

M. Anandha Rao

Rheology of Fluid AND Semisolid Foods

PRINCIPLES AND APPLICATIONS

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Rheology of Fluid and Semisolid Foods

Principles and Applications

M. Anandha Rao, PhD

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Cornell University
Geneva, New York

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*To Jan
for her unlimited and unconditional love;
and Hari
for bringing much joy into my life.*

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Preface

Considering that the science of rheology of fluid and semisolid foods has advanced considerably during the past few decades, food professionals need to appreciate the basic principles of rheological behavior and proper measurement of rheological properties, as well as the influence of composition and structure on those properties. Fluid and semisolid foods encompass a wide range of composition and structure and exhibit rheological behavior, including simple Newtonian, shear-thinning, shear-thickening, time-dependent shear-thinning and shear-thickening, as well as viscoelastic behavior. In addition, many manufactured solid foods are often in a fluid state at some stage during their manufacture; thus, rheological changes during phase transitions are also important. A sound appreciation of food rheology should be helpful in quality control and product development of foods. This book is intended to be an introduction to the science of the rheology of fluid foods and its application to practical problems.

One goal of this book is to introduce to interested students and scientists the principles of rheological behavior (Chapter 1), rheological and functional models applicable to fluid foods (Chapter 2), and measurement of the viscous and viscoelastic rheological behavior of foods (Chapter 3). The first three chapters cover the basic principles necessary to understand food rheology, to conduct rheological experiments, and to interpret properly the results of the experiments. They also contain many functional relationships that are useful in understanding the rheological behavior of specific foods. The science of rheology is based on principles of physics of deformation and flow, and it requires a reasonable knowledge of mathematics. Readers are urged to refresh their mathematics and physics backgrounds to understand the importance of several functional relationships. The science of rheology has been touched on by many eminent scientists, including Newton, Maxwell, Kelvin, Reiner, Einstein (1921 physics Nobel laureate), Flory (1974 chemistry Nobel laureate), de Gennes (1991 physics Nobel laureate), and Chu (1997 physics Nobel laureate).

Rheological behavior of food gum and starch dispersions is covered in Chapter 4 and that of many processed foods is covered in Chapter 5, with emphasis on the important developments and relationships with respect to the role of composition and structure on rheological behavior. In Chapter 4, the rheological changes taking place during starch gelatinization as a result of changes in starch granule size

are covered. In both Chapters 4 and 5, generally applicable results are presented. At the end of Chapter 5, an extensive compilation of literature values of the rheological properties of fluid foods is also provided, along with the experimental techniques and ranges of important variables covered in a specific study.

Novel and important applications of rheology to food gels and gelation phenomena are covered in Chapter 6. In this chapter, the pioneering studies of Paul Flory and Pierre de Gennes are introduced. Many foods are gel systems, so the theoretical and practical aspects of these subjects are important and useful in understanding the role of gelling polymers on rheological properties of homogeneous and phase-separated gel systems.

Every food professional should recognize that sensory assessment of foods is important. Chapter 7 covers the role of rheological behavior in the sensory assessment of viscosity and flavor of fluid foods. It should be noted that food rheologists have made many unique contributions to sensory assessment of viscosity.

Lest one ignore the important role of rheological behavior and properties of fluid foods in handling and processing foods, these are covered in Chapter 8, including applications under isothermal conditions (pressure drop and mixing) and under nonisothermal conditions (heat transfer: pasteurization and sterilization). In particular, the isothermal rheological and nonisothermal thermorheological models discussed in Chapter 3 and 4 are applied in Chapter 8.

Last but not least, I thank Paul Okechukwu and José Antonio Lopes da Silva for collaborating in Chapters 5, 6, and 7. I am very grateful to the many graduate students and visiting scientists who have worked with me and contributed to my better understanding of rheology of fluid and semisolid foods. Several references listed at the end of each chapter are studies conducted with my students, who have made valuable contributions. Herb Cooley has helped me with many figures used in this book and in the conduct of several studies in my laboratory. Many persons have helped me during my career, especially my professor at Ohio State, Bob Brodkey, and my colleagues, Alfredo A. Vitali, ITAL, Brazil, and Ashim Datta, Cornell. I thank the editors at Aspen Publishers, Inc., for their invaluable help. Any mistakes in this book are mine.

