluid mechanics generally requires us to formulate the stress and strain fields using tensorial representation. But the subject of rheology does not require tensor representations of stress and strain because we always specify the mode of deformation (e.g., shear or extension).

xxvi Introduction

For two reasons this book does not include tensor analyses. First, many who would like to learn about the subject of polymer rheology often turn away upon opening the first two chapters of a typical book on rheology because they mistakenly think that the subject is highly mathematical and beyond their level of preparation. Second, no tensors are needed anywhere because we discuss simple shear and uniaxial extension separately. Once the mode of deformation is specified, all the mathematical treatments actually involve only scalar quantities. The present book thus departs from the tradition that invokes tensor analyses and matrix representations to introduce the subject of polymer rheology.

7. Emerging Trends

It is at least challenging if not risky to infer microscopic processes from macroscopic nonlinear responses of polymeric liquids to fast large deformation. We have arrived at a coherent molecular picture after a careful examination of the accumulated phenomenology. In the end, we are forced to suggest existence of an entropic barrier in Chapter 16 that provides the cohesion of the entanglement network against finite external deformation. Because of this cohesion barrier, after a sudden stepwise deformation of moderate magnitude chain deformation remains pinned down until reptative relaxation restores the chain conformation. This conclusion may be regarded as deductive and therefore speculative. To bridge the gap of six orders of magnitude in length scale we need to resort to microscopic observations such as neutron scattering measurements and computer simulations. As this book approached the finish line, we learned that new small-angle neutron scattering (SANS) measurements had recently been performed along with innovative model-independent analysis⁴⁴ that directly compares the SANS spectrum with the tube model prediction. During stress relaxation from stepwise extension of moderate magnitude, chains remain stretched on length scales larger than the averaged equilibrium tube segment according to the SANS spectrum even after 20 times Rouse time. Such measurements prompt us to suggest that chain deformation and stress arising from molecular deformation should be described at different length scales instead of a single scale of the equilibrium tube segment. The tube model assumed or made approximation that chain deformation and accompanying stress only needs to be characterized using a single length scale given by the equilibrium tube segment (or equilibrium entanglement strand). Consequently, the tube model may be highly unrealistic for nonlinear polymer rheology, as much of the experimental evidence presented in this book seems to indicate.

8. Summary

This book presents the subject in the order of phenomenology first and theory second. In contrast to other treatments in the literature that collect phenomenology based on the assumption that the deformation field could be prescribed *a priori*, this book shows new phenomenology obtained from the independent and separate characterization of the deformation field and the state of stress. To accomplish such a task, many inherent experimental limitations have been overcome. The emergent phenomenology motivates a physical picture of the nonlinear rheology of entangled polymers that is rather different from pictures associated with the tube theory. This phenomenology allows us to refocus on the two central questions in nonlinear rheology of entangled polymers: (a) Why do polymer chains deform elastically at the beginning in response to a macroscopic strain? (b) When do polymers cease to undergo further elastic deformation so that flow can commence. In the search for the answers, some new questions arise that are equally important to address: (c) What happens to chain entanglement when the elastic deformation is terminated at a considerable strain, for example, after a few strain units? (d) What is the role of melt elasticity in polymer rheology? This book describes the approaches taken to answer these foundational questions.

The book is divided into four parts: (a) Linear viscoelasticity and experimental methods; (b) Yielding – primary nonlinear response to ongoing deformation; (c) Decohesion and elastic yielding after large deformation; and (d) Emerging conceptual framework and beyond. The subject is discussed with minimal mathematical equations and without tensor analysis. The bulk of the book is a description of phenomenology, collected from state-of-the-art macroscopic rheometric measurements and particle-tracking velocimetric observations. The reader can find this phenomenological component in Parts 2 and 3 of the book. Part 4 explores the molecular foundation for nonlinear rheology of entangled polymers, based on the available phenomenological information described in Parts 2 and 3. Although the materials in Chapters 1-3 are not new, perhaps even too lengthy and simple for many readers, Chapters 1 and 2 provide the definitions and information needed for the developments in the subsequent Parts 2 through 4. Readers familiar with standard linear rheology may simply start reading from Chapter 4 or 6 and use Part 1 as a reference as needed. Conversely, for readers less fluent with the theoretical background, Chapters 1 and 2 are just a compilation of classical results from the established theories of polymer dynamics. Instead of going through the "derivations" in these chapters, the readers only need to go to these chapters for definitions of relevant concepts and quantities that appear in the reminder of the book. In short, the key chapters of the book are 6, 7, 9, 11, 12, 16, and 18, respectively, on wall slip, yielding behavior, particle-tracking velocimetric observations of shear banding, various forms of strain localization in startup melt extension, elastic yielding phenomenon, the theoretical foundation, and troubles with existing frameworks (a summary of different worldviews). To have a complete overview of the subject, it is better not to skip any chapter. For a short review of the new worldview described in this book, the reader may go to listen to a research seminar posted at https://www.youtube.com/watch?v=ffbhZYlkWcA.

In closing, a very specific comment needs to be made about how the content of this book is presented and discussed. To establish a correct and reliable conceptual foundation for the nonlinear rheology of entangled polymers, we must first describe the key phenomenology. This phenomenology will motivate the discussions of the theoretical concepts, leading to our molecular-network paradigm. To verify such a theoretical framework, we need to discuss further supporting phenomenology, including phenomenology that was uncovered as predictions of the new paradigm. In the chapters prior to Chapter 16 some phenomenology is presented and discussed using concepts that are only rigorously described in Chapters 15 and 16. These concepts include yielding, chain disentanglement, entropic barrier, and finite cohesion. These central phrases form the new language in which we discuss nonlinear polymer rheology. A reader may simply follow the discussion of the phenomenology, using the literal meanings of these terms. A reader may alternatively go to Chapter 16 to find more precise definitions and associated discussions for these terms as he or she reads through Parts 2 and 3.

