

The News and Information Publication of The Society of Rheology  
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*Help with Ringing, Dumbbells, Relaxation Times*



**Also:**

**Technical Program Salt Lake City, Utah USA**  
**Notable Passing: Hershel Markovitz**  
**Report on Portland**



**Rheology Bulletin**

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### **On the Cover:**

SOR member Prof. Tom McLeish of the University of Leeds UK demonstrates the elongational behavior of colored slime. Prof. McLeish's current research interests are in the dynamics of branched entangled polymers, phase separation in polymeric fluids, and the structure and dynamics of wormlike micelles, peptide nanotapes (amyloid fibrils) and proteins.

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# Creep Ringing in Rheometry or How to Deal with Oft-discarded Data in Step Stress Tests!

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## Introduction

Inertial effects are ubiquitous and unavoidable in stress-controlled rheometry. Many readers of this *Bulletin* will have seen the kind of phenomena shown in the experimental data of Figure 1. If the fluid is sufficiently viscoelastic, inertio-elastic ‘ringing’ events (*i.e.* damped oscillations) are observed in the angular displacement measured at the start of a creep test, as a result of the coupling of instrument inertia and sample elasticity. Even if the fluid is a simple viscous Newtonian fluid one may have noticed that the initial strain response of any real creep test is always quadratic in time, rather than the simple linear response  $J(t) = \gamma(t)/\tau_0 = t/\mu$  that is always taught in class. Although well-understood theoretically, effectively dealing with the consequences of inertio-elastic ringing is something with which practitioners of the coarse art of rheometry may not always be comfortable. This note is intended to remind the reader of the sources of these phenomena, and review some methods for extracting useful rheological information from the data rather than simply discarding or deleting them.

Inertial effects are often interpreted as undesirable, because inertia limits the ability to measure the theoretical creep response of an unknown test material at short times. However, effects such as inertio-elastic creep ringing can be exploited in order to rapidly estimate viscoelastic properties. Creep ringing can be deliberately exploited to slightly extend the accessible range of oscillatory measurements, and the data extracted can also be compared with the viscoelastic material properties measured in forced oscillation tests in order to check for self-consistency.

## Review

The analysis of inertio-elastic vibrations arising in viscoelastic materials has been practiced for some time. It was apparently one of the most popular methods of (attempting to) extract viscoelastic moduli, especially for low frequencies and low-loss samples, when it was difficult to measure the phase angle (see, *e.g.*, the opening remarks by Markovitz [1]). The earliest protocols were to perform the test under *free* vibrations; that is, a predetermined force was released, and the system was then allowed to return to equilibrium as it underwent damped vibrations (often referred to as ‘free damped vibrations’ in the literature). Some early rheometer designs incorporated torsional springs, which would exhibit free (and weakly damped) vibrations even when the sample itself had no elasticity. Instrument elasticity complicated the experimental procedure, as pointed out by Walters [2], who noted that the free vibration technique was generally only useful for extracting a viscosity coefficient. Without the torsional spring, however, the analysis and experiments are less difficult. By measuring the ringing frequency  $\omega_*$  and the *logarithmic decrement*  $\Delta$  associated with the ringing (to be defined in detail below), Struick [3] showed that the viscoelastic moduli can be *approximated* for small  $\Delta$ , negligible instrument elasticity, and negligible sample inertia by the following expressions:

$$\begin{aligned} G' &\approx \frac{I\omega_*^2}{b} \left(1 + (\Delta/2\pi)^2\right) \\ G'' &\approx \frac{I\omega_*^2}{b} \left(\frac{\Delta}{\pi}\right) \\ \tan \delta &\approx \frac{\Delta}{\pi} \left(1 + (\Delta/2\pi)^2\right) \end{aligned} \quad (1)$$

where  $I$  is the moment of inertia of the system,  $\omega_*$  is the ringing frequency, and  $\Delta$  is the logarithmic decrement. This is defined as the natural logarithm of the ratio of two successive peaks, or more generally  $\Delta = (1/n) \ln(A_1/A_{n+1})$ , where  $A$  is the amplitude of the ringing above the equilibrium displacement and  $n$  is the number of cycles between peaks.

In these expressions,  $b$  is a geometry factor given by  $\gamma/\tau = b\phi/\Gamma$  that relates the raw (or measured) angular displacement  $\phi$  and torque  $\Gamma$  to the rheological quantities of interest, *i.e.* the strain  $\gamma$  and stress  $\tau$  (hence  $b = F_\gamma/F_\tau$  where  $\tau = F_\tau\Gamma$  and  $\gamma = F_\gamma\phi$ ). For example, the geometry factor for a cone-plate is  $b_{c-p} = 2\pi R^3 / (3\tan\theta)$ , and for a plate-plate,  $b_{p-p} = \pi R^4 / 2h$ . Struick also gives higher order correction

