TA Instruments

Thermal Analysis & Rheology

RHEOLOGY SOFTWARE MODELS
(OSCILLATION)

RH064

Introduction

If any kind of quantitative analysis is to be made of the results of an oscillation experiment, then it is useful to fit the experimental data using a mathematical model. Many commercial software packages contain curve-fitting procedures that could be used for the purpose, but a reliable model should both provide a good fit to the data, and be physically realistic. No matter how well an arbitrarily chosen model may comply with the first of these criteria, it is unlikely to comply with the second.

Most of the models contained in the TA Instruments software are rheologically plausible for low strain amplitudes, but several non-rheological models are also included. The latter should be used with caution if the purpose of using models is anything other than straightforward curve fitting. The rheological models require that the condition of linear viscoelasticity is observed, i.e. that at a particular oscillation frequency the amplitude of the applied stress is directly proportional to the amplitude of the measured strain. [The software requires that either storage modulus, G', or out-of-phase component of the complex viscosity, η'', and either loss modulus, G'', or dynamic viscosity, η', are plotted against either frequency in Hertz, or angular frequency, ω, in rads/sec.] For model fitting purposes it is more convenient to use angular frequency. The model fitting software will calculate and display the conventionally defined standard error of the fit. The greater the standard error, the worse the fit; a reasonable fit gives a value of less than about twenty.

Although it is not essential, some rheologists find it helpful to regard the various mathematical models as describing mechanical systems. The simplest mechanical model is the spring, which represents a solid material obeying Hooke's law, i.e.:

$$\sigma = G\gamma \tag{1}$$

where σ is the applied shear stress, γ is the resulting shear strain, and G is the modulus of rigidity, or shear modulus (Figure 1).

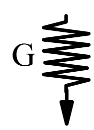

Figure 1: spring representing solid of modulus G.

The dashpot, a piston filled with a Newtonian liquid, which obeys Newton's law of viscous flow, i.e.:

$$\sigma = \eta\dot{\gamma} \tag{2}$$

where η is the viscosity and $\dot{\gamma}$ is the shear rate, defined as $d\gamma/dt$ (Figure 2).

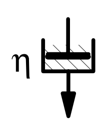

Figure 2: dashpot representing liquid of viscosity η

The Newtonian liquid is the simplest model to be included in the TA Instruments software, and the loss and storage moduli are given by $G'' = \omega\eta$ and $G' = 0$.

The single element Maxwell model

More elaborate models are constructed from these basic units, connected in various ways. A single-element Maxwell is a spring and a dashpot connected in series (Figure 3).

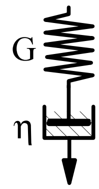

Figure 3: single element Maxwell model

This is the simplest form of viscoelastic model, and can be defined by the viscosity of the dashpot, and the modulus of the spring. Since the modulus has units of Pa, and the viscosity has units of Pa.s, division of the second by the first gives a quantity with units of seconds, known as the relaxation time, λ. A Maxwell element can also be fully described by the relaxation time, and either the modulus or the viscosity of the individual units. TA Instruments software reports the relaxation time and viscosity. The modulus can, of course, be calculated easily if required. For a single-element Maxwell, the storage and loss moduli are given by:

$$G' = \frac{\eta\lambda\omega^2}{1+\omega^2\lambda^2} \tag{3}$$

$$G'' = \frac{\eta\omega}{1+\omega^2\lambda^2} \tag{4}$$

It is worth noting as an aside that it follows from these expressions that $d\log G'/d\log\omega \rightarrow 2$ and $d\log G''/d\omega \rightarrow 1$ as $\omega \rightarrow 0$, and that $d\log G'/d\omega \rightarrow 0$ and $d\log G''/d\log\omega \rightarrow -1$ as $\omega \rightarrow \infty$. It happens that these limits set the ranges of physically possible values of the moduli for all systems over all frequencies. In other words the slope of the curve of G′ plotted against ω on logarithmic axes must be between 0 and 2, and that of G″ must be between -1 and 1. These constraints can provide a quick and useful check on the quality of experimental data. Another point of interest is that the model gives a maximum in G″ at an angular frequency of $1/\lambda$ rads / sec.

Figure 4 shows oscillation data for a typical commercial hair shampoo fitted with a single element Maxwell model. The software gave $\eta = 97.70$ Pa s, $\lambda = 0.1620$ s (from which G = 603.1 Pa), with a standard error of 148.8. It can be seen that, although the correct trends are predicted, and the peak in G″ is at approximately the right frequency, the fit is moderate, as the standard error indicates.

