Rheology of Fluid and Semisolid Foods
Principles and Applications

Second Edition
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Rheology of Fluid and Semisolid Foods
Principles and Applications
Second Edition

M. Anandha Rao
Department of Food Science and Technology
Cornell University
Geneva, NY, USA
To Jan
   for her unlimited and unconditional love;
   and Hari for bringing much joy into my life.
To my late father
   who made sacrifices so that I could study.
Preface to the First Edition

Considering that the science of rheology of fluid and semisolid foods has advanced considerably during the past few decades, it is educational for food professionals to appreciate the basic principles of rheological behavior and proper measurement of rheological properties, as well as the influence of composition and structure on the 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, often, many manufactured solid foods are 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 text is intended to be an introduction to the science of the rheology of fluid foods and its application to practical problems.

One goal in writing 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 science of rheology is based on principles of physics of deformation and flow, and requires a reasonable knowledge of mathematics. Thus these 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. 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 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 Steven Chu (1997 physics Nobel laureate).

Rheological behavior of food gum and starch dispersions are covered in Chapter 4 and that of many processed foods are 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 that 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. Therefore in Chapter 7, the role of rheological behavior in the sensory assessment of viscosity and flavor of fluid foods is covered. 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, they are covered in Chapter 8. Here, the topics covered include applications under isothermal conditions (pressure drop and mixing) and under non-isothermal conditions (heat transfer: pasteurization and sterilization). In particular, the isothermal rheological and nonisothermal thermorheological models discussed in Chapters 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 of 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. The mistakes in this book are mine and I hope that many of them can be corrected in a future edition.

M. Anandha Rao, PhD
Department of Food Science and Technology
Cornell University
Geneva, NY, USA
December 8, 1998
Preface to the Second Edition

Following the very good acceptance of the first edition of *Rheology of Fluid and Semisolid Foods: Principles and Applications*, it is a pleasure to present the second edition.

Again, the book is divided into eight chapters: Chapter 1—Introduction: Food Rheology and Structure, Chapter 2—Flow and Functional Models for Rheological Properties of Fluid Foods, Chapter 3—Measurement of Flow and Viscoelastic Properties, Chapter 4—Rheology of Food Gum and Starch Dispersions, Chapter 5—Rheological Behavior of Processed Fluid and Semisolid Foods, Chapter 6—Rheological Behavior of Food Gels, Chapter 7—Role of Rheological Behavior In Sensory Assessment of Foods and Swallowing, and Chapter 8—Application of Rheology to Fluid Food Handling and Processing.

Many changes and additions have been incorporated in this edition. In fact, every chapter has been revised. These revisions should help readers better appreciate the important role rheological properties play in food science as well as to utilize them to characterize foods. Some of the new topics covered in the second edition include:

Chapter 1. Role of structure/microstructure, glass transition, and phase diagram.
Chapter 2. Structural analyses and structure-based models.
Chapter 3. In-plant measurement of flow behavior of fluid foods. Using a vane-in-a-cup as a concentric cylinder system. The vane yield stress test can be used to obtain data at small- and large-deformations. Critical stress/strain from the non-linear range of a dynamic test. Relationships among rheological parameters. First normal stress difference and its prediction.
Chapter 4. Yield stress of starch dispersions, and network and bonding components, effect of sugar on rheology of starch dispersion, and rheology of starch-gum dispersions.
Chapter 5. Structural analyses and structure-based models of processed foods are discussed. In addition, in Appendix A, data on milk concentrates and viscoelastic properties of tomato concentrates were added.
Chapter 6. Besides strengthening the coverage on dissolved-polymer gels, a section was added on theoretical treatment of starch gels as composites of starch granules in an amylose matrix.
Chapter 8. Heat transfer in continuous flow sterilization and to canned foods under intermittent agitation.

I am grateful to the USDA-NRI, various companies, and international scientific agencies for supporting my research. I am very grateful to the 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 of studies conducted with my students who have made valuable contributions. I thank Paul Okechukwu and José A. L. da Silva for collaborating in Chapters 5, 6, and 7. Many persons have helped me during my career, especially my professor at Ohio State, Bob Brodkey, and my colleague, Alfredo A. Vitali, ITAL, Brazil. The mistakes in this book are mine and I hope that many of them can be corrected in a future edition.