Although this book focused on phenomenology derived from entangled polymers, many characteristics are expected to appear in other chain-like systems such as associative polymer solutions and melts as well as self-assembled aggregating systems including wormlike micelles. These systems must also yield upon large conformation. They could also undergo stress overshoot and various formations of strain location in either shear or extension or more complex configurations.

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Part I

Linear Viscoelasticity and Experimental Methods

Part of the physics on Earth is remarkably simple: There exists a subworld of linear response. The best-known example is Newton's second law: $\underline{F} = M\underline{a}$. In the field of mechanics, there are other famous examples of linear response, that is, Hooke's law for the deformation of elastic solids and Newton's law for the flow of viscous liquids. Here, the output, such as the degree of deformation or rate of deformation, is linearly proportional to the input, such as the imposed force, and vice versa.

1

It is conceptually interesting to note that viscoelastic materials including entangled polymeric liquids undergo yielding even in the limit of linear response. Since yielding implies removal of a constraining barrier, the structural state after yielding is different from the equilibrium state. In the linear response regime, the structural change is apparently insignificant. Indeed, all current theories that depict linear response assume that the structures of the liquids responsible for the linear viscoelasticity remain intact during a weak external deformation.

In this part of the book, we describe linear viscoelasticity of polymeric liquids, experimental characterization methods, and rheometric setups. Specifically, Chapter 1 provides a phenomenological discussion of linear viscoelasticity in terms of basic concepts and elementary models such as the Maxwell model, as well as a simple account of the rubber elasticity theory. Chapter 2 focuses on a theoretical description of various molecular models for polymer dynamics, for example, Rouse, Zimm, and reptation models as well as the packing and percolation models for polymer entanglements. Chapter 3 is devoted to a brief account of the various rheometric apparatuses and related methods that are applicable when deformation is homogeneous. Chapter 4 extends Chapter 3 by emphasizing that the objective of rheology is to characterize the mechanical responses *and* determine the deformation field. It introduces the particle-tracking velocimetric method that enables a comprehensive characterization of rheological behavior. Chapter 5 describes additional rheometric devices as well as apparatuses that involve more complicated geometries.

Phenomenological Description of Linear Viscoelasticity

It has been known since James Clerk Maxwell's period that deformation and flow behavior of materials may not fall into two simple categories: ideally elastic solid and purely viscous liquid. Elastic solids were extensively studied by Robert Hooke (1635–1703). As a contemporary of Hooke, Isaac Newton (1643–1727) discovered the basic law for the motion of viscous liquids. Many materials are neither elastic solids nor viscous liquids. Their mechanical behavior exhibits time-dependent properties; that is, they appear solid-like on short time scales and liquid-like on long time scales. Such materials are clearly non-Newtonian. This viscoelastic behavior is actually a property of a wide range of structured materials, including colloids, liquid crystals, micelles, foams, gels, granular matter, emulsions and membranes, and, of course, polymers. Viscoelasticity arises from the existence of slow relaxation associated with material's structural change.

Linear viscoelasticity, by definition, depicts behavior that is phenomenologically simple: the mechanical resistance is linearly proportional to the degree of external perturbation. A linear response is possible when the external world does not cause the material to deviate so much away from its equilibrium state as to display obvious nonequilibrium properties. In the linear regime, the perturbation is so weak that the material response is uniform and homogeneous, making the phenomenology straightforward to interpret.

In the reminder of this chapter, we first discuss three protocols commonly used to probe the viscoelastic behavior of structured materials including polymers. Then we describe how the Boltzmann superposition principle and Maxwell model can be applied to describe the linear response behavior of viscoelastic materials. This chapter ends with a section on the classical network picture of rubber elasticity, showing the entropic origin of polymer viscoelasticity.

1.1 Basic Modes of Deformation

External deformation occurs in various forms such as simple shear, uniaxial extension, and compression. For each of these three types, there are at least three different ways to impose the deformation: (a) startup deformation where the boundaries of the body under deformation are suddenly displaced at some specified speed at t = 0; (b) stepwise deformation where a startup deformation is abruptly terminated at a specified magnitude of strain; and (c) oscillatory deformation where the moving boundary is made to undergo sinusoidal linear displacement. Only simple shear and uniaxial extension are extensively discussed in the book. Compression leading to squeezing or planar extension will first be discussed in Sections 5.3.2 and 5.3.3 and considered again in Sections 10.3 and 10.4 as well as in Section 13.5. In this chapter, we use simple shear to illustrate the three modes (a) to (c).