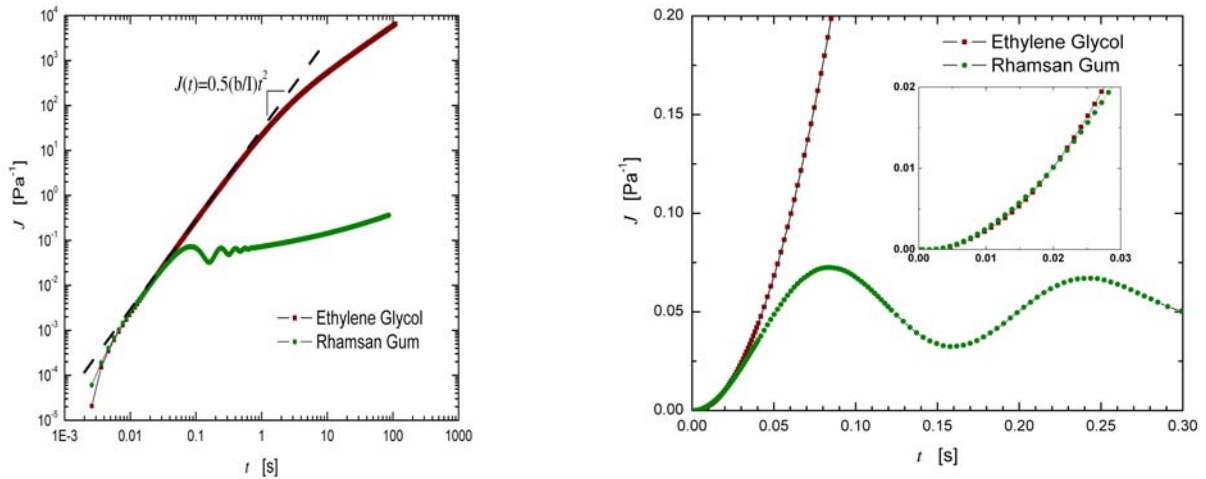


Figure 1: The transient creep response of a viscous Newtonian fluid and a viscoelastic polymeric gel with equivalent instrument inertia and geometry. The viscoelastic fluid exhibits underdamped oscillations but little flow at long times as shown in Figure 1(a). The short time creep response, shown in Figure 1(b), is identical for the two fluids and is completely determined by instrument inertia and geometry. A short time asymptotic solution proportional to  $t^2$  is also shown by the broken line. Creep ringing is caused by the coupling of instrument inertia with the elasticity of the viscoelastic sample (Rhamsan gum (courtesy of CPKelco, San Diego, CA) at 0.75 wt% 250mM NaCl, AR-G2, D=6 cm 2° cone, T=25°C,  $\tau_0=1$  Pa for each).

terms to the approximation given above. These corrections are proportional to  $\Delta$ ,  $\omega_s$ , and derivatives with respect to frequency (to access a range of frequencies, one would need to vary the instrument inertia). Struick also presents a plot of maximum relative error versus logarithmic decrement. For example, at  $\Delta = 1.0$  (or equivalently  $\tan \delta \approx 0.33$  from eq. (1)) the maximum relative error for the elastic modulus is 7%, and for the loss modulus it is 23%. These ideas are also reviewed in the treatise by Ferry [4].

Forced oscillations with precise harmonic control and measurements over many orders of magnitude in frequency are now readily provided by commercial rheometers, and therefore the free vibration technique is no longer a common method of measuring viscoelastic moduli. However, the ringing caused by the coupling of instrument inertia and sample elasticity is still part of the everyday lives of experimental rheologists. Zölzer & Eicke [5] used creep data obtained on a modern controlled-stress instrument to revisit the early ideas of ringing under step-stress loadings, and used the approximations developed for free vibrations to interpret their data; however, this work is not widely known or cited. Another option for obtaining estimates of viscoelastic moduli from observations of free ringing is to assume a specific rheological constitutive model for the material. The differential equation governing the evolution in the sample stress is then coupled with the differential equation of motion for the system, and the resulting time-dependent response can then be solved analytically (or numerically) and regressed to the experimental measurements in order to obtain best-fit material parameters. The resulting equation of motion is of the general form:

$$\frac{I}{b} \ddot{\gamma} = H(t)\tau_0 - \tau_s(t) \quad (2)$$

where  $I = I_{\text{geometry}} + I_{\text{rheometer}}$ ,  $H(t)$  is the Heaviside step function characterizing the imposition of the instrument stress, and  $\tau_s(t)$  is the shear stress in the sample arising from deformation. It is immediately apparent that the sample stress is *not* a step function,  $\tau_s(t) \neq H(t)\tau_0$ , due to the finite inertia of any real rheometric instrument, although it eventually reaches the constant, desired value after the inertial transient has decayed. The constitutive equation for sample stress is coupled with this equation of motion, and the full system of (differential) equations must be solved simultaneously. Arigo & McKinley [6] presented numerical solutions for a four-mode upper-convected Maxwell model in parallel with a solvent viscosity, along with the analytical solution for the single-mode formulation (a convected Jeffreys model). Additional rheological models were considered by Baravian & Quemada [7], including the Kelvin-Voigt and Maxwell models. Baravian & Quemada noted that creep ringing was advantageous in extending the accessible frequency range in measurements on biopolymer gels (they reported ringing at up to 75 Hz) since inertial effects limited the frequency range accessible by forced oscillations.