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CHAPTER 1

Introduction

M. Anandha Rao

By definition, rheology is the study of the deformation and flow of matter. The science of rheology grew considerably due to research work done on synthetic polymers and their solutions in different solvents, which, in turn, was necessary due to the many uses of the polymers ("plastics") in day-to-day and industrial applications. Nevertheless, because of the biological nature of foods, food rheology offers many unique opportunities of study and a large body of food rheology literature exists. Rheological properties are based on flow and deformation responses of foods when subjected to stress. A thorough study of the rheology of fluid foods requires knowledge of tensors and the basic principles of fluid flow, such as the equation of continuity (conservation of mass) and the equation of motion (conservation of momentum). The necessary basic equations can be derived (Bird et al., 1960; Macosko, 1994) by conducting a balance of either mass or momentum on a stationary volume element of finite dimensions (e.g., Δx , Δy , Δz in rectangular coordinates) through which the fluid is flowing.

$$\text{Input} + \text{Generation} = \text{Output} + \text{Accumulation} \quad (1.1)$$

Because mass is not generated, in the derivation of the equation of continuity, the second term on the left-hand side of Equation 1.1 can be omitted. The applicable partial differential equations are obtained in the limit as the dimensions of the control volume tend to zero. The primary objective here is to point out to readers the origins of useful relationships and the assumptions made in deriving them. Appendix 1-A presents the equation of continuity and the equations of motion in Cartesian, cylindrical, and spherical coordinates; however, for the actual derivation of the transport equations, the aforementioned references should be consulted. The use of some of these equations in deriving equations for specific measurement geometries will be illustrated in Chapter 3 and in processing applications in Chapter 8. In vector and tensor form, the transport equations are quite concise (Appendix 1-A).

Foods can be classified in different manners, including as solids, gels, homogeneous liquids, suspensions of solids in liquids, and emulsions. Fluid foods are those that do not retain their shape but take the shape of their container. Fluid foods that contain significant amounts of dissolved high molecular weight compounds (polymers) and/or suspended solids exhibit non-Newtonian behavior. Many non-Newtonian foods also exhibit both viscous and elastic properties, that is, they exhibit viscoelastic behavior.

Fluid and semisolid foods exhibit a wide variety of rheological behavior ranging from Newtonian to time dependent and viscoelastic. Fluid foods containing relatively large amounts of dissolved low molecular weight compounds (e.g., sugars) and no significant amount of a polymer or insoluble solids can be expected to exhibit Newtonian behavior. A small amount ($\sim 1\%$) of a dissolved polymer can substantially increase the viscosity and also alter the flow characteristics from the Newtonian behavior of water to the non-Newtonian behavior of an aqueous dispersion. It is interesting to note that whereas the rheological properties are altered substantially, magnitudes of the thermal properties (e.g., density and thermal conductivity) of the dispersion remain relatively close to those of water. Further, with one or two exceptions, for example, food polymer dispersions, it is difficult to predict precise magnitudes of viscosity of fluid foods, mainly because foods are complex mixtures of biochemical compounds that show a wide variation in composition. Therefore, studies on rheological properties of foods are useful and important for applications that include handling and processing, quality control, and sensory assessment of foods. The latter is an important field of study to which food scientists have made significant contributions.

When studying the rheological behavior of a food, knowledge of the composition of the food, especially the important structuring components (e.g., dissolved polymers, suspended solids), the structure of the food itself (e.g., homogeneous or phase-separated gel, emulsion), and the processing and storage conditions would be helpful because they all often affect the behavior. In dispersions, however, the structure of the food particles plays a major role in defining the rheological behavior. Either large molecules or finely subdivided bulk matter could be considered to be colloidal matter; that is, the particles are in the range 10^{-9} to 10^{-6} m in dimension. Therefore, principles of colloidal science are also useful in understanding the rheological behavior. For example, colloids can be classified as lyophilic (solvent loving) or lyophobic (solvent fearing), and when the solvent is water they are called hydrophilic and hydrophobic, respectively.