1.1.1 Startup shear

Let us consider a sample of interest sandwiched between two parallel plates, as depicted in Fig. 1.1(a). To produce startup shear, the lower plate is held stationary, while the upper plate is made to suddenly displace in the X direction. We assume that the sample's upper boundary of area Σ will move by X = Vt at time t when the upper plate is given a velocity V at time t = 0, as characterized in Fig. 1.1(b,c). Specifically, we consider no slip at the interfaces between the sample and two confining plates. During each time interval Δt , the upper plate moves by $\Delta x = V\Delta t$, producing an elemental shear strain of

$$\Delta \gamma = \Delta x / H \tag{1.1}$$

so that the shear rate is

$$\dot{\gamma} = \Delta \gamma / \Delta t \to V / H,$$
 (1.2)

where $\Delta x/\Delta t|_{\Delta t \to 0} \to V$ by definition. This introduction of shear strain and shear rate rests on an important premise: The shear deformation is uniform along the thickness direction (Y axis) as depicted in Fig. 1.1(a). Assuming that the shear deformation is imposed at t = 0, with surface velocity V, then the accumulative external shear strain at time t is $\gamma(t) = \dot{\gamma}t$. As shown in Fig. 1.1(a), in response to shear deformation, a shear stress emerges – a force F is required to maintain shearing (Eq. (1.6)). In steady state, which is achieved when the stress responses no longer vary in time, we also need to argue about the validity to assume homogeneous shear. The illustration in Fig. 1.1(d) assumes a constant shear rate in every layer along the Y axis. We will defer a detailed discussion of the shear homogeneity assumption in Chapter 4.

From the onset, let us introduce a key yet elementary concept in rheology associated with the startup shear depicted in Fig. 1.1(a,b). Let us figure out how long it takes to produce a sizable deformation, for example, a shear strain of $\gamma_1 = 1.0$. At a displacement velocity V as shown in Fig. 1.1(d), the time t_{1exp} it takes for the moving plate to travel a distance of H is given by

$$t_{1 \exp} = H/V = 1/\dot{\gamma},\tag{1.3}$$

where the second equality follows from Eq. (1.2). This experimental time scale, t_{1exp} , is the time required to impose 100% shear deformation at given shear rate $\dot{\gamma}$. It is worth noting that Eq. (1.3) provides useful information only if homogeneous shear prevails. Two questions naturally arise: (a) When is shear deformation regarded slow enough to ensure linear response? (b) When does the assumption of shear homogeneity break down? We will answer (a) in Section 1.2.7 and defer (b) to Part 2.



Figure 1.1 (a) Depiction of simple shear in three dimensions, showing two parallel surfaces at y = 0 (fixed) and H (displaced by X over time *t*). The force F required to hold the bottom surface stationary can be measured to define shear stress in Eq. (1.6) where Σ is the total area of the shearing surface. (b) Displacement X of the upper surface as a function of time at a constant shear rate V/H. (c) Startup shear shown by the step function of V versus time *t*. (d) Homogeneous continuous simple shear, produced by either the moving plate at speed V or a force F on the plate. (e) Step strain realized by the displacement of the moving surface by X over a period of t_0 for a gap distance of H, so that $\gamma = X/H$.

1.1.2 Step Strain and Shear Cessation from Steady State

Step strain is the simplest rheological experiment. As shown in Fig. 1.1(e), step strain is a variation of startup deformation, achieved by terminating the displacement in Fig. 1.1(a) after a certain amount of strain, $\gamma = X/H$. This protocol is commonly applied to characterize stress relaxation behavior after shear cessation of viscoelastic materials, including entangled polymeric liquids. Ideally, the step strain should be made to take place instantly. In the experimental reality, it always takes a finite period given by $t_0 = X/V = \gamma/(V/H)$. How short does t_0 need to be to avoid molecular relaxation during step strain? How small does γ need to be to ensure linear response? These questions are discussed in more detail in Section 1.2.7. Relaxation from steady shear is also a valuable protocol, which can be depicted in Fig. 1.1(e) by having $X/H \gg 1$ until steady state is reached. In summary, step strain tests are most often carried out to learn how stress relaxation takes place through molecular diffusion (in linear response regime) and how viscoelastic materials undergo structural changes due to large deformation, to which the entire Part 3 is devoted.

1.1.3 Dynamic or Oscillatory Shear

Oscillatory shear, also known as dynamic shear, is the most frequently applied method to probe viscoelasticity, particularly linear viscoelasticity. Instead of displacing the upper plate with a constant velocity, the top boundary moves according to a sine wave

$$\mathbf{x}(t) = \mathbf{X}_0 \sin \omega t \tag{1.4a}$$

with a velocity of $v(t) = V_0 \cos \omega t$, where $V_0 = X_0 \omega$. In other words, the imposed strain $\gamma(t)$ is a sinusoidal function of time

$$\gamma(t) = \gamma_0 \sin \omega t, \tag{1.4b}$$

where ω is the oscillation frequency so that the period *T* is $2\pi/\omega$, and γ_0 is the amplitude of the oscillatory deformation: $\gamma_0 = X_0/H$. Assuming homogeneous shear, the time-dependent shear rate $\dot{\gamma}(t)$ is simply the time derivative of the right-hand side of Eq. (1.4b):

$$\dot{\gamma}(t) = \gamma_0 \omega \cos \omega t \equiv \dot{\gamma}_0 \cos \omega t, \tag{1.5}$$

where the amplitude $\dot{\gamma}_0$ is given by the product of γ_0 and ω , that is, $\dot{\gamma}_0 = V_0/H$. Here, γ_0 and ω can be varied independently to explore viscoelastic responses.

1.2 Linear Responses

Both ideal elastic solids and viscous liquids are known to exhibit linear response as reviewed in the following paragraphs. Viscoelastic materials can also show linear responses, which may be characterized by the Maxwell and Voigt models. While a low magnitude of strain in stepwise deformation and oscillatory shear ensures linear response, sufficiently low rate of deformation or oscillation frequency is another way to make sure that the elastic structures remain intact during continuous or sinusoidal deformation.