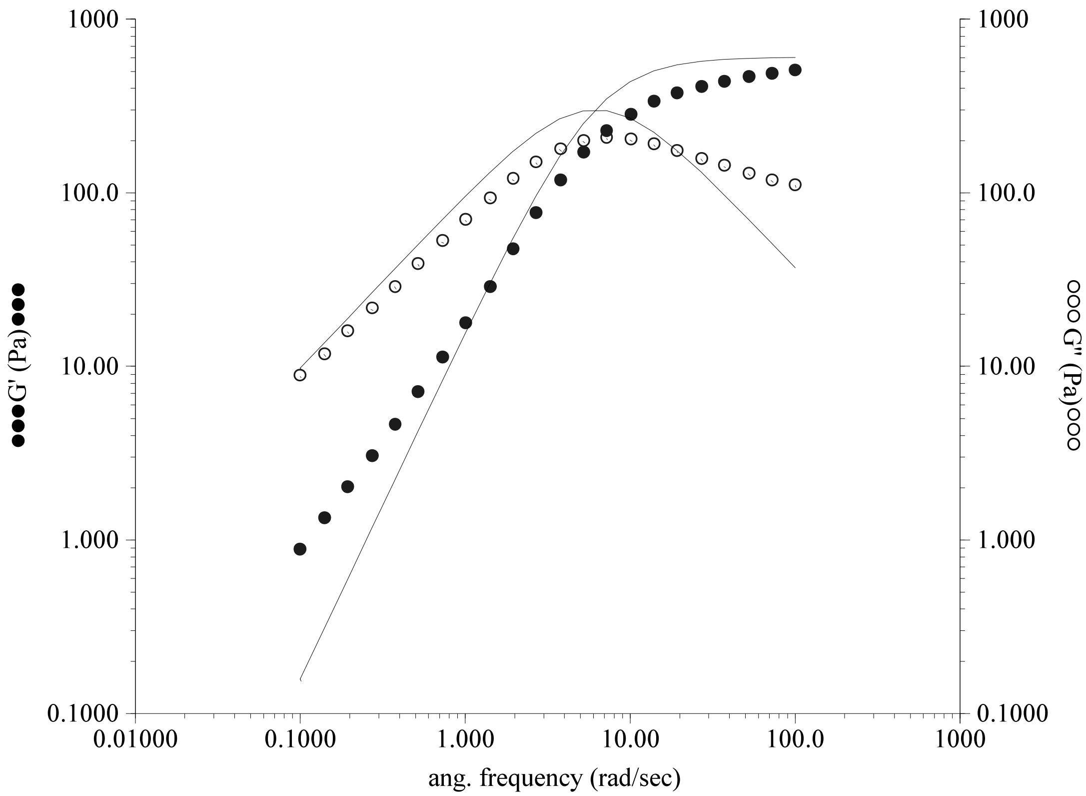

Figure 4: oscillation data for hair shampoo fitted with a single element Maxwell model

Models with a higher number of Maxwell elements

A two element Maxwell is constructed by placing two single element Maxwells in parallel (Figure 5).

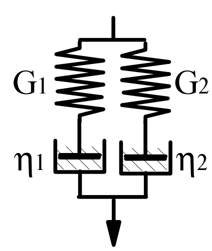

Figure 5: two element Maxwell model

The response of elements placed in parallel to an oscillatory stress is simply additive, so:

$$G' = \frac{\eta_1 \lambda_1 \omega^2}{1+\omega^2 \lambda_1{}^2} + \frac{\eta_2 \lambda_2 \omega^2}{1+\omega^2 \lambda_2{}^2} \tag{5}$$

and
$$G'' = \frac{\eta_1 \lambda_1 \omega}{1+\omega^2 \lambda_1{}^2} + \frac{\eta_2 \lambda_2 \omega}{1+\omega^2 \lambda_2{}^2} \tag{6}$$

where the subscripts refer the first and second Maxwell elements. In principle an n element Maxwell model can be constructed, where n can take any value (Figure 6).