### Illustrative Examples

We turn now to some examples of creep ringing behavior. Figure 2 shows the creep response for three common rheological models: Newtonian, Kelvin-Voigt, and Jeffreys. For each model the ideal creep response is shown (with  $I = 0$  in eq. (2)) alongside the actual response that arises due to a finite moment of inertia. For completeness, the analytical solutions for the Kelvin-Voigt and Jeffreys models are given in Table 1 (see e.g. [7] for detailed development of solutions). The Kelvin-Voigt model contains two parameters (a spring of modulus  $G_K$  in parallel with a dashpot  $\eta_K$ ) and is the canonical model for a viscoelastic solid because it attains a finite strain at

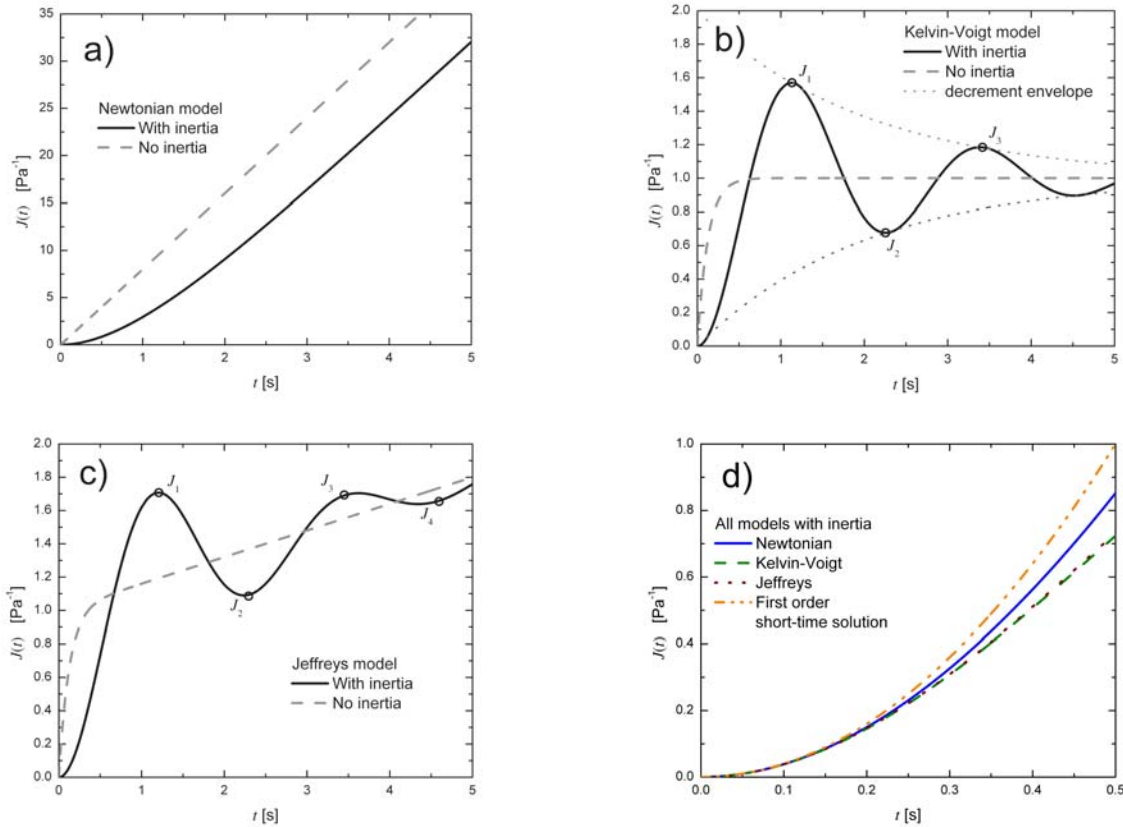


Figure 2: Typical data (simulated) for inertial creep responses compared to ideal non-inertial responses: a) Newtonian; b) Kelvin-Voigt viscoelastic solid, under-damped; c) Jeffreys viscoelastic fluid, under-damped; d) an enlargement of the response near the origin shows that all models have the same quadratic response at short times, which is determined purely by the instrument inertia and geometry factor.

steady state. The Jeffreys model contains three-parameters (one spring and two dashpots), and at steady state shows a steady rate of creep as expected in a viscoelastic fluid. The three elements of the Jeffreys model can be arranged as either a Kelvin-Voigt unit in series with a dashpot, or equivalently as a Maxwell unit (i.e. a spring in series with a dashpot) in parallel with a dashpot [8]. In this work we use the former formulation because it is convenient to see how the results reduce to the Kelvin-Voigt model in the limit  $\eta_2$  approaches infinity. Ringing is only observed in the under-damped case, corresponding to the sample having sufficient elasticity,  $G_K, G_J > G_{critical}$ , where  $G_{critical}$  is given in Table 1 for each model.