Figure 1.1(a–d) explicitly depicts startup deformation in the displacement-controlled mode of simple shear. A liquid or solid resists the shear so that a finite horizontal force arises along the X axis. In the present case of simple shear, shear stress σ can be defined as the total resistance force on the bottom surface divided by the surface area Σ

$$\sigma_{xy} = F/\Sigma, \tag{1.6}$$

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where σ_{xy} includes the conventional tensorial subscript "xy" to indicate that the force along the direction of shear, that is, along the X axis, is exerted on a plane whose normal is along the Y axis. Throughout this book, we will drop the subscript in σ_{xy} . The unit of stress is force per unit area, in SI units, N/m², which is Pascal (Pa), named after French mathematician Blaise Pascal (1623–1662).

1.2.1 Elastic Hookean Solids

Ideal "perfectly elastic" solids can undergo a finite amount of deformation instantaneously when a stress σ is suddenly applied. At small enough deformations, a linear relationship often exists between the elastic deformation and the stress σ , as studied by Hooke. Let us consider the case of simple shear as illustrated in Fig. 1.1(a). Hookean solids obey a linear relationship

 $\sigma(t) = G\gamma(t), \tag{1.7}$

where G is the elastic modulus. In Fig. 1.2, G is the slope of the inclined straight line. Since the shear strain γ is dimensionless, G has the same dimension as that of stress. Thus, G may be expressed as energy per unit volume as well as force per unit area.

1.2.2 Viscous Newtonian Liquids

Liquids differ from solids in that deformation can proceed indefinitely. A viscous liquid undergoes flow instantly, whereas the flow of viscoelastic liquids (polymeric liquids being the primary example and focus of this book) is preceded by *elastic deformation* during startup deformation. Thus, it should be clear at the onset about the difference between *flow* and *deformation*. Throughout this book, deformation means something general, while flow has a very specific meaning, namely, *irrecoverable* deformation. In contrast to flow, elastic deformation is recoverable: an elastically deformed sample may return to its nondeformed state upon removing the external stress from the sample.

We begin by considering the simplest case of simple shear in viscous liquids. In terms of Fig. 1.1(d), Newton discovered for certain liquids such as water and milk that the force F required to make the upper plate move with velocity V is proportional to V. Since the total F is also proportional to the total area Σ of the top surface in Fig. 1.1(a), it is convenient to use the definition for shear stress given by Eq. (1.6). Newton's law for viscous liquids relates the shear stress σ to the shear rate $\dot{\gamma} = V/H$ depicted in Fig. 1.1(d) as

$$\sigma = n\dot{\gamma}.$$
 (1.8)

Equation (1.8) also gives the basic definition for the viscosity η of liquids. For viscous Newtonian liquids, η is a constant, and Eq. (1.8) holds true at all times, as shown by the horizontal line in Fig. 1.2, starting at the moment when the shear is first applied. Newtonian liquids show *linear response*, as shown in Eq. (1.8), just as elastic solids show linear response, as shown by Eq. (1.7).





Equation (1.8) also explicitly indicates the unit of viscosity: Pa.s. In presenting Eq. (1.8), we assumed that the velocity field is uniform with a constant gradient as depicted in Fig. 1.1(d). While true for Newtonian liquids by definition, the assumption that the velocity gradient is a constant may be wrong for entangled polymeric liquids, except at very low shear rates, which are conditions to be treated in Section 1.2.7. Part 2 will consider whether the linear velocity profile of Fig. 1.1(d) remains true under all different shearing conditions in all systems. Section 4.1.1 discusses the assumption of homogeneous shear as a working principle for rheometric measurements. Chapter 9 shows when this assumption fails.

Viscoelastic Responses 1.2.3

1.2.3.1 Boltzmann Superposition Principle for Linear Response

Equations (1.7) and (1.8) are simplest examples of laws for linear response behavior, where the stress scales linearly with either strain or strain rate, respectively. By analogy with these equations, linear viscoelastic behavior can be generically described by applying the Boltzmann superposition principle, which generalizes the special cases of ideal viscous liquids and elastic solids. The specific phenomenological model for linear viscoelasticity was developed by James Clark Maxwell.

For viscoelastic materials, the concept of elastic modulus, for example, G in Eq. (1.7), is generalized to be time dependent: G(t) is typically a decreasing function of time t. To illustrate viscoelasticity, let us consider a sudden step strain $\Delta \gamma(t_1)$ made over a vanishingly short period of Δt at time t_1 . The sample may deform elastically and resist with a stress increment given by

$$\Delta \sigma(t) = G(t - t_1) \Delta \gamma(t_1), \text{ for } t > t_1.$$
(1.9)

Here, the relaxation modulus G(t) replaces the elastic modulus G that appears in Eq. (1.7). Let us imagine imposing a series of small step strains $\Delta \gamma(t_i)$ at times t_i , i = 1, 2, ..., n, where t_1 can be taken to be the infinite past $(-\infty)$ and t_n defines the present time *t*. Ludwig Boltzmann (1844–1906) recognized that *for linear response* the stress $\sigma(t)$ produced by these consecutive steps of deformation should be additive, leading to^{1,2}

$$\sigma(t) = \sum_{i=1}^{n} G(t - t_i) [\Delta \gamma(t_i) / \Delta t] \Delta t = \int_{-\infty}^{t} G(t - t') \dot{\gamma}(t') dt'.$$
(1.10a)