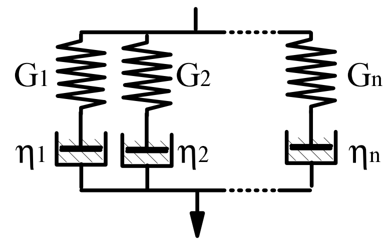

Figure 6: n element Maxwell model

The storage and loss moduli are then given by the summations.

$$G' = \sum_n \frac{\eta_n \lambda_n \omega^2}{1+\omega^2 \lambda_n{}^2} \tag{7}$$

$$G'' = \sum_n \frac{\eta_n \omega}{1+\omega^2 \lambda_n{}^2} \tag{8}$$

TA Instruments software permits up to four Maxwell elements to be fitted, an eight parameter model. The inclusion of further elements would be unlikely to be of much practical value, since it is rare to run a frequency sweep over more than about four decades of angular frequency, or with more than ten data points per decade.

Figure 7 shows the data of Figure 4 fitted with a four element Maxwell model. (Rule of thumb is to use one Maxwell unit per decade of Frequency) It can be seen that an excellent fit is achieved, as indicated by the standard error of 6.302. The software gave $\eta_1 = 24.78$ Pa s, $\lambda_1 = 0.4523$ s, (i.e. $G_1 = 54.79$ Pa); $\eta_2 = 15.03$ Pa s, $\lambda_2 = 5.893$ s, ($G_2 = 2.550$ Pa); $\eta_3 = 2.278$ Pa s, $\lambda_3 = 0.01377$ s, ($G_3 = 165.4$ Pa); $\eta_4 = 47.46$ Pa s, $\lambda_4 = 0.1326$ s, ($G_4 = 357.9$).

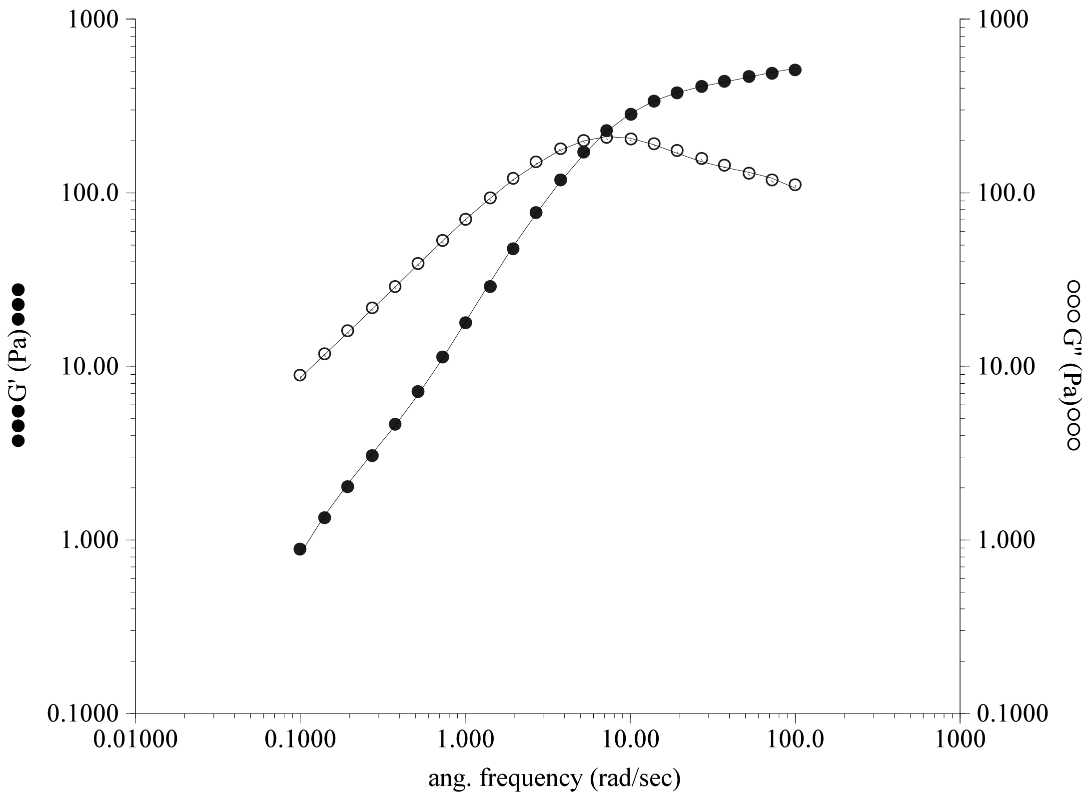

Figure 7: data of Figure 4 fitted with a four element Maxwell model

A more meaningful way of introducing more than four Maxwell elements is to fix the intervals of relaxation times between each element. This is done in the Spriggs model, which consists of an infinite number of Maxwell elements, each with the same value of G, but with relaxation times related by the inverse power series (Equation 9):