The envelope for determining the logarithmic decrement is also shown for the Kelvin-Voigt model in Figure 2(b). For a viscoelastic solid creep response of the approximate form  $J(t) \approx X e^{\frac{\Delta \omega t}{2\pi}} \sin(\omega t + \psi) + Y$ , the logarithmic decrement  $\Delta$  can be determined from the absolute value of three peaks,  $J_1, J_2, J_3$  (as shown in Figure 2b) by the formula  $\Delta = 2\ln((J_1 - J_2) / (J_3 - J_2))$ , which eliminates the need to know the offset bias  $Y$ . The logarithmic

decrement  $\Delta$  may then be used in conjunction with eq. (1) to approximate the viscoelastic moduli.

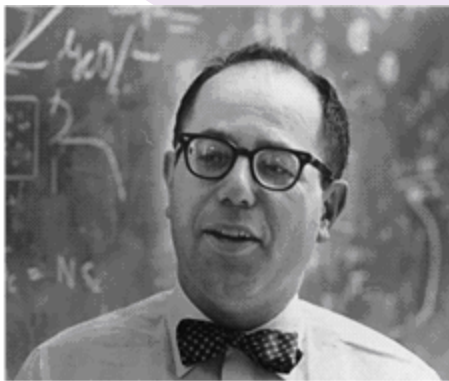
It is apparent from Figure 2(c) that the logarithmic decrement may be more difficult to obtain for a viscoelastic *fluid*, since an irreversible flow component is part of the response. For this case an approximate viscoelastic response is of the prototypical form  $J(t) \approx X e^{\frac{\Delta \omega t}{2\pi}} \sin(\omega t + \psi) + Y + Zt$ . In this case, the logarithmic decrement can be determined from the absolute value of four peak points,  $J_1, J_2, J_3, J_4$  (shown in Figure 2c) without knowledge of  $Y$  or  $Z$ , by the formula

$$\Delta = 2\ln((J_1 - 2J_2 + J_3) / (-J_2 + 2J_3 - J_4)) \quad (3)$$

Figure 2(d) is a close-up of the short time responses of each constitutive model presented in Figures 2(a) – (c). This graphically shows that the initial short time response of any model is related only to the inertia of the system and is quadratic in time. This can be readily observed from eq. (2). Provided the sample being probed does not exhibit

(continues page 22)





Photograph by Clyde Hare, courtesy AIP Emilio Segre Visual Archives

## Hershel Markovitz (1921-2006)

Hershel Markovitz, Emeritus Professor of Mechanics and Polymer Science in the Department of Chemistry of Carnegie Mellon University, died on 29 August in Jerusalem, where he had been living since 1987 with his wife Marion. Born 11 October 1921 in McKeesport, PA, he resided in Pittsburgh, PA, until moving to Jerusalem. Preceded in death by Marion, he is survived by their three children, and his brother.

The contributions Hershel made to rheology were recognized by the 1967 Bingham Medal of the Society of Rheology. Here, and throughout, we adopt the informal “Hershel”, in keeping with both his personality and how he was universally known among his contemporaries in the SoR. They will remember him for his pleasant and always helpful demeanor, his careful scholarship, his thoughtful and effective contributions to education in rheology, with encyclopedia articles and films on rheology that remain in circulation to this date, his insightful theoretical and experimental research in linear and nonlinear viscoelasticity, and, equally as characteristic, his bow ties, handmade for him by Marion using excess fabric from her seamstress projects. Hershel created the experiments and devised the equipment used in the demonstrations in his educational films, and was the principal in all of them (complete with his trademark bow tie). Collaborations in rheology with Hershel had a strong and highly beneficial influence on the research of several of his colleagues at the Mellon Institute,

including the four authors of this obituary, each of whom learned much and greatly enjoyed collaborative research and coauthorship with him.

Following a B.S. in Chemistry from the University of Pittsburgh (1942), Hershel earned a Ph.D. from Columbia University (1949) with a dissertation in physical chemistry, written under the direction of G. B. Kimball, on the influence of salts on the viscosity of solutions of polyacrylic acid. After his graduate studies, he joined the Mellon Institute of Industrial Research in Pittsburgh (1949) to work on a Fellowship on synthetic rubber sponsored by the Synthetic Rubber Division of the Reconstruction Finance Corporation. His coworkers on the projects of that Fellowship included scientists and engineers familiar to many in the SoR, e.g., Thomas W. DeWitt, Frank J. Padden Jr. and Lewis J. Zapas.

