CONSTITUTIVE MODELING OF VISCOELASTIC FLUIDS

Faith A. Morrison
Department of Chemical Engineering, Michigan Technological University, Houghton, MI USA

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Contents

Summary

In this paper we review the context in which rheological constitutive equations are used in the continuum approach to fluid modeling. The Newtonian fluid is an excellent model for materials that are simple, including oil, water, and most organic liquids. For non-Newtonian fluids, three groups of constitutive models are identified: inelastic, linear-viscoelastic, and non-linear viscoelastic. The inelastic models are quite useful for pressure-drop/flow-rate calculations. They are also the easiest with which to compute. The linear-viscoelastic models are all equivalent, and are excellent in being able to describe the behavior of non-Newtonian fluids in the linear-viscoelastic regime. The non-linear viscoelastic models are both difficult to compute with and incomplete in their ability to mimic fluid behavior. The strengths and weaknesses of individual non-linear

viscoelastic models must be considered when making predictions with these models.

1. Introduction

The fluid state of matter is produced when forces between molecules are just so: large enough that the molecules remain in close proximity but too small to force the molecules to remain in fixed locations. When outside forces act on a fluid, it moves and deforms. How fluids move and deform and the forces that are generated when fluids move and deform is the subject of fluid mechanics and of rheology.

There are two common approaches to modeling the fluid state, the molecular approach and the continuum approach. In the molecular approach, the various intermolecular forces are accounted for, and the positions of individual molecules are calculated. In the continuum approach individual molecules are not considered, but rather a few field variables, for example density, local velocity, and stress, are defined and tracked using models that are constructed to mimic molecular behavior.

In both the molecular approach and the continuum approach the final goal is the same: to calculate how fluids move and deform. The difference in the approaches is in how the motion and forces are accounted for. In the continuum approach, forces in a fluid are accounted for by a field variable, the stress tensor, which lumps together all the molecular forces that are at play in a fluid. The stress tensor must be deduced from observations of a fluid of interest, and in this paper we discuss the equations for stress, the stress constitutive equations, that have been used to model many different types of materials. For Newtonian fluids the stress constitutive equation is well known; for viscoelastic fluids there are many different constitutive equations that have been developed, each with advantages and disadvantages. These are discussed.

2. Fluid Mechanics Basics of Rheology

2.1. Conservation Equations

Modeling in fluid mechanics and rheology is based on three conservation laws, the laws of conservation of mass, momentum, and energy. Performing balances on an arbitrary volume in a flowing fluid leads to the three equations that encode these conservation laws, the continuity equation, the Cauchy momentum equation, and the equation of conservation of energy.

Continuity equation (mass balance)

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \left(\rho \underline{v} \right) = 0$$

Cauchy momentum equation (momentum balance)

$$\rho \left(\frac{\partial \underline{v}}{\partial t} + \underline{v} \cdot \nabla \underline{v} \right) = -\nabla p + \nabla \cdot \underline{\underline{\tau}} + \rho \underline{g}$$

Conservation of energy

$$\rho \hat{C}_p \left(\frac{\partial T}{\partial t} + \underline{v} \cdot \nabla T \right) = k \nabla^2 T + \hat{S}$$

where ρ is the fluid density, t is time, $\underline{v}$ is the fluid velocity, pis pressure, $\underline{\underline{\tau}}$ is the stress tensor, g is the acceleration due to gravity, $\hat{C}_p$ is the specific heat capacity, T is temperature, k is thermal conductivity, and $\hat{S}$ is the rate of energy production per unit volume. Both the continuity equation and the equation of conservation of energy are scalar equations. The Cauchy momentum equation, which is the momentum balance, is a vector equation, and thus has three components. All three equations are written above in Gibbs notation (vector/tensor notation), which is discussed thoroughly in the literature. When solving a problem, the equations can be written in any coordinate system, and the components of these equations in common coordinate systems may be found in the literature.