This formula, known as the Boltzmann superposition principle, offers a general relationship between the strain history and stress, in the linear response regime, for all viscoelastic materials. For startup shear at t = 0 with a constant rate $\dot{\gamma}$, Eq. (1.10a) can be rewritten to show the stress growth as

$$\sigma(t) = \dot{\gamma} \int_{0}^{t} G(s) ds \equiv \dot{\gamma} \eta(t).$$
(1.10b)

This stress increase is related to the relaxation modulus through the integration. The curve labeled "elastoviscous" in Fig. 1.2 illustrates the transition from the initial elastic deformation to the eventual flow state, a transition that we may call "voluntary yielding." In the steady state, the zero-shear viscosity is given by

$$\eta_0 = \frac{\sigma(\infty)}{\dot{\gamma}} = \int_0^\infty G(s) ds.$$
(1.10c)

It can be noted from Eq. (1.10c) that a viscosity can be given as a product of modulus and time.

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1.2.3.2 General Material Functions in Oscillatory Shear

When an oscillatory external deformation, as described by Eqs. (1.4b) (1.5), is imposed onto a viscoelastic material, we can be certain in the linear response regime that the stress should also be oscillatory, given by

$$\sigma(t) \equiv \sigma_0(\omega) \sin[\omega t + \delta(\omega)] = \gamma_0(G' \sin \omega t + G'' \cos \omega t) \equiv G'(\omega)\gamma(t) + \eta'(\omega)\dot{\gamma}(t).$$
(1.11)

Here the introduction of storage and loss moduli $G' = (\sigma_0/\gamma_0) \cos \delta$ and $G'' = (\sigma_0/\gamma_0) \sin \delta$ arises naturally. By definition,

$$\tan \delta \equiv G''/G', \tag{1.12a}$$

and

$$\eta'(\omega) = \mathbf{G}''(\omega)/\omega. \tag{1.12b}$$

By inserting Eq. (1.6) into Eq. (1.10a), we arrive at generic formulas relating the storage and loss moduli to the relaxation modulus G(t):

$$G'(\omega) = \omega \int_{0}^{\infty} G(s) \sin(\omega s) ds$$
(1.13a)

and

$$G''(\omega) = \omega \int_{0}^{\infty} G(s) \cos(\omega s) ds.$$
(1.13b)

These formal relationships imply that G' and G'' provide the same information on the linear viscoelastic characteristics of the system that the relaxation modulus G(t) does. According to Eq. (1.11), the linear stress response to small-amplitude oscillatory shear (SAOS) is a combination of elastic deformation (the first term) and viscous flow (the second term).

1.2.3.3 Stress Relaxation from Step Strain or Steady-State Shear

Stress relaxation after step strain is one of few elementary experiments to probe viscoelastic behavior. Upon sudden imposition of a strain γ that occurs instantaneously at t = 0, that is, as t_0 in Fig. 1.1(e) approaches zero, we measure the residual stress $\sigma(t)$ for $t > t_0 \sim 0$. When γ is sufficiently small, linear response behavior is observed, so that for $t \ge 0$

$$\sigma(t) = \mathcal{G}(t)\gamma. \tag{1.14}$$

The magnitude $\sigma(t)$ of the relaxing stress is linearly proportional to the imposed strain γ . The materials function G(t) is known as the relaxation modulus that first appeared in Eq. (1.10a). In an ideal experiment, the step strain takes place infinitely quickly. A realistic experiment can only impose a finite rate of deformation, that is, X/t_0 in Fig. 1.1(e) is finite rather than infinite. If there is a wide spectrum of relaxation times, then Eq. (1.14) may not hold true because fast relaxation modes may not contribute to G(t). Consequently, if there is a broad spectrum of relaxation times, different (nonideal) relaxation functions $G_{NI}(t)$ can be found, as though linear response were lost despite small step strains that do not alter the internal structure of the system. We will pick up this subtle issue in 1.2.5.2 after the introduction of the generalized Maxwell model in the following section.

1.2.4 Maxwell Model for Viscoelastic Liquids

Long before synthetic polymeric materials have been around, various natural materials were known to possess the duality of viscoelasticity. Molten cheese and chocolate can be viscoelastic.

Figure 1.3 (a) An abstract representation of the Maxwell element, made of a dashpot of viscosity η and spring of modulus G in series. (b) A shear setup made a layer of solid (or liquid) over a layer of liquid (or solid) with thickness H_s and H_i, which mimics the Maxwell model. A top surface displacement of X is a sum of the displacements x_i and x_s associated with the liquid and solid layers, respectively.

Maxwell (1831–1879) is the first to propose a *phenomenological* treatment of viscoelastic phenomena, famously known in the field as Maxwell model. Indeed, a piece of viscoelastic material can be modeled as an assembly of alternating solid and liquid layers. Conventionally, we simply assign a spring with Hookean elastic constant G and a dashpot with viscosity η to depict the Maxwell model,² as shown in Fig. 1.3(a).