M. Anandha Rao, PhD
Department of Food Science and Technology
Cornell University
Geneva, NY, USA
December 26, 2006
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Contributors

M. Anandha Rao, Ph.D. Department of Food Science and Technology Cornell University Geneva, New York

J.A. Lopes da Silva, Ph.D. Department of Chemistry University of Aveiro 3810-193 Aveiro, Portugal

Paul E. Okechukwu, Ph.D. Anambra State Polytechnic Oko, Anambra State, Nigeria
By definition, rheology is the study of 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 that 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 there exists a large body of food rheology literature. Many foods are composed mainly of biopolymers and aqueous solutions containing dissolved sugars and ions. The former are large molecules, often called macromolecules, such as proteins, polysaccharides, and lipids from a wide range of plant and animal sources. In addition, water is an important component in many foods and plays a major role in the creation of edible structures and their storage stability (Rao, 2003). Processed foods may be viewed as edible structures that are created as a result of the responses of proteins, polysaccharides, and lipids in aqueous media to different processing methods, such as thermal processing, homogenization, and other physical treatments. Most, if not all, of those responses are physical in nature. The measured rheological responses are those at the macroscopic level. However, they are directly affected by the changes and properties at the microscopic level (Rao, 2006). Thus, it would be helpful to understand the role of structure of foods on their rheological behavior.

Rheological properties are based on flow and deformation responses of foods when subjected to normal and tangential stresses. 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 of fluid flow can be derived (Bird et al., 1960) by conducting a balance of either mass or momentum on a stationary volume element of finite dimensions (e.g., $\Delta x$, $\Delta y$, $\Delta z$ 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, and present the equation of continuity in Appendix 1–A, and the equation of motion in cartesian, cylindrical, and spherical coordinates in Appendixes 1–B, 1–C, and 1–D, respectively; 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 (~1%) of a dissolved polymer can substantially increase the viscosity and also alter the flow characteristics from Newtonian of water to non-Newtonian of the 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, such as that of food polymer dispersions, it is difficult to predict precisely the magnitudes of the viscosity of fluid foods mainly because foods are complex mixtures of biochemical compounds that exhibit a wide variation in composition and structure. 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.

The classification of rheological behavior and the measurement of rheological properties of fluid foods were reviewed among others by Sherman (1970), Ross-Murphy (1984), Rao (1977a, 1977b, 2005), Rao and Steffe (1992), 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 on the role of fundamental properties 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 experimental efforts covered in Van Wazer et al. (1963) would be educational for 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 also 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 desk-top computers, it is essential that food rheologists 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 \( \mathbf{\tau} \) of force imposed on unit surface area of a test material can be resolved in terms of nine components \( (\sigma_{ij}) \), three normal and six tangential stresses. In simple shearing (viscometric) flow that is encountered in the flow geometries: capillary, Couette, cone-and-plate, and parallel plate, \( \sigma_{12} = \sigma_{21} \) while the other four tangential components, \( \sigma_{13}, \sigma_{23}, \sigma_{31}, \) and \( \sigma_{32} \) are equal to zero, so that the stress tensor may be written as:

\[
\mathbf{\tau} = \begin{bmatrix}
\sigma_{11} & \sigma_{12} & 0 \\
\sigma_{21} & \sigma_{22} & 0 \\
0 & 0 & \sigma_{33}
\end{bmatrix}
\] (1.2)

The stresses, \( \sigma_{11}, \sigma_{22}, \) and \( \sigma_{33} \) 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, \( \mathbf{\varepsilon} \), in viscometric flows are:

\[
\mathbf{\varepsilon} = \begin{bmatrix}
0 & \dot{\gamma} & 0 \\
\dot{\gamma} & 0 & 0 \\
0 & 0 & 0
\end{bmatrix}
\] (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 which 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.
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 understand rheological properties of foods in a systematic manner, it is convenient to first study the principles of rheological behavior of fluid and solid foods. Viscosity data must be obtained with well designed viscometers and expressed in fundamental units. Viscosity data in units that are specific to a particular brand viscometer, such as the time to flow out of a specific cup or the manufacturer’s arbitrary viscosity, will not be applicable universally, and the viscosity values are of limited value. Viscosity is best determined using geometries in which the shear rate can be calculated from the dimensions of the measuring system and experimental data, such as the velocity or volumetric flow rate of a fluid or the rotational speed of a rotating cylinder, cone or plate. In general, the determination of stress corresponding to the shear rates is not very difficult. However, calculation of applicable shear rate requires effort. Unfortunately,
there have been too many instances in which such effort has not been expended. In addition to the dynamic viscosity determined in shear fields, one can also determine viscosity in extensional shear fields (Padmanabhan, 1995) as discussed later.

**UNITS IN RHEOLOGICAL MEASUREMENT**

Shear Rate, denoted by the symbol, \(\dot{\gamma}\), is the velocity gradient established in a fluid as a result of an applied shear stress. It is expressed in units of reciprocal seconds, \(s^{-1}\). Shear Stress is the stress component applied tangentially. It is equal to the force vector (a vector has both magnitude and direction) divided by the area of application and is expressed in units of force per unit area (Pa). The nomenclature committee of the Society of Rheology recommends that the symbol \(\sigma\) be used to denote shear stress. However, the symbol \(\tau\) that was used to denote shear stress for a long time can still be encountered in rheology literature.

Viscosity, is the internal friction of a fluid or its tendency to resist flow. It is denoted by the symbol \(\eta\) for Newtonian fluids, whose viscosity does not depend on the shear rate, and for non-Newtonian fluids to indicate shear rate dependence by \(\eta_a\). Depending on the flow system and choice of shear rate and shear stress, there are several equations to calculate. Here, it is defined by the equation:

\[
\eta_a = \frac{\text{shear stress}}{\text{shear rate}} = \frac{\sigma}{\dot{\gamma}}
\]  

(1.7)

The preferred units of viscosity are Pa s or mPa s. Some of the older units and their relation to the SI unit are given in Table 1–1. It is clear that the shear rate employed in the calculation must be specified when the magnitude of apparent viscosity is discussed. Apparent viscosity has many useful applications in characterizing a fluid food; in particular, in the characterization of shear-thinning fluids, the apparent viscosity at low shear rates, called the zero-shear rate viscosity \((\eta_0)\), is a useful parameter.

---

**Table 1–1 Conversion Factors for Viscosity, Kinematic Viscosity, and Activation Energy of Flow**

The SI unit for viscosity is Pa s

<table>
<thead>
<tr>
<th>Unit</th>
<th>Conversion Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Pa s</td>
<td>1000 cP = 1 N s m(^{-2}) = 1 kg m(^{-1}) s(^{-1}) = 0.67197 lbm ft(^{-1}) s(^{-1})</td>
</tr>
<tr>
<td>1 poise (P)</td>
<td>1 dyne s cm(^{-2}) = 0.1 Pa s</td>
</tr>
<tr>
<td>1 cP</td>
<td>0.001 Pa s = 1 mPa s = 0.01 P</td>
</tr>
<tr>
<td>1 lbm ft(^{-1}) s(^{-1})</td>
<td>1.4882 kg m(^{-1}) s(^{-1}) = 1.4882 Pa s = 1488.2 cP</td>
</tr>
<tr>
<td>Kinematic viscosity (cSt) = viscosity (cP)/density (g cm(^{-3}))</td>
<td>1 St = 100 cSt = 0.0001 m(^2) s(^{-1})</td>
</tr>
<tr>
<td>1 calorie</td>
<td>4.1868 joule (J)</td>
</tr>
<tr>
<td>The gas constant, (R)</td>
<td>8.314 (J mol(^{-1}) K(^{-1}))</td>
</tr>
<tr>
<td>Boltzmann constant, (k)</td>
<td>(1.38 \times 10^{-23}) N m K(^{-1})</td>
</tr>
</tbody>
</table>
Because much work was done with viscosity expressed in poise in sensory assessment of viscosity, the same tradition will be continued in Chapter 7 on sensory assessment of viscosity.

**TYPES OF FLUID FLOW BEHAVIOR**

The major types of fluid flow behavior can be described by means of basic shear diagram of shear rate versus shear stress, such as Figures 1–2 and 1–3. In Figure 1–2, the shear stresses are plotted against the shear rates (independent variable) which is the conventional method. However, some authors plot shear rates against the shear stresses (independent variable) as shown in Figure 1–3. With the introduction of controlled-stress rheometers, the use of shear stress as the independent variable is often desirable.

**Newtonian Behavior**

With Newtonian fluids, the shear rate is directly proportional to the shear stress and the plot begins at the origin. Typical Newtonian foods are those containing compounds of low molecular weight (e.g., sugars) and that do not contain large concentrations of either dissolved polymers (e.g., pectins, proteins, starches) or insoluble solids. Examples of Newtonian foods include water, sugar syrups, most honeys, most carbonated beverages, edible oils, filtered juices and milk.

All other types of fluid foods are non-Newtonian which means that either the shear stress–shear rate plot is not linear and/or the plot does not begin at the origin,
or the material exhibits time-dependent rheological behavior as a result of structural changes. Flow behavior may depend only on shear rate and not on the duration of shear (time-independent) or may depend also on the duration of shear (time-dependent). Several types of time-independent flow behavior of foods have been encountered.

Shear-Thinning Behavior

With shear-thinning fluids, the curve begins at the origin of the shear stress–shear rate plot but is concave upwards, that is, an increasing shear rate gives a less than proportional increase in shear stress. Shear-thinning fluids are popularly called pseudoplastic. The expression shear-thinning is preferred compared to pseudoplastic because it is an accurate description of the shear rate–shear stress curve. Shear-thinning may be thought of being due to breakdown of structural units in a food due to the hydrodynamic forces generated during shear. Most non-Newtonian foods exhibit shear thinning behavior, including many salad dressings and some concentrated fruit juices.

Yield Stress

The flow of some materials may not commence until a threshold value of stress, the yield stress ($\sigma_0$) (see Figures 1–2 and 1–3), is exceeded. Although the concept of yield stress was questioned recently (Barnes and Walters, 1985), within the time scales of most food processes the concept of yield stress is useful in food process design, sensory assessment, and modeling. Shear-thinning with yield stress behavior
is exhibited by foods, such as tomato concentrates, tomato ketchup, mustard, and mayonnaise. In the event, the shear rate–shear stress data follow a straight line with a yield stress, the food is said to follow the Bingham plastic model.

Shear-Thickening Behavior

In shear-thickening behavior also, the curve begins at the origin of the shear stress–shear rate plot and is concave downwards, that is, an increasing shear stress gives a less than proportional increase in shear rate. This type of flow has been encountered in partially gelatinized starch dispersions. The expression dilatant is popularly and incorrectly used to describe shear-thickening. However, because dilatancy implies an increase in the volume of the sample during the test, it is incorrect to use it to describe shear-thickening rheological behavior. Strictly speaking, shear-thickening should be due to increase in the size of the structural units as a result of shear.

Time-Dependent Behavior

Foods that exhibit time-dependent shear-thinning behavior are said to exhibit thixotropic flow behavior. Most of the foods that exhibit thixotropic behavior are heterogeneous systems containing a dispersed phase that is often very fine. At rest, the particles or molecules in the food are linked together by weak forces. When the hydrodynamic forces during shear are sufficiently high, the inter-particle linkages are broken resulting in reduction in the size of the structural units that in turn offer lower resistance to flow during shear (Mewis, 1979). This type of behavior is common to foods such as salad dressings and soft cheeses where the structural adjustments take place in the food due to shear until an equilibrium is reached. Time-dependent shear-thickening behavior is called antithixotropic behavior. Formerly, it was called rheopectic behavior, but the Society of Rheology recommended the expression antithixotropic. This type of behavior, although rare, is being detected in many foods due to the development of sensitive automated rheometers. When shear rate versus shear stress data are obtained first in ascending order of shear rate and immediately afterwards in descending order, the two curves will not coincide and values of the latter will be lower than the former for thixotropic foods (Figure 1–4). Repetition of the experiments will result in an equilibrium hysteresis loop.

In antithixotropic behavior, the shear stress values in descending order of shear rates are higher than those in ascending order (Figure 1–5). The characterization of these types of flow is an important research problem at this time. The primary difficulty in obtaining reliable thixotropic or antithixotropic data is that often loading of the test sample in to a measuring geometry induces structural changes that cannot be either controlled or expressed quantitatively. Therefore, considerable caution should be exercised in using the area of hysteresis loop as a measure of thixotropic behavior and a characteristic of the food sample because the magnitude of the area will depend on the shear to which the sample is subjected to prior to and during loading of the sample into a viscometer.
Figure 1-4 Time-Dependent Shear-Thinning (thixotropic) Behavior of a Tapioca Starch Dispersion Heated at 67°C for 5 min, Data of Tattiyakul (1997).

Figure 1-5 Time-Dependent Shear-Thickening (antithixotropic) Behavior of a Cross-linked Waxy Maize Starch Dispersion Heated at 120°C for 30 min, Data of Chamberlain (1996). Note that the decreasing shear curves of the samples had higher stress values than the increasing shear curves.
APPARENT VISCOSITY

Additional information can be obtained from a basic shear (shear stress–shear rate) diagram (see Figure 1–2) and the equations that describe the data in it. The yield stress $\sigma_0$ (if present) can be read off the diagram. One can calculate the apparent viscosity at any given shear rate. For example, the apparent viscosity at a shear rate of 50 s$^{-1}$ is:

$$\eta_{a,50} = \frac{\sigma_{50}}{\gamma_{50}}$$

where, $\sigma_{50}$ is the shear stress corresponding to a shear rate of 50 s$^{-1}$. The zero-shear viscosity $\eta_0$, is an important parameter in the study of shear-thinning fluids. It is the limiting viscosity at very low shear rates. The important role of $\eta_0$ in the study of biopolymer dispersions will be discussed in Chapters 2 and 4.

INTRINSIC VISCOSITY

Many foods contain high-molecular weight polymers, such as proteins, pectins, and others. Often, they contribute significantly to the structure and viscosity of foods. In dilute solutions, the polymer chains are separate and the intrinsic viscosity, denoted as $[\eta]$, of a polymer in solution depends only on the dimensions of the polymer chain. Because $[\eta]$ indicates the hydrodynamic volume of the polymer molecule and is related to the molecular weight and to the radius of gyration, it reflects important molecular characteristics of a biopolymer. The concentrations of polymers used should be such that the relative viscosities ($\eta/\eta_s$) of the dispersions are from about 1.2 to 2.0 to assure good accuracy and linearity of extrapolation to zero concentration (Morris and Ross-Murphy, 1981; da Silva and Rao, 1992). Intrinsic viscosity can be determined from dilute solution viscosity data as the zero concentration-limit of specific viscosity ($\eta_{sp}$) divided by concentration ($c$):

$$[\eta] = \lim_{c \to 0} \left( \frac{\eta_{sp}}{c} \right)$$

where, $\eta_{sp} = [(\eta - \eta_s)/\eta_s]$, and $\eta$ and $\eta_s$ are the viscosities of the solution and the solvent, respectively. When a dilute solution exhibits shear-thinning behavior, its zero shear viscosity, $\eta_0$, at very low shear rates, sometimes referred to as “vanishing shear rates,” may be used in place of the Newtonian viscosity $\eta$. We note that there are several ways of determining the intrinsic viscosity $[\eta]$ from experimental dilute solution viscosity data (Tanglertpaibul and Rao, 1987). The two equations commonly employed for determining $[\eta]$ of food gums are those of Huggins (Equation 1.10) and Kraemer (Equation 1.11):

$$\frac{\eta_{sp}}{c} = [\eta] + k_1 [\eta]^2 c$$

$$\ln (\eta_r/c) = [\eta] + k_2 [\eta]^2 c$$

In Equation (1.11), $\eta_r$ is the relative viscosity ($\eta/\eta_s$). Equations 1.10 and 1.11 imply that plots of $\eta_{sp}/c$ versus $c$ and $\ln(\eta_r/c)$ versus $c$ would result in straight lines,
respectively. The extrapolations are usually done for relative viscosity values between 1.2 and 2.0 when the corresponding specific viscosities are between about 0.2 and 1.0. The Huggins constant \( k_1 \) is considered to be an index of the polymer–polymer interaction with a large number of the reported values being between 0.3 in good solvents and 1.0 in theta solvents; the higher values are attributed to the existence of association between the macromolecules. The Huggins and Kraemer constants \( (k_1 \text{ and } k_2) \) are theoretically related by the equation:

\[
k_1 = k_2 + 0.5
\]

The Huggins equation has been used much more extensively and in Figure 1–6 intrinsic viscosity determination of mesquite seed gum, a galactose-mannose polymer, based on the equation is illustrated (Yoo et al., 1994).

For polyelectrolytes (charged polymers), a plot of \( \eta_{sp}/c \) versus \( c \) may be a curve. An alternate expression of Fuoss and Strauss (1948) can be used (Chamberlain and Rao, 2000):

\[
\frac{\eta_{sp}}{c} = \frac{[\eta]}{(1 + Bc^{1/2})}
\]

When \( (c/\eta_{sp}) \) is plotted against \( c^{1/2} \), a straight line is obtained with an intercept of \( 1/[\eta] \) and a slope of \( B/[\eta] \).

The Mark-Houwink empirical equation relates intrinsic viscosity and the average molecular weight \( (M) \):

\[
[\eta] = K (M)^{\alpha}
\]

---

**Figure 1–6** Intrinsic Viscosity Determination of Mesquite Seed Gum, a Galactose-Mannose Polymer, Based on the Huggins equation.
where $K$ and $a$ are constants at a specific temperature for a given polymer-solvent system. The magnitude of the constant $a$ is generally in the range 0.5 to 0.8 when conformation of the polymer is random coil (Launay et al., 1986); for polymers that assume compact conformations, the magnitudes of the exponent $a$ are lower than 0.5. Magnitudes of higher than 0.8 are encountered when hydrodynamic interactions are absent (free draining random coil), that is, when the solvent can drain freely between the macromolecules, as is the case when the conformations are elongated and rigid (rod like polymers). A large number of models have been used to deduce intrinsic viscosity-molecular weight relationships (Launay et al., 1986), including the equivalent sphere model (Flory–Fox equation), the random flight model for flexible chain molecules, the worm-like chain model, and rigid elongated molecules. Rigid elongated conformations have been associated with large values of the Mark-Houwink exponent with values of 1.7–1.8 being reported for some polyelectrolytes at low ionic strength and high degree of disassociation. The magnitudes of intrinsic viscosity and of molecular weight of several biopolymers are given in Table 1–2 (da Silva and Rao, 1992). It is seen that significant differences in the magnitudes are encountered depending on the structural characteristics, such as molecular mass (length of the chain) and different degrees of substitution. For polymers with charges, $[\eta]$ and rheological behavior are also affected by the pH and the ionic strength of the solution; therefore, their values should be controlled in studies of $[\eta]$ and their rheological behavior.

### Table 1–2: Examples of Magnitudes of Intrinsic Viscosity $[\eta]$ and Average Molecular Weight ($M$) of Some Biopolymers

<table>
<thead>
<tr>
<th>Biopolymer</th>
<th>Solvent</th>
<th>$M$</th>
<th>$[\eta]$ (dl/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apple pectin</td>
<td>NaCl 0.155 M</td>
<td>155,000</td>
<td>6.13</td>
<td>Michel (1982)</td>
</tr>
<tr>
<td>DE*—72.9%</td>
<td></td>
<td>113,000</td>
<td>4.45</td>
<td></td>
</tr>
<tr>
<td>DE—60.5%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xanthan gum</td>
<td>Water</td>
<td>168</td>
<td>36.7</td>
<td>Launay et al. (1984)</td>
</tr>
<tr>
<td>NaCl 2%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium alginate</td>
<td>Ionic force</td>
<td>200,000</td>
<td>5.99</td>
<td>Smidsrød (1970)</td>
</tr>
<tr>
<td>0.01</td>
<td></td>
<td>500,000</td>
<td>17.2</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td></td>
<td>200,000</td>
<td>3.72</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>500,000</td>
<td>8.26</td>
<td></td>
</tr>
<tr>
<td>Locust bean gum</td>
<td>Water</td>
<td>1,600,000</td>
<td>11.2</td>
<td>Doublier (1975)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,100,000</td>
<td>7.70</td>
<td></td>
</tr>
<tr>
<td>Guar gum</td>
<td>Water</td>
<td>440,000</td>
<td>4.5</td>
<td>Robinson et al. (1982)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,650,000</td>
<td>12.5</td>
<td></td>
</tr>
</tbody>
</table>

*DE stands for degree of esterification.
Intrinsic viscosity is very useful as a measure of the hydrodynamic volume of food polymers and has been used for studying the role of polymer concentration on zero-shear viscosity of several food polymers (Chapter 4).

STRESS-STRAIN BEHAVIOR OF SOLID FOODS

Equations 1.2 to 1.4 represent material functions under large deformations (e.g., continuous shear of a fluid). One may recall a simple experiment in an introductory physics course where a stress \( \sigma \) is applied to a rod of length \( L \) in a tension mode and that results in a small deformation \( \Delta L \). The linear relationship between stress \( \sigma \) and strain \( \gamma \) (also relative deformation, \( \gamma = \Delta L / L \)) is used to define the Young's modulus of elasticity \( E \) (Pa):

\[
\sigma = E \gamma
\]  

(1.15)

If the solid does not show time-dependent behavior, that is, it deforms instantaneously, one has an ideal elastic body or a Hookean solid. The symbol \( E \) for the modulus is used when the applied strain is extension or compression, while the symbol \( G \) is used when the modulus is determined using shear strain. The conduct of experiment such that a linear relationship is obtained between stress and strain should be noted. In addition, for an ideal Hookean solid, the deformation is instantaneous. In contrast, all real materials are either viscoplastic or viscoelastic in nature and, in particular, the latter exhibit time-dependent deformations. The rheological behavior of many foods may be described as viscoplastic and the applicable equations are discussed in Chapter 2.

LINEAR VISCOELASTICITY

One convenient manner of studying viscoelasticity is by stress relaxation where the time-dependent shear stress is studied for step increase in strain. In Figure 1–7, the stress relaxation of a Hookean solid, and a viscoelastic solid and liquid are shown when subjected to a strain instantaneously and held constant. The relaxation modulus can be calculated as:

\[
G(t, \gamma) = \frac{\sigma(t, \gamma)}{\gamma}
\]  

(1.16)

Because a Hookean solid deforms instantaneously, the imposed strain has a time-dependent profile similar to that of the stress. For relatively small strains, shear normal stresses and the type of deformation (e.g., linear or shear) will not be important. Further, the extensional and the shear relaxation moduli are related as:

\[
E(t) = 3G(t)
\]  

(1.17)
Boltzmann suggested that when the changes in stress and strain are small, one can express the change in stress as:

$$d\sigma = \gamma dG$$

(1.18)

Defining the memory function as: $M(t) = -dG(t)/dt$, one can express a large linear deformation as the sum of all the small linear deformations that in turn can be written as the integral over all past times:

$$\sigma = -\int_{-\infty}^{t} M(t-t')\gamma(t')dt'$$

(1.19)

where, $t'$ is the past time variable in the range $-\infty$ to the present time $t$. The elapsed time is denoted as $s = (t - t')$, and Equation 1.17 can be written as:

$$\sigma = -\int_{-\infty}^{t} M(s) \gamma(t-s)ds$$

(1.20)

The above equation is a one-dimensional model of linear viscoelastic behavior. It can be also written in terms of the relaxation modulus after noting that:

$$d\sigma = G d\sigma = G\frac{d\gamma}{dt} dt = G\dot{\gamma} dt$$

(1.21)

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

(1.22)
Therefore, the stress is an integral over past time of the product of the relaxation modulus and the rate of strain. The relaxation modulus can be expressed in terms of a series of relaxation times, $\lambda_n$, and the constants, $G_n$:

$$G(t) = \sum_{n=1}^{N} G_n \exp(-t/\lambda_n)$$  \hspace{1cm} (1.23)

In the unlikely event of $G(t)$ being described by a single exponential term:

$$G(t) = G_0 \exp(-t/\lambda)$$  \hspace{1cm} (1.24)

From the above equation, one obtains the simple Maxwell model:

$$\sigma = -\int_{-\infty}^{t} G_0 e^{-(t-t')/\lambda} \dot{\gamma} dt'$$  \hspace{1cm} (1.25)

One can express linear viscoelasticity using the relaxation spectrum $H(\lambda)$, that is, using the relaxation time $\lambda$. The relationship between the relaxation modulus and the spectra is:

$$G(s) = \int_{0}^{\infty} \frac{H(\lambda)}{\lambda} e^{-s/\lambda} d\lambda$$  \hspace{1cm} (1.26)

**Linear Viscoelasticity in Differential Form**

Three equations are basic to viscoelasticity: (1) Newton’s law of viscosity, $\sigma = \eta \dot{\gamma}$, (2) Hooke’s law of elasticity, Equation 1.15, and (3) Newton’s second law of motion, $F = ma$, where $m$ is the mass and $a$ is the acceleration. One can combine the three equations to obtain a basic differential equation. In linear viscoelasticity, the conditions are such that the contributions of the viscous, elastic, and the inertial elements are additive. The Maxwell model is:

$$\sigma + \lambda \frac{d\sigma}{dt} = \eta \dot{\gamma} = \lambda G_0 \dot{\gamma}$$  \hspace{1cm} (1.27)

A convenient manner of interpreting viscoelastic behavior of foods is in terms of a spring that has a modulus $E$ and a dashpot that represents a Newtonian fluid with viscosity $\eta$ that can be arranged either in series (Maxwell model) (Figure 1–8, left) or in parallel (Kelvin–Voigt model). In the Maxwell model, for slow motions the dashpot, that is, Newtonian behavior dominates. For rapidly changing stresses, that is, at short times, the model approaches elastic behavior. The use of models such as the Maxwell and the Kelvin–Voigt (Figure 1–8, right) and their combinations is valid only when the experimental data are obtained within the linear viscoelastic range. Many studies on foods have reported measurements in the linear viscoelastic range.
so that the Maxwell and the Kelvin–Voigt models and their combinations were used in the interpretation of results of such studies (Chapters 3 and 5).

The relaxation time for a Maxwell element (Figure 1–8, left) is defined as:

$$\tau_1 = \frac{\eta}{E}$$  \hspace{1cm} (1.28)

From data in a stress relaxation experiment (Chapter 3), where the strain is constant and stress is measured as a function of time, $\sigma(t)$, the relaxation time may be estimated from the time necessary for $[\sigma(t)/\sigma(0)]$ to become $1/e = 0.368$. Typically, several Maxwell elements are used to fit experimental data, $\sigma(t)$. For the Kelvin–Voigt element (Figure 1–8, right) under stress, the equation is:

$$\frac{dy}{dt} = \frac{\eta}{\tau_2} \gamma + E \gamma$$  \hspace{1cm} (1.29)

For constant stress, the above equation can be integrated to describe the deformation:

$$\lambda = \frac{\sigma}{E} [1 - \exp(-E/\eta)t]$$  \hspace{1cm} (1.30)

In terms of the retardation time, $\tau_2$, the above equation is:

$$\gamma = \frac{\sigma}{E} [1 - \exp(-t/\tau_2)]$$  \hspace{1cm} (1.31)

The Kelvin–Voigt elements are used to describe data from a creep experiment and the retardation time ($\tau_2$) is the time required for the spring and the dashpot to deform to $(1 - 1/e)\), or 63.21\% of the total creep. In contrast, the relaxation time is that required for the spring and dashpot to stress relax to $1/e$ or 0.368 of $\sigma(0)$ at constant strain. To a first approximation, both $\tau_1$ and $\tau_2$ indicate a measure of the time to complete about half of the physical or chemical phenomenon being investigated (Sperling, 1986).

**LENGTH SCALE OF FOOD MOLECULES AND FOODS**

When studying the rheological behavior of a food, knowledge of the composition of the food, especially the important structuring components (e.g., dissolved polymers,