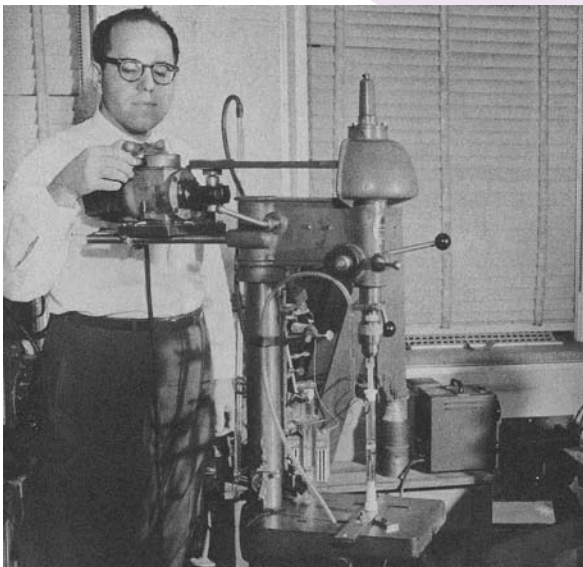
In his eight years with the Synthetic Rubber Fellowship, Hershel worked on problems in the rheology of polymers and their solutions demonstrating the strategies that would mark his research, including the construction and employment of equipment to measure dynamic mechanical properties, and the theory needed to properly understand the implications of results obtained in the use of such instruments. He became a Senior Fellow of Mellon Institute in 1951, and was the Head of the Fellowship from 1954 until its conclusion in 1957 upon the termination of the funding agency. In that period he published several papers on the rheology of solutions of polyisobutylene, including a comprehensive study with DeWitt, Padden, and Zapas, and wrote important papers about the theory and measurement of normal stress effects. He recruited Edward F. Casassa for research on dilute polymer solutions and began collaborations with him on a statistical mechanical theory of the second virial coefficient of polymer solutions.

A restructuring of the research activities in the Mellon Institute commenced in 1957 with the arrival of Paul J. Flory as the Executive Director of Research and Thomas G Fox as a Staff Fellow in charge of fundamental and applied polymer research. The restructuring brought an expansion of research in fundamental polymer science. Casassa was promoted to the position of Senior Fellow, and Bernard D. Coleman was recruited in that position. Among the newly recruited Fellows were Donald J. Plazek and Meyer H. Birnboim to work with Hershel, and Guy C. Berry to work with Casassa and Fox, and to later collaborate with Hershel.



In the next decade Hershel deepened his interests in normal stress effects and nonlinear rheology in general and continued his experimental research in linear viscoelasticity with Plazek with the emphasis laid on the frequency and temperature dependence of the (linear) dynamical properties of polyethylene (1961). He published an experimental study with David R. Brown of normal stress effects in solutions of polyisobutylene (1963) and wrote with Coleman a paper on the continuum theory of normal stress effects in second-order fluids that demonstrated the presence of a (at the time surprising) relation between a particular normal stress effect and certain linear viscoelastic parameters (1964). He and Coleman collaborated with Walter Noll, of the faculty of the Carnegie Institute of Technology (CIT), to write the monograph *Viscometric Flows of Non-Newtonian Fluids, Theory and Experiment* (1966). In this period, Hershel was a Visiting Lecturer at the Johns Hopkins University (1958-9) and a Fulbright Fellow at the Weizmann Institute (1964-5).

In the period 1968 through 1985 he published several papers on the history of rheology, and his dedication to education led him to publish three encyclopedia articles and produce and be the principal in films on rheology that remain in circulation to this date. The merger of the Mellon Institute and CIT to create Carnegie Mellon University in 1967 brought a professorship to Hershel, and the opportunity to create courses in rheology and viscoelasticity in the new graduate program in polymer science at Carnegie Mellon; he taught these courses until his retirement in 1986, being recognized for his excellence in this endeavor by the Julius Ashkin



Teaching Award from the Mellon College of Science of Carnegie Mellon in 1982. This is not to imply that he discontinued his research in this period. His research continued apace, including experimental studies on the linear viscoelastic properties of polymer solutions (with Plazek and others), semicrystalline polysiloxane (with a Ph.D. student), and polymer dispersions (with Berry and another Ph.D. student), along with a number of theoretical studies including work with Coleman on the theory of fluids with gradually fading memory.

Hershel was active in scientific affairs: he was chairman of the American Physical Society's Division of High Polymer Physics (1961-2), president of the Society of Rheology (1969-71), served on a number of editorial boards, and had editorial positions with the Transactions of the Society of Rheology (1967-9) and the Journal of Polymer Science (1965-88).

Over the years 1949-88, Hershel interacting informally with many at Carnegie Mellon and elsewhere, while publishing research papers with some 26 different co-authors. He was generous with his time and knowledge, attributes much appreciated by the many students with whom he worked, as well as by those of us who had the much-valued opportunity to be his colleague and friend.

Guy C. Berry  
Carnegie Mellon University  
Pittsburgh, PA

Bernard D. Coleman  
Rutgers University  
New Brunswick, NJ

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University of Pittsburgh  
Pittsburgh, PA

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# Teaching with FENE Dumbbells

by R. Byron Bird

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A few years ago there appeared a book entitled *How Fluids Unmix*, by Johanna Levelt Sengers (Koninklijke Nederlandse Akademie van Wetenschappen, Amsterdam (2002)). In this book she shows what a wealth of qualitative information is contained in the simple van der Waals equation of state for binary gas mixtures, with just four constants. This book also is an excellent historical study of the powerful school of Dutch physicists who contributed so much to our understanding of the equation of state of gas mixtures, phase relations, and critical phenomena. This beautiful book prompted me to ask "Is there a similar story to tell in rheology?"

When one thinks of simple mechanical models for describing polymer molecules, the elastic dumbbell models immediately come to mind. Such bead-spring models were used by Werner Kuhn and collaborators beginning in the 1930s. The simplest model involves two beads connected by a Hookean spring whose instantaneous length and orientation is given by the vector  $\mathbf{Q}$ . The force in the spring is  $\mathbf{F} = H\mathbf{Q}$ , where  $H$  is the Hookean spring constant. In 1966, Hanswalter Giesekus showed how to get a constitutive equation for this model by essentially doing the following. We write two forms of the stress-tensor expression:

Kramers form[1]:

$$\boldsymbol{\tau}_p = -n\langle \mathbf{FQ} \rangle + nkT\boldsymbol{\delta} = -nH\langle \mathbf{QQ} \rangle + nkT\boldsymbol{\delta} \quad (1)$$

$$\text{Giesekus form[2]: } \boldsymbol{\tau}_p = +\frac{1}{4}n\zeta\langle \mathbf{QQ} \rangle_{(1)} \quad (2)$$

Here  $\boldsymbol{\tau}_p$  is the polymer contribution to the stress tensor,  $n$  is the number density of dumbbells,  $\zeta$  is the friction coefficient of a single bead,  $\boldsymbol{\delta}$  is the unit tensor, and the subscript (1) indicates a convected time derivative. The angular brackets indicate statistical averages.

To get a constitutive equation, we take the convected time derivative of  $\langle \mathbf{QQ} \rangle$  in the first equation and use  $\boldsymbol{\delta}_{(1)} = -\dot{\boldsymbol{\gamma}}$ , where  $\dot{\boldsymbol{\gamma}}$  is the rate-of-



Bob Bird at the Portland SOR meeting, October 2006.

strain tensor. We then combine the resulting equation with Eq. 2 to eliminate  $\langle \mathbf{QQ} \rangle$  to get[2]:

$$\boldsymbol{\tau} = \boldsymbol{\tau}_s + \boldsymbol{\tau}_p$$

$$\text{with } \boldsymbol{\tau}_p + \lambda_H \boldsymbol{\tau}_{p(1)} = -nkT\lambda_H \dot{\boldsymbol{\gamma}} \quad (3)$$

Here  $\boldsymbol{\tau}_s = -\eta_s \dot{\boldsymbol{\gamma}}$  is the solvent contribution to the stress tensor, and  $\lambda_H = \zeta/4H$  is the time constant for the fluid. When Eq. 3 is solved for steady shear flow, we get for the viscosity  $\eta_0 = \eta_s + nkT\lambda_H$ . All other rheological properties can then be expressed in terms of two constants:  $\eta_0$  and  $\lambda_H$ . Equation 3 can describe qualitatively many observed rheological phenomena but *not* the shear-rate dependence of the viscosity and first normal stress coefficient.

In 1972, Hal Warner[3] began to explore the kinetic theory of finitely extensible dumbbells, to try to get a shear-rate-dependent viscosity. He chose to describe the spring force by the expression

$$\mathbf{F} = H\mathbf{Q}/[1-(Q/Q_0)^2] \quad (Q \leq Q_0) \quad (4)$$

in which  $Q_0$  is the maximum allowable length for the connector. For this model a new dimensionless group arises, the finite extensibility parameter  $b = HQ_0^2/kT$ , which is generally between 30 and 300, and infinity in the Hookean spring limit. He christened this model the FENE dumbbell (Finitely Extensible Nonlinear Elastic). Then the two forms of the polymer contribution to the stress tensor are:

$$\boldsymbol{\tau}_p = -nH \left\langle \frac{\mathbf{QQ}}{1-(Q/Q_0)^2} \right\rangle + nkT\boldsymbol{\delta} \quad (5)$$

$$\boldsymbol{\tau}_p = +\frac{1}{4}n\zeta\langle \mathbf{QQ} \rangle_{(1)} \quad (6)$$

It is not possible to get the complete constitutive equation as was done for Hookean dumbbells. Hence Hal solved the differential equation for the distribution of orientation vectors by a perturbation method and thus got the following expansions for the

viscosity and normal stress coefficients at small shear rates with  $\eta_0$ ,  $\lambda_H$ , and  $b$  as parameters, where now  $\eta_0 = \eta_s + [b/(b+5)] nkT\lambda_H$ .

$$\frac{\eta - \eta_s}{\eta_0 - \eta_s} = \left[ 1 - \frac{2b^2(4b+17)}{(b+5)(b+7)(b+9)(2b+7)} (\lambda_H \dot{\gamma})^2 \dots \right] \quad (7)$$

$$\frac{\Psi_1}{\eta_0 - \eta_s} = \frac{2b\lambda_H}{(b+7)} \times \left[ 1 - \frac{2b^2(20b^3 + 315b^2 + 1578b + 2569)}{(b+5)(b+7)(b+9)(b+11)(2b+7)^2} (\lambda_H \dot{\gamma})^2 \dots \right] \quad (8)$$

and  $\Psi_2 = 0$ . For steady elongational flow, Ole Hassager showed that for small and large elongational rates  $\dot{\epsilon}$ , respectively:

$$\frac{\bar{\eta} - 3\eta_s}{\eta_0 - \eta_s} = 3 \left[ 1 + \frac{b}{b+7} (\lambda_H \dot{\epsilon}) + \dots \right], \quad (\lambda_H \dot{\epsilon} < 1) \quad (9)$$

$$\frac{\bar{\eta} - 3\eta_s}{\eta_0 - \eta_s} = 2(b+5) \left[ 1 - \frac{b+3}{2b} \frac{1}{\lambda_H \dot{\epsilon}} + \dots \right], \quad (\lambda_H \dot{\epsilon} > 1), \quad (10)$$

After Hal presented his paper to The Society of Rheology, one young professor (who shall remain nameless) said something like "I don't understand why you are wasting your time on this stuff."

In 1975, Roger Tanner[4] suggested assuming that the distributions of orientations and chain lengths peak sharply around some configuration  $\mathbf{S}(t)$ . If we describe this sharply peaked distribution by a delta function, Eqs. 5 and 6 become:

$$\boldsymbol{\tau}_p = -nH \frac{\mathbf{SS}}{1 - (\mathcal{S}/Q_0)^2} + nkT\boldsymbol{\delta} \quad (11)$$

$$\boldsymbol{\tau}_p = +\frac{1}{4}n\zeta(\mathbf{SS})_{(1)} \quad (12)$$

The dyadic product  $\mathbf{SS}$  as well as  $\mathcal{S}^2$  can be eliminated among these two equations and the trace of the first equation, thereby giving a constitutive equation:

$$Z\boldsymbol{\tau}_p + \lambda_H \boldsymbol{\tau}_{p(1)} - [\boldsymbol{\tau}_p - nkT\boldsymbol{\delta}] \lambda_H \frac{D \ln Z}{Dt} = -nkT\lambda_H \dot{\gamma} \quad (13)$$

where  $Z = 1 + (3/b)[1 - (\text{tr}\boldsymbol{\tau}_p/3nkT)]$ , and  $D/Dt$  is the substantial derivative. Thus we have a constitutive

equation containing the parameter  $b$ . The zero-shear-rate viscosity is given by  $\eta_0 = \eta_s + [b/(b+3)]nkT\lambda_H$ , which does not quite agree with Eq. 7.

Several years later, in 1980, Paul Dotson, Norm Johnson, and I did something very similar[5]. We replaced the average of the ratio in Eq. 5 by the ratio of the averages (which we call the Peterlin approximation), and then eliminated the average values as Tanner had done with  $\mathbf{SS}$  and  $\mathcal{S}^2$ . We called the resulting equation the FENE-P equation.

Although I had sat in on Roger Tanner's presentation to The Society of Rheology, and (if my memory is correct) he attended mine, it was some time before we realized that we had arrived at the same result, because of differences in notation.

In the second edition of *Dynamics of Polymeric Liquids*, we added a small refinement by replacing the  $\langle \dots \rangle$  expression in Eq. 5 by [6]

$\langle \mathbf{QQ} \rangle / (1 - \langle Q^2/Q_0^2 \rangle) + \epsilon Q_0^2 \boldsymbol{\delta}$  to make the zero-shear-rate viscosity match Warner's expression (Eq. 7) by taking  $\epsilon = 2/[b(b+2)]$ . The resulting constitutive equation resembles Eq. 13, but with  $nkT$  replaced by  $nkT(1-\epsilon b)$ , and 1 replaced by  $(1-\epsilon b)$  in  $Z$ . After a flow problem has been solved, we can then calculate the average molecular stretching at every point in the flow field from  $\langle Q^2/Q_0^2 \rangle = (1-Z^{-2})$ . Unfortunately there will always be a small number of dumbbells that are stretched out beyond the maximum length  $Q_0$ , but this causes little trouble in describing rheological phenomena.

Let us now examine some of the results of the FENE-P model. For the zero-shear-rate viscosity and the viscosity at infinite shear rates, respectively, we found[6] (with  $\eta_0 = \eta_s + [b/(b+5)]nkT\lambda_H$ ):

$$\frac{\eta - \eta_s}{\eta_0 - \eta_s} = 1 \quad (14)$$

$$\frac{\eta - \eta_s}{\eta_0 - \eta_s} = \left( \frac{b+5}{b} \right) \left( \frac{b}{2} \right)^{1/3} \left( \frac{1}{\lambda_H \dot{\gamma}} \right)^{2/3} \quad (15)$$

The viscosity decreases as  $\dot{\gamma}^{-2/3}$ , agreeing with experimental data for many polymer solutions. The model also gives  $\Psi_1$  decreasing as  $\dot{\gamma}^{-4/3}$ , which seems to be appropriate. The second normal stress coefficient  $\Psi_2$  is given as zero; since  $\Psi_2$  is generally considerably smaller than  $\Psi_1$ , we consider this model result to be not altogether unreasonable.

For elongational flow we get[6]

$$\frac{\bar{\eta}(0) - 3\eta_s}{\eta_0 - \eta_s} = 3; \quad \frac{\bar{\eta}(\infty) - 3\eta_s}{\eta_0 - \eta_s} = 2(b+5);$$

$$\frac{\bar{\eta}(-\infty) - 3\eta_s}{\eta_0 - \eta_s} = \frac{1}{2}(b + 5) \quad (16)$$

and the slope of  $\bar{\eta}(\dot{\epsilon})$  at  $\dot{\epsilon} = 0$  is positive. Thus the model predicts a large elongational viscosity as the elongation rate increases, and a somewhat smaller increase as the elongation rate becomes negative (biaxial stretching).

Many more problems have been solved. Yoshihiro Mochimaru[7] in 1981 obtained qualitatively reasonable results for shear and normal stresses at the sudden inception of shear flow as well as for steady shear flow with superposed oscillatory motion. In addition he has solved the problem of fast squeezing flow between two parallel disks. In 1983, he also obtained the developing velocity profiles at the inception of Couette flow; he predicted that there would be “velocity overshoot”—that is, the velocity goes beyond the final linear profile, and then oscillates about the final linear profile. Newtonian fluids, on the other hand, approach the final linear profile monotonically. In 1989, Steven Burdette[8] observed this velocity overshoot experimentally in polymeric liquids.

Numerous modifications of the FENE-P constitutive equation have been proposed. In 1988, Chilcott and Rallison, instead of equating the right sides of Eqs. 11 and 12, wrote[9]

$$\frac{n\zeta}{4}(\mathbf{SS})_{(1)} = \frac{-nHSS + nkT\delta}{1 - (S^2/Q_0^2)} \quad (17)$$

to describe Boger fluids with constant viscosity. Subsequent authors called the resulting constitutive equation the FENE-CR equation, which implies (incorrectly) that it has something to do with FENE dumbbells.

In 1991, Lew Wedgewood, Dan Ostrov, and I suggested a generalization of the model to a linear chain of  $N$  beads and  $N-1$  nonlinear springs[10]. The model contains four parameters:  $\eta_0$ ,  $\lambda_H$ ,  $b$ , and  $N$ . In the limit as  $b$  becomes infinite, this FENE-PM model reduces to the Rouse chain model; the “M” stands for “multibead.” This model also gives shear-rate-dependent viscosity with slope  $-2/3$  on a log-log plot and a first-normal-stress coefficient with a slope of  $-4/3$ . Monotone increasing elongational viscosity is also predicted. The shapes for the components of the complex viscosity are much more realistic than those for dumbbells. Inclusion of hydrodynamic interaction is also possible, so that the data for small-amplitude oscillatory motion are more faithfully reproduced. Many papers have appeared in the literature comparing the behavior of various kinds of finitely

extensible chains, starting with Ben van den Brule’s article in *JNNFM* in 1993[11]. Nowadays Brownian dynamics provides a means for making calculations for much more complicated mechanical models and for taking into account polymer-wall interactions. We have seen that the simple FENE dumbbell model has provided a nice playground for getting a *qualitative* understanding of a wide range of rheological phenomena in terms of molecular motions. It is particularly helpful as a tool for teaching[12]. With just three parameters,  $\eta_0$ ,  $\lambda_H$ , and  $b$  you can go a long way!

The author wishes to thank Professor A. J. Giacomin for his suggestions in preparing this manuscript.

#### References

1. H. A. Kramers, *Physica*, **11**, 1-19 (1944).
2. H. Giesekus, *Rheol. Acta*, **2**, 50-62 (1962).
3. H. R. Warner, Jr., *Ind. Eng. Chem. Fundamentals*, **11**, 379-387 (1972).
4. R. I. Tanner, *Trans. Soc. Rheol.*, **19**, 37-65 (1975).
5. R. B. Bird, P. J. Dotson, and N. L. Johnson, *J. Non-Newtonian Fluid Mechanics*, **7**, 213-235 (1980)—Eqs. 58-85 are in error.
6. R. B. Bird, C. F. Curtiss, R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids, Vol. 2, Kinetic Theory*, Wiley, New York (1987), pp. 89 and 87 (the development on p. 87 is due to O. Hassager).
7. Y. Mochimaru, *J. Non-Newtonian Fluid Mechanics*, **9**, 157-178, 179-184 (1981), **12**, 135-152 (1983).
8. S. R. Burdette, *J. Non-Newtonian Fluid