Instead of considering a set of spring and dashpot, let us imagine placing a layer of elastic solid of modulus G on top of a liquid layer of viscosity η , as shown in Fig. 1.3(b), or vice versa. Suppose that the upper boundary is displaced with velocity V. Then, the solid layer elastically deforms according to

$$\sigma = G(x_s/H_s), \tag{1.15}$$

and the liquid layer flows as

$$\sigma = \eta(\dot{\mathbf{x}}_l / \mathbf{H}_l),\tag{1.16}$$

because the shear stresses are the same in the two layers. The time derivative of the total displacement X of the upper plate

$$X(t) = x_s + x_l \tag{1.17a}$$

is related to the overall shear rate $\dot{\gamma}$ as $\dot{X}/H \equiv V/H$. Upon differentiating both sides of Eqs. (1.15) and (1.17a), we find by adding both sides of the resulting Eqs. (1.15) and (1.16)

$$\sigma + \tau \dot{\sigma} = 2\eta \dot{\gamma},\tag{1.18}$$

where the Maxwell relaxation time τ is given by

$$\tau = \eta/G, \tag{1.19}$$

which follows upon setting $H_l = H_s = H/2$ so that $\gamma = (\gamma_s + \gamma_l)/2$. In a standard exposition of the Maxwell model, the strain is linearly additive.

$$\gamma = \gamma_s + \gamma_l, \tag{1.17b}$$

that is, $X = \gamma H = x_s(H/H_s) + x_l(H/H_l)$ instead of Eq. (1.17a). In this case, the extra factor $H/H_l = 2$ would not appear on the right-hand side of Eq. (1.18). A construct analogous to Fig. 1.3(b) can be made for uniaxial extension. The same extra factor of 2 also shows up. Apart from this numerical discrepancy, construction of Fig. 1.3(b) offers a concrete way to contemplate viscoelasticity using a combination of purely viscous and purely elastic materials. Here in the Maxwell model, a relaxation time τ naturally emerges from a ratio of viscosity η to modulus G. The Maxwell model of Eq. (1.18) allows us to depict each of the three tests reviewed in Section 1.1.

1.2.4.1 Stress Relaxation from Step Strain

The Maxwell model allows us to depict the essence of a step strain test of magnitude $\gamma = X/H$, which is to evaluate stress relaxation. Since shear ceases at time t_0 as shown in Fig. 1.1(e) in such a test, we can set the right-hand side of Eq. (1.18) to zero for $t > t_0$ and solve this most common



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differential equation for the initial condition given by

$$\sigma(0) = G\gamma(H/H_s). \tag{1.20}$$

The solution is an exponential function:

$$\sigma(t) = \sigma(0) \exp(-t/\tau), \text{ for } t > t_0.$$
(1.21a)

The "instantaneous" strain γ is imposed on the solid layer during a time scale $t_0 \ll \tau$; for the liquid layer to suffer the strain γ would correspond to emergence of a stress level larger than $\sigma(0)$ in Eq. (1.20) by a factor of $(\tau/t_0) \gg 1$, which could not feasibly occur. The condition of $t_0 \ll \tau$ translates to $\gamma/Wi \ll 1$, where the dimensionless parameter $Wi = \dot{\gamma}\tau$ is the Weissenberg number (to be formally introduced in Section 1.2.7). As long as $\gamma \ll 1$, the condition for instantaneous strain can be met for Wi > 1. During the step strain, the liquid layer experiences little flow: the amount of strain taking place in the liquid layer can be estimated to be $\gamma_l \sim \dot{\gamma}_l t_0 \sim \gamma(t_0/\tau) \ll \gamma$, where use is made of $\eta \dot{\gamma}_l \sim G\gamma$. Defining the relaxation modulus G(t) as shown in Eq. (1.14), we have, according to Eqs. (1.20) and (1.21a),

$$G(t) = G \exp(-t/\tau), \tag{1.21b}$$

whereas the factor of (H/H_s) was omitted if we adopt the familiar convention, that is, using Eq. (1.17b) instead of Eq. (1.17a). Because according to Eq. (1.21a) the stress decreases to zero exponentially, the Maxwell model cannot describe viscoelastic solids. This should also be obvious from the construction of the model depicted in Fig. 1.3.

1.2.4.2 Startup Deformation

Taking the case of simple shear, according to the Maxwell model, viscoelastic materials must always initially undergo elastic deformation upon a startup shear for any values of *Wi*. This can be demonstrated by equating Eqs. (1.15) with (1.16) and expressing x_s in terms of x_l through Eq. (1.17a) to obtain the following equation for x_l :

$$\mathbf{x}_l + \tau \dot{\mathbf{x}}_l = \mathbf{X}(t),\tag{1.22}$$

which is similar in the form to Eq. (1.18) for σ . It is straightforward to solve this elementary differential equation, given the initial condition $x_l(t=0) = 0$, which states that the liquid layer suffers no deformation at t = 0. We have

$$\mathbf{x}_{l}(t) = \mathbf{X}(t)\{1 + [\exp(-t/\tau) - 1]/(t/\tau)\},\tag{1.23a}$$

where X(t) = Vt as shown in Fig. 1.1(b). It is clear that as long as $t/\tau \ll 1$ we have, upon Taylor expansion, $x_l(t) \sim X(t)(t/2\tau)$, that is, $x_l/X \sim t/\tau \ll 1$, independent of $Wi = \dot{\gamma}\tau$. Numerically, we see from Fig. 1.4(a) that x_l is only 10% of the total displacement x(t) at $t = 0.2\tau$. The condition of $x_l/x \ll 1$ implies the lack of flow and dominance of elastic deformation.