The conservation equations fundamentally seek to tell us how three important field variables are distributed in space and time: density, velocity, and temperature. The use of field variables to describe a fluid system is part of the continuum model of fluid mechanics. In the continuum model, a fluid is visualized as having properties that are continuous in space. Density of a fluid, for example, is the mass per unit volume. The density of a fluid can vary with position and time, and thus density is a function of $x,\ y,\ z,$ and t. The function that gives density, $\rho(x, y, z, t)$, is a field variable.

The continuity equation comes from the basic principle that matter can neither be created nor destroyed. When this principle is applied to a small volume in a flow, the continuity equation results: there is no additional physics needed to arrive at the result. The Cauchy momentum equation comes from Newton's second law applied to a small volume in a flow. This volume is called the control volume. Newton's second law says that the sum of the forces on a body is equal to the mass times the acceleration of the body, $\sum \underline{f} = m\underline{a}$. When this law is applied to the control volume, the Cauchy momentum equation results. The three terms on the right-hand side of the Cauchy momentum equation represent the forces on the control volume: pressure forces, molecular forces other than pressure, and gravity forces.

2.2. Constitutive Equations

In order to apply the momentum balance to a flow, and to subsequently solve for the velocity field, more must be known about the middle term on the right-hand side of the Cauchy momentum equation. This term accounts for molecular forces other than pressure; these molecular forces are codified in an additional field variable, the stress tensor $\underline{\underline{\tau}}(x, y, z, t)$.

The stress tensor is a mathematical construct that allows us to calculate the molecular stresses at a point in a flow as a function of the velocity field. The stress tensor is a very powerful and useful system for keeping track of molecular effects. Just as density is a field variable that represents in a continuous function certain molecular effects (the distribution of mass in space), stress is a field variable that represents in a continuous function the molecular effects that result in forces in a fluid. In the case of density, the distribution of mass in space may be adequately accounted for by a scalar function that varies with position and time. The velocity field is another field variable, one that represents in a continuous function the local fluid velocity as a function of position and time. At each position we need to know both magnitude of the local fluid velocity and the direction of the local fluid velocity, and thus we use a vector function for the field variable $\underline{v}$. For stress, it is neither possible to adequately account for molecular forces with a single scalar function of position and time, nor with a single vector function of position and time. For stress, to express the forces present in a fluid at a location, we must specify both the orientation of the surface on which the forces are acting and the direction and magnitude of the force itself. The mathematical entity that can keep track of these three things – the orientation of the surface, the direction of the force, and the magnitude of the force – is the tensor.

The simplest way to think of a tensor is as a 3x3 matrix of tensor components that acts on vectors as 3x1 or 1x3 matrices. Thus, the dot product of the unit vector $\hat{n}$ with the tensor $\underline{\underline{\tau}}$ can be written as

$$\hat{n}\cdot\underline{\underline{\tau}}=\begin{bmatrix} n_1 & n_2 & n_3 \end{bmatrix}\cdot\begin{bmatrix} \tau_{11} & \tau_{12} & \tau_{13} \\ \tau_{21} & \tau_{22} & \tau_{23} \\ \tau_{31} & \tau_{32} & \tau_{33} \end{bmatrix}=\begin{bmatrix} \sum_{j=1}^{3} n_j\tau_{j1} & \sum_{j=1}^{3} n_j\tau_{j2} & \sum_{j=1}^{3} n_j\tau_{j3} \end{bmatrix}$$

where the n_i and τ_{km} are the coefficients $\hat{n}$ and $\underline{\underline{\tau}}$ in some orthonormal coordinate system. The fundamental meaning of the stress tensor in fluid mechanics is that the force $\underline{f}$ on a small area dA in a flow is given by

$$\underline{f}=\left(\hat{n}\cdot\underline{\underline{\tau}}\right)dA$$

where $\hat{n}$ is the unit vector normal to dA. It is in this form that the stress tensor enters into the derivation of the momentum balance and subsequently comes to occupy its position on the right-hand side of the Cauchy momentum equation.

The stress tensor is not a constant, but is variable, and it is a function of the velocity field. Thus the momentum balance cannot be solved until the functional form of $\underline{\underline{\tau}}(\underline{v})$ is known. The equation that gives $\underline{\underline{\tau}}(\underline{v})$ for a chosen fluid is called the stress constitutive equation or simply, the constitutive equation.

2.3. Newtonian Fluids

The constitutive equation is a mathematical relationship that gives the stress tensor as a function of the velocity field for a particular fluid. It is applicable to any flow, but it is specific to a particular fluid. For the simplest types of fluids, incompressible Newtonian fluids, the constitutive equation is known.

Newtonian constitutive equation $\underline{\underline{\tau}}\left(\underline{v}\right)=\mu\left[\nabla\underline{v}+\left(\nabla\underline{v}\right)^{\mathrm{T}}\right]$

This equation, called the Newtonian constitutive equation, is written in Gibbs notation, which can be translated to any coordinate system by using standard tables. The Newtonian constitutive equation contains one material parameter, μ, the viscosity, which is a constant.

If the Newtonian constitutive equation is substituted into the momentum balance, the Cauchy momentum equation becomes

Navier-Stokes equation

$$\rho\left(\frac{\partial\underline{v}}{\partial t}+\underline{v}\cdot\nabla\underline{v}\right)=-\nabla p+\mu\nabla^{2}\underline{v}+\rho\underline{g}$$

This equation, called the Navier-Stokes equation, is the momentum balance for incompressible, Newtonian fluids. In combination with the continuity equation and the equation of conservation of energy, the Navier-Stokes equation can be solved and all the field variables $\left(\rho,\underline{\underline{\tau}},\underline{v},T\right)$ determined for a chosen flow. The Newtonian constitutive equation works well for fluids such as water, oil, air, and most other small-molecule pure liquids.

2.4. Non-Newtonian Fluids

For many fluids, the Newtonian constitutive equation does not make accurate predictions. For materials that are not pure (suspensions, emulsions), for large molecule liquids (polymers, gels), and for liquids with special intermolecular forces (ionic liquids, magnetic liquids), the Newtonian constitutive equation is inadequate. Materials that generate velocity and stress effects that are not represented by the Newtonian constitutive equation are called non-Newtonian fluids.

The remaining three sections of this article are descriptions of constitutive equations for non-Newtonian fluids. There is not just one non-Newtonian constitutive equation; rather, there are an infinite number of such equations, since there are an infinite number, or at least a very large number, of fluids that are not represented by the Newtonian equation. For each fluid that is non-Newtonian there may be a different constitutive equation.

The types of constitutive equations that are discussed fall into three categories: inelastic models, linear-viscoelastic models, and nonlinear-viscoelastic models. These three categories represent physics of increasing complexity and consequently increasing difficulty of both comprehension and implementation. The inelastic models and the linear-viscoelastic models are well understood; the nonlinear-viscoelastic models represent an area of current research, although much groundwork has been laid and there are many practical nonlinear-viscoelastic models. For more details on these topics, please see the references cited at the end of this article.

3. Inelastic Models

The principal shortcoming of the Newtonian constitutive equation is that it relies on a single, constant material parameter, the viscosity. For many materials, the viscosity is not constant but varies with flow conditions. Thus, one approach to improving the applicability of the Newtonian constitutive equation is to develop models that allow for variable viscosity. Such a model is the generalized Newtonian model.

Generalized Newtonian model $$\underline{\underline{\tau}} = \eta \left[\nabla \underline{v} + \left(\nabla \underline{v} \right)^{\mathrm{T}} \right]$$

The function $\eta(\underline{v})$ is called the non-Newtonian viscosity, and it is a function of the velocity field.

The generalized Newtonian fluid model is actually a family of models, since different equations are created for different choices of the function η. We have a great deal of flexibility in choosing the function η, but there are constraints. First, the constitutive equation must be able to be meaningfully translated into any coordinate system. Thus, when we write the function η in terms of the velocity field, we may not reference components of $\underline{v}$ in any particular coordinate system. Second, the constitutive equation is applicable to any flow; thus the choice of η must not be exclusive to one particular flow. Third, once η is chosen, the predictions of the constitutive equation should be correct, that is, should be what is observed for a fluid of interest.

To meet these criteria, we note that vector magnitudes are independent of coordinate system and may therefore appear in functions such as η. Similarly, tensors have scalars associated with them that are independent of coordinate system; these scalars are called a tensor's invariants, and there are three invariants for tensors of the type we are discussing here.

Tensor invariants of $\underline{\underline{A}}$

$$I_{\underline{\underline{A}}} \equiv tr\,\underline{\underline{A}} = \sum_{j=1}^{3} A_{jj}$$

$$II_{\underline{\underline{A}}} \equiv tr\left(\underline{\underline{A}} \cdot \underline{\underline{A}}\right) = \sum_{j=1}^{3} \sum_{k=1}^{3} A_{kj} A_{jk}$$

$$III_{\underline{\underline{A}}} \equiv tr\left(\underline{\underline{A}} \cdot \underline{\underline{A}} \cdot \underline{\underline{A}}\right) = \sum_{j=1}^{3} \sum_{k=1}^{3} \sum_{m=1}^{3} A_{mj} A_{jk} A_{km}$$

The tensor invariant that is found to capture the effect of the flow on the viscosity is the second invariant of the rate of deformation tensor.

Rate of deformation tensor $\underline{\underline{\dot{\gamma}}} \equiv \nabla \underline{v} + \left(\nabla \underline{v}\right)^{\mathrm{T}}$

Note that the rate-of-deformation tensor appears in both the Newtonian constitutive equation and the generalized Newtonian constitutive equation. The usual way to write the functionality of η is to write it in terms of $\dot{\gamma}$, the magnitude of the rate of deformation tensor, which is related to the second invariant of $\underline{\underline{\dot{\gamma}}}$ as follows:

Magnitude of $\underline{\underline{\dot{\gamma}}}$ $\dot{\gamma} = \left|\underline{\underline{\dot{\gamma}}}\right| \equiv \sqrt{\frac{1}{2} II_{\underline{\underline{\dot{\gamma}}}}}$

Thus, the non-Newtonian viscosity is written as $\eta(\dot{\gamma})$, and the generalized Newtonian constitutive equation becomes

Generalized Newtonian fluid (GNF) constitutive equation $\underline{\underline{\tau}} = \eta\left(\dot{\gamma}\right)\left[\nabla \underline{v} + \left(\nabla \underline{v}\right)^{\mathrm{T}}\right]$

The quantity $\dot{\gamma}$ is read as “gamma dot” and is called the rate of deformation. In shear flows, $\dot{\gamma}$ is called the shear rate.

3.1. Power-Law Model

A common choice for the viscosity function is the power-law equation;

Power-law viscosity function $\eta = m\dot{\gamma}^{n-1}$

where m and n are parameters of the model. The pre-factor m is called the consistency index, and the exponent n is called the power-law index. The power-law function appears as a straight line when viscosity versus $\dot{\gamma}$ is plotted on a log-log graph. Note that for $n=1$ the viscosity is constant, and thus $n=1$ corresponds to the Newtonian case with viscosity equal to m.

It is fairly easy to make calculations of flow and stress fields with the power-law generalized Newtonian fluid constitutive equation. For many polymer melts values of $n<1$ correctly capture flow behavior at high rates of deformation. The overall predictions of the power-law GNF are found to be adequate when pressure-drop/flow-rate information is desired. GNF models are incapable of predicting memory or other elastic effects, however; also it is not possible to estimate a relaxation time from any of the parameters of the power-law GNF.

3.2. Carreau-Yassuda Model

The variation of viscosity with $\dot{\gamma}$ often follows a shape shown in Figure 1. The power-law model only captures the high-rate portion of this curve. An equation that captures the entire curve is the Carreau-Yassuda model.

Carreau-Yassuda viscosity function

$$\eta = \eta_\infty + \left(\eta_0 - \eta_\infty\right)\left[1 + \left(\lambda\dot{\gamma}\right)^a\right]^{\frac{n-1}{a}}$$

where the five parameters of the model are the zero-shear viscosity η_0, the infinite-shear viscosity η_∞, the relaxation time λ, the power-law index n, and the shape parameter a. The zero-shear viscosity captures the low-$\dot{\gamma}$ plateau; the infinite-shear viscosity captures the high-$\dot{\gamma}$ plateau; the relaxation time determines the value of $\dot{\gamma}$ at which the low-$\dot{\gamma}$ plateau ends; the power-law index determines the slope of the rapidly decreasing portion of the curve; and the shape parameter determines the shape of the transition between the upper plateau and the rapidly-increasing portion of the curve.

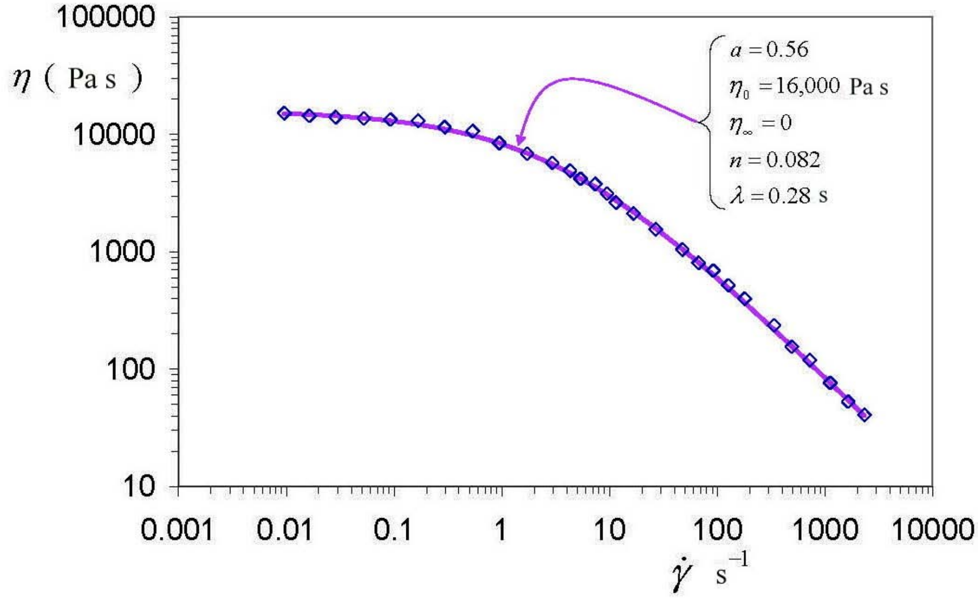

Figure 1. Most polymer melts are shear-thinning, showing a zero-shear plateau at low rates and a power-law region at high rates. A viscosity function that captures these features well is the Carreau-Yassuda viscosity function, which is shown fit to data for polydimethylsiloxane above (Data are from Piau et al.).

The Carreau-Yassuda model does a better job of capturing the shape of the viscosity function but at the expense of calculations becoming considerably more difficult. Because the Carreau-Yassuda model is a generalized Newtonian fluid model, it shares with the power-law model the inability to predict memory or other elastic effects.

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Biographical Sketch

Faith A. Morrison was born in Bethlehem, PA USA in 1962. She received her B.S. in chemical engineering from Princeton University in 1983 and her Ph.D. in chemical engineering from the University of Massachusetts, Amherst in 1988.

In 1988 she did postdoctoral work with Shiro Matsuoka and Ronald Larson at ATT Bell Laboratories and in 1989 she performed research at ESPCI in Paris, France under the supervision of Claudine Noel and Lucien Monnerie. Since 1990 she has been on the faculty of the Department of Chemical Engineering at Michigan Technological University. She has also spent research sabbaticals at 3M Company (St. Paul, MN) and at Korea University (Seoul, Korea). She is the author of the beginner’s rheology textbook *Understanding Rheology*, published by Oxford University Press in 2001. She is currently writing an undergraduate fluid mechanics text and conducting research on the rheology of highly filled systems.

Prof. Morrison is the Vice President of The Society of Rheology and editor of the *Rheology Bulletin*. She is a member of the American Institute of Chemical Engineers, the American Physical Society, the American Chemical Society, and Sigma Xi.