$$\lambda_Q = \frac{\lambda_1}{Q^\alpha} \tag{9}$$

In practice the series is truncated at n = 100 in the TA Instruments software. This gives

$$G' = \frac{\eta_0 \lambda \omega^2}{\zeta} \sum_{k=1}^{\infty} \frac{1}{k^{2\alpha} + \lambda^2 \omega^2} \tag{10}$$

$$G'' = \frac{\eta_0 \omega}{\zeta} \sum_{k=1}^{\infty} \frac{k^\alpha}{k^{2\alpha} + \lambda^2 \omega^2} \tag{11}$$

where $\zeta = \sum_{k=1}^{\infty} \frac{1}{k^{\alpha}}$. The Spriggs is a three parameter model, since only a single relaxation time and modulus (or viscosity), and the index α are required.

A further model of the Maxwell type is that referred to as the Oldroyd. The complete Oldroyd was developed for the general case of large strains in three dimensions; reduced to small shear strains, when the condition of linear viscoelasticity is observed, it yields for the moduli:

$$G'' = \eta_0 \omega \left(\frac{1 + \lambda_1 \lambda_2 \omega^2}{1 + \lambda_1{}^2 \omega^2} \right) \tag{12}$$

$$G' = \eta_0 \omega \left(\frac{(\lambda_1 - \lambda_2) \omega^2}{1 + \lambda_1{}^2 \omega^2} \right) \tag{13}$$

It happens that these expressions also describe a Maxwell element and dashpot in parallel (Figure 8), but with the redefinition of parameters:

$$G_M = \frac{\eta_0 (\lambda_1 - \lambda_2)}{\lambda_1{}^2} \tag{14}$$

$$\lambda_M = \lambda_1 \tag{15}$$

$$\eta_D = \frac{\eta_0 \lambda_2}{\lambda_1} \tag{16}$$

In this form the model is alternatively known as the Jeffreys.

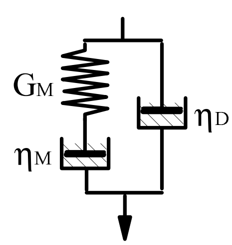

Figure 8: Oldroyd model written as combination of dashpot and Maxwell element

Other models

The power law model fits G″, to the power law relationship:

$$G'' = k\omega^n \tag{17}$$

where $1 > n > 0$. G′ is fitted to the same power law, but with the prefactor cot (nπ/2), i.e.:

$$G' = k \cot(n\pi/2)\,\omega^n \tag{18}$$

The prefactor can take values from 0 to ∞: for $n = 0.5$, $\cot(n\pi/2) = 1$, $G'=G''$. For $1>n > 0.5$, $1 > \cot(n\pi/2) < 0$, $G'' > G'$. For $0.5 > n > 0$, $\infty>\cot(n\pi/2)>1$, $G' > G''$. Strictly speaking the power law is not a physically realistic model in this form, but it approximates to certain cases where the series of Maxwell elements is replaced by a continuous function. Typical data to which a power law model can be applied are those of a set yogurt, given in Figure 9.