Accompanying the initial elastic deformation, stress rises from zero instead of having a finite value from the onset. It is easy to integrate Eq. (1.18) or to insert Eq. (1.21b) into Eq. (1.10a) and show both stress growth upon startup and stress relaxation after shear cessation, by setting $\dot{\gamma}(t)$ as $\dot{\gamma}$ for $t < t_1$ and 0 for $t > t_1$, respectively. Specifically, we have the stress growth given by

$$\sigma = \sigma_{\infty} [1 - \exp(-t/\tau)] \text{ for } t < t_1$$
(1.23b)

and the stress relaxation given by

$$\sigma = \sigma_{\infty} \{ [\exp[-(t - t_1)/\tau] - \exp(-t/\tau)] \} \text{ for } t > t_1,$$
(1.23c)

where $\sigma_{\infty} = \eta \dot{\gamma}$ is the steady shear stress. Experiment reveals that many types of viscoelastic liquids, including entangled polymer melts and solutions, show initial elastic response to startup



Figure 1.4 (a) Illustration of Eq. (1.23a). (b) Maxwell model's depiction of stress growth and relaxation (dashed curve) according to Eqs. (1.23b) and (1.23c), respectively.

shear, followed by flow at long times. This initial elastic strain γ grows with *Wi*. In the Maxwell model, the stress σ also initially grows with strain as shown by Eq. (1.23b) in Fig. 1.4(b). Thus, the Maxwell model qualitatively captures the initial rheological response of entangled polymers. On the other hand, being a model for linear response, the Maxwell model cannot anticipate and depict how the relation between stress and strain depends on *Wi*. According to Fig. 1.4(b), the initial stress growth associated with elastic deformation persists for a strain that is proportional to *Wi*. Viscoelastic fluids such as entangled polymers cannot remain elastic for a strain that linearly increases with *Wi*. Thus, the Maxwell model cannot describe fast deformation behavior at high strains.

The Maxwell model prescribes a smooth transition from elastic deformation to flow for any value of Wi. Thus, even Maxwell-like materials should show a sign of (voluntary) yielding. In the steady-shear limit, that is, $t/\tau \gg 1$, the solid component in the Maxwell element of Fig. 1.3(b) suffers a fixed amount of deformation $x_s(\infty) = X(\infty) - x_l(\infty) = V\tau$, corresponding to $\sigma_{\infty} = G(x_s/H_s) = (H/H_s)G(\tau \dot{\gamma}) \sim \eta \dot{\gamma}$. This depiction is reasonably close to reality for $Wi \ll 1$. But for Wi > 1, there is something missing in the Maxwell model: Rewriting Eq. (1.23b) as $\sigma = GWi[1 - \exp(-t/\tau)]$, we see σ/G becoming Wi at $t/\tau > 1$, that is, σ getting much larger than G for $Wi \gg 1$. This unphysical situation occurs because for $Wi \gg 1$ the Maxwell model is incapable of describing when and how elastic deformation is replaced by irrecoverable deformation, which is flow. To delineate the nature of the transition from elastic deformation to flow is the main focal point of this book. In solid mechanics, yielding refers to a material transitioning from elastic deformation to plastic deformation. If we do not distinguish between plastic deformation and flow and simply label them as irrecoverable deformation and if we can extend the concept of yielding to refer to a transition from elastic deformation to irrecoverable deformation, then we can legitimately use the phrase yielding to speak about the rheological behavior of any viscoelastic liquids, including entangled polymeric liquids.

1.2.4.3 Oscillatory (Dynamic) Shear

The stress response of an elastic solid to a strain sine wave is also a sine wave, while the stress response of a viscous liquid to a strain sine wave is a cosine wave. Viscoelastic materials will display a sinusoidal stress in steady state as indicated in Eq. (1.11), provided that γ_0 is low enough so that σ_0 is linearly proportional to γ_0 . When the "phase lag" angle δ is vanishingly small, we see a solid-like response. Conversely, when δ is almost $\pi/2$, $\sigma(t)$ is nearly a cosine function and therefore in phase with the shear rate of Eq. (1.5), so the sample behaves like a liquid.

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The Maxwell model has a specific quantification of how $\delta(\omega)$ and $\sigma_0(\omega)$ in Eq. (1.11) depend on ω . As shown in a standard textbook on viscoelasticity,³ Eq. (1.18) can be readily solved using complex variable notation to obtain the functional forms of δ and σ_0 . We may also perform the analysis in real variables. Inserting Eqs. (1.5) and (1.11) into Eq. (1.18), we have

$$\sigma_0(\omega)[\sin(\omega t + \delta) + \omega\tau\cos(\omega t + \delta)] = \gamma_0 G\omega\tau\cos\omega t, \qquad (1.24)$$

where we ignore the extra factor of H/H_l from Eq. (1.18) to conform to the conventions used in the Maxwell model. Since there cannot be a term proportional to $\sin \omega t$ on the left-hand side of Eq. (1.24), we immediately find, by expanding the sine and cosine functions,

$$\tan \delta = 1/\omega\tau. \tag{1.25}$$

This equation implies $1 = \sin \delta \sqrt{1 + (\omega \tau)^2}$ and $\omega \tau = \cos \delta \sqrt{1 + (\omega \tau)^2}$, which can be, respectively, substituted into the left-hand side of Eq. (1.24) in front of each of the two terms giving a summation of $[\sin \delta \sin(\omega t + \delta) + \cos \delta \cos(\omega t + \delta)] = \cos \omega t$. This substitution allows us to determine σ_0 as

$$\sigma_0(\omega) = \frac{\gamma_0 G\omega\tau}{\sqrt{1 + (\omega\tau)^2}} \equiv \gamma_0 |G^*|, \qquad (1.26)$$

where $G^* = G' + iG''$ is known as the complex modulus. According to the second equality of Eq. (1.11), the storage and loss moduli G' and G'' are simply related to σ_0 as

$$G' = [\sigma_0(\omega)/\gamma_0] \cos \delta = G(\omega \tau)^2 / [1 + (\omega \tau)^2]$$
(1.27a)

and

$$\mathbf{G}'' = [\sigma_0(\omega)/\gamma_0] \sin \delta = \mathbf{G}(\omega \tau)/[1 + (\omega \tau)^2]. \tag{1.27b}$$

Here, the first equality holds true in general. The second two equalities represent a specific prediction of the Maxwell model. The specific predictions can also be derived by inserting Eq. (1.21b) into the generic expressions Eqs. (1.13a) and (1.13b).

Figure 1.5 depicts G' and G'' from Eqs. (1.27a) and (1.27b) as functions of ω . Depending on the imposed frequency ω , a Maxwellian material may behave like a solid displaying a rubbery plateau or a liquid showing a negligible G'. Such a material may be truly regarded as a solid as long as it is being mechanically examined on time scales much shorter than τ . Note that Eq. (1.11) gives the time-dependent stress in steady state. The initial transient response is not depicted by Eq. (1.11).

1.2.5 General Features of Viscoelastic Liquids

1.2.5.1 Generalized Maxwell Model

The Maxwell model offers a most useful and simplest phenomenological continuum-level description of viscoelastic liquids that possess a dominant relaxation time. In reality, a viscoelastic liquid may possess more than one elementary relaxation time. A generalized Maxwell



Figure 1.5 Schematic illustration on double-log of the Maxwell model description of the storage and loss moduli G'' and G'' as a function of the oscillation frequency ω . For $\omega \tau \ll 1$, G' $\sim \omega^2$ and G'' $\sim \omega$ and G' = G'' at $\omega \tau = 1$.

model² can be useful to describe linear viscoelastic processes in real systems. In particular, the storage and loss moduli G', G" in the generalized Maxwell model have the following forms:

$$G'(\omega) = \sum_{q=1}^{\infty} \frac{G_q(\omega\tau_q)^2}{1 + (\omega\tau_q)^2}$$
(1.28)

and

$$G''(\omega) = \sum_{q=1}^{\infty} \frac{G_q \omega \tau_q}{1 + (\omega \tau_q)^2},$$
(1.29)

where $\{\tau_q\}$ gives a spectrum of relaxation times. Conventionally, q = 1 represents the longest relaxation time, with shorter time τ_q involving a larger number q > 1. Moreover, the relaxation modulus G(t) is a summation of exponential functions

$$G(t) = \sum_{q=1}^{\infty} G_q \exp(-t/\tau_q).$$
(1.30)

Finally, the Newtonian viscosity η_0 of a generalized Maxwellian liquid is given by

$$\eta_0 = \sum_{q=1}^{\infty} G_q \tau_q, \tag{1.31}$$

which can be obtained by inserting Eq. (1.30) into the Boltzmann formula Eq. (1.10a). As we will see, most molecular models for polymer dynamics also share the same mathematical forms as given in Eqs. (1.28)–(1.31). Since the generalized Maxwell model is a phenomenological account, it cannot explain the molecular origin of the viscoelastic behavior, for example, it cannot determine how τ_q may depend on the chain length or molecular weight and how it varies with the mode index q and where the elasticity arises from.

1.2.5.2 Lack of Linear Response in Small Step Strain: A Dilemma

In realistic experiments, it takes a finite time to produce a step strain of magnitude γ_0 . During t_0 , fast relaxation modes compete with the imposed straining. The shorter the duration t_0 , the less relaxation of the fast modes can take place. Step strain in real experiments amounts to shearing a sample for a very short time t_0 at high rate $\dot{\gamma}$ to a magnitude of $\gamma = \dot{\gamma}t_0$ before shear cessation at t = 0. Inserting this step strain condition and Eq. (1.30) into Eq. (1.10a), we have

$$\sigma(t) = \dot{\gamma} \sum_{q=1}^{\infty} G_q \tau_q [1 - \exp(-t_0/\tau_q)] \exp(-t/\tau_q), \text{ for } t \ge 0.$$
(1.32)

Thus, the relaxation modulus G_{NI} under the nonideal but realistic step strain condition follows from Eq. (1.32)

$$G_{\rm NI}(t,\gamma_0) = \sigma(t)/\dot{\gamma}t_0 = \sum_{q=1}^{\infty} G_q \exp(-t/\tau_q) f(t_0/\tau_q),$$
(1.33)

where the function $f(x) = (1 - e^{-x})/x$ decreases monotonically from unity at x = 0 toward zero. Equation (1.33) differs from the ideal relaxation modulus G(t) of Eq. (1.30) and is an explicit function of t_0/τ_q . When t_0/τ_q is not vanishingly small, the higher relaxation mode q makes a smaller contribution to the overall stress relaxation because f is unity only in the limit of $t_0/\tau_q = \gamma/(\dot{\gamma}\tau_q) \ll 1$. In other words, $G_{\rm NI}$ approaches Eq. (1.30) only when $t_0/\tau_q \ll 1$ for all the contributing modes indexed by q. Thus, when the relaxation dynamics are dictated by a series of time scales, $G_{\rm NI}$, obtained from small step-strain with $\gamma \ll 1$, is explicitly dependent on