The classification of rheological behavior and the measurement of rheological properties of fluid foods were reviewed by Sherman (1970), Ross-Murphy (1984), Rao (1992, 1995), Steffe (1996), and others. In addition to these references, one must consult books on synthetic polymer rheology for valuable information on viscoelastic behavior, measurement techniques, and the role of fundamental prop-

erties such as molecular weight on viscoelastic behavior. In particular, the texts by Bird et al. (1977a, 1977b), Ferry (1980), and Tschoegl (1989) have much useful information on viscoelasticity. Barnes et al. (1989) discussed rheology in a lucid manner. Techniques for measuring rheological properties, especially flow properties, were well covered by Van Wazer et al. (1963) and those of viscoelastic properties by Walters (1975), Whorlow (1980), Dealy (1982), and Macosko (1994). An examination of the early efforts would provide an education on the innovations in experimental techniques and developments in interpretation of rheological behavior. In this respect, a review (Markovitz, 1985) of the studies conducted soon after the Society of Rheology was formed provides a fascinating picture of the development of the science of rheology. While one should appreciate the ease with which many rheological measurements can be performed today, primarily due to the availability of powerful desktop computers, it is essential that food rheologists really understand the underlying principles in rheological measurements and interpretation of results. In addition, low-friction compressed-air bearings, optical deformation measurement systems, and other developments also have contributed to measurements on foods and other low viscosity materials.

STRESS AND STRAIN TENSORS

While scalar quantities have magnitudes, vectors are defined in terms of both direction and magnitude and have three components. Tensors are second-order vectors and have nine components. In a Cartesian system of coordinates, a stress tensor ($\tilde{\tau}$) of force imposed on unit surface area of a test material can be resolved in terms of nine components (σ_{ij}): three normal and six tangential stresses. In simple shearing (viscometric) flow that is encountered in the flow geometries (capillary, Coette, cone-and-plate, and parallel plate), $\sigma_{12} = \sigma_{21}$, while the other four tangential components, σ_{13} , σ_{23} , σ_{31} , and σ_{32} , are equal to zero, so the stress tensor may be written as

$$\tilde{\tau} = \begin{vmatrix} \sigma_{11} & \sigma_{12} & 0 \\ \sigma_{21} & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{vmatrix} \quad (1.2)$$

The stresses, σ_{11} , σ_{22} , and σ_{33} are normal stresses that are equal to zero for Newtonian fluids and may be of appreciable magnitudes for some foods, such as doughs. The components of the deformation tensor, $\tilde{\epsilon}$, in viscometric flows are

$$\tilde{\epsilon} = \begin{vmatrix} 0 & \dot{\gamma} & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix} \quad (1.3)$$

where $\dot{\gamma}$ is the shear rate.

Rheological properties of food materials over a wide range of phase behavior can be expressed in terms of viscous (viscometric), elastic, and viscoelastic functions that relate some components of the stress tensor to specific components of the strain or shear rate response. In terms of fluid and solid phases, viscometric functions are generally used to relate stress with shear rate in liquid systems, while elastic functions are related to the appropriate stress function to strain in solids. Viscoelastic properties cover the combination where a material exhibits both viscous and elastic properties.

VISCOMETRIC PROPERTIES

Three material functions—the viscosity function, η , and the first and second normal stress coefficients, Ψ_1 and Ψ_2 —can be evaluated from the stress tensor using Equations 1–4 through 1–6, which relate specific stress components σ_{ij} to the shear rate $\dot{\gamma}$:

$$\sigma_{21} = \eta(\dot{\gamma}) \quad (1.4)$$

$$\sigma_{11} - \sigma_{22} = \Psi_1(\dot{\gamma})^2 \quad (1.5)$$

$$\sigma_{22} - \sigma_{33} = \Psi_2(\dot{\gamma})^2 \quad (1.6)$$

Steady state experiments employing rotational, capillary, and tube flow viscometers are commonly used to generate data for evaluation of these material properties. Reported values of the viscometric coefficients for many materials, especially synthetic polymers, indicate that η and Ψ_1 are large and positive, whereas Ψ_2 is small and negative (Macosko, 1994). While the first normal stress difference is known to be responsible for the climbing fluid film phenomenon often referred to as the “Weissenberg effect,” extrudate swell, and normal force pump, the second normal stress difference determines where the free surface of a fluid flowing down a trough would be convex (Barnes et al., 1989; Macosko, 1994). Typical magnitudes of Ψ_1 of foods are shown in Figure 1–1 (Dickie and Kokini, 1982).