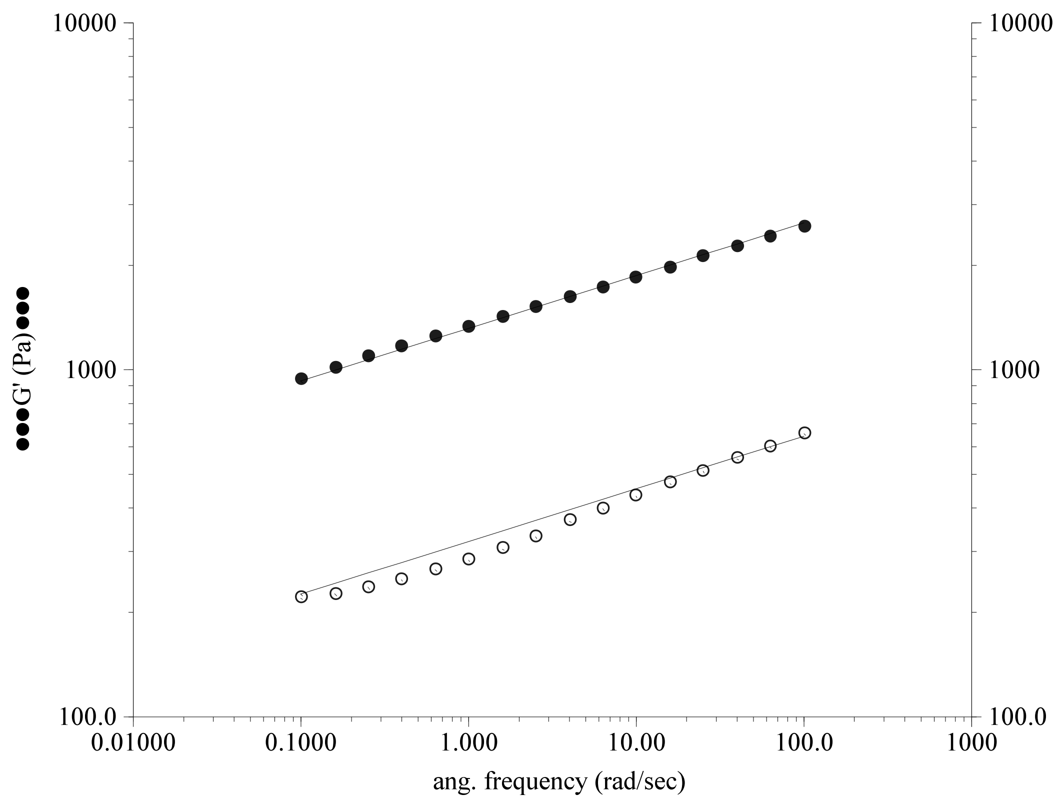

Figure 9: oscillation data for a set yogurt fitted with a power law model

The software gave a value of $k = 320.4\ (\text{Pa s})^n$, and $n = 0.1518$., with a standard error of 21.47.

The Williams Landel Ferry (WLF) and Arrhenius models are applicable only to data reduced using the principle of time-temperature superposition, and are discussed in a separate note. (RN11)

The straight line and polynomial, of order selectable up to eight, are sometimes useful for interpolation, but do not necessarily represent physically realistic systems.

Materials conforming to the various models

Very few materials conform well to a single element Maxwell; some liquid crystals and soap solutions provide the best examples. But four Maxwell elements is sufficient for many polymer solutions and melts, and most classes of particulate dispersion, over a range of about three decades of frequency.

The Spriggs model derives from dilute polymer solution theory, for example Rouse theory gives $\alpha = 2$, and is normally applied to materials of that type.

The Oldroyd (Jeffreys) model is best suited to dispersions of deformable particles, for example emulsions.

Although physically unrealistic, as the slightly inferior fit to the loss modulus in the above example demonstrates, the power law usually provides the best fit for flocculated dispersions and polymeric gels.

References

Among the introductory texts which give details of some of the models described above, in particular the Maxwells, are:

Barnes, H.A., Hutton, J.F. and Walters, K., An Introduction to Rheology, Elsevier, Amsterdam, 1989.
Ferguson, J. and Kemblowski, Z., Applied Fluid Rheology, Elsevier, London, 1991.
Macosko, C., Rheology, Principles, Measurements and Applications, VCH, New York, 1994.

The use of models in polymer rheology is discussed in:

Larson, R.G., Constitutive Equations for Polymer Melts and Solutions, Butterworths, Boston, 1988.
Bird, R.B., Armstrong, R.C. and Hassager, O, Dynamics of Polymeric Liquids, vol 1, John Wiley, New York, 1987.

The rationale behind the application of the Oldroyd model is given in:

Oldroyd, J.G., The Elastic and Viscous Properties of Emulsions and Suspensions, Proceedings of the Royal Society, A218, p122, 1953.

The Spriggs model is described in:

Spriggs, T.W., Chemical Engineering Science, 20, p931, 1965.

An example of the use of the power law model is given by:

Bremer, L.G.B, van Vliet, T. and Walstra, P., Theoretical and Experimental Study of the Fractal Nature of the Structure of Casein Gels, Journal of the Chemical Society, Faraday Transactions, 85, p3359, 1989.

For more information or to place an order, contact:
TA Instruments, Inc., 109 Lukens Drive, New Castle, DE 19720, Telephone: (302) 427-4000, Fax: (302) 427-4001
TA Instruments S.A.R.L., Paris, France, Telephone: 33-01-30489460, Fax: 33-01-30489451
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Internet: http://www.tainst.com
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