Most rheological studies have concentrated on the viscosity function and dynamic viscoelastic properties and much less on normal stress differences (Rao, 1992). Since about the mid 1960s, there has been a gradual paradigm shift from normal stresses to dynamic rheological properties as measures of viscoelastic properties. One reason for the shift appears to be the difficulties in obtaining reliable magnitudes of normal stresses and, compared to dynamic rheological properties, their limited practical application. Another reason is that with the availability of automated rheometers, measurement of dynamic rheological parameters has become very popular and manageable. Therefore, one rarely encounters data on normal stress functions of foods.

The relationships between stress and strain, and the influence of time on them, are generally described by constitutive equations or rheological equations of state

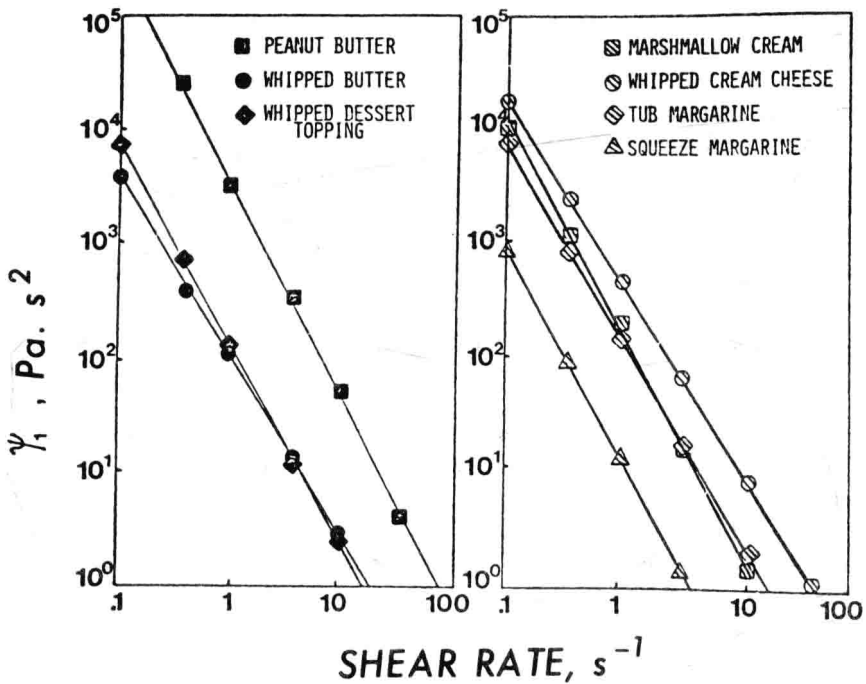


Figure 1-1 First Normal Stress Coefficient Data of Several Foods as a Function of Shear Rate. Source: Reprinted with permission from A.M. Dickie and J.L. Kokini, Use of the Bird-Leider Equation in Food Rheology, *Journal of Food Processing and Engineering*, Vol. 5, pp. 157-184. © 1981, Food and Nutrition Press.

(Ferry, 1980). When the strains are relatively small (i.e., in the linear range), the constitutive equations are relatively simple. Equations 1.5 and 1.6 are constitutive equations of viscoelastic behavior under continuous shear (nonlinear range). In the limit of low strains, relationships exist between the above material functions and those obtained from dynamic and creep experiments. Constitutive equations will be discussed further in Chapter 4.

SHEAR STRESS-SHEAR RATE RELATIONSHIPS

To study rheological properties of foods in a systematic manner, it is convenient to first learn the principles of rheological behavior of fluid and solid foods. Viscosity data must be obtained with well-designed viscometers and be expressed in fundamental units. Viscosity data in units that are specific to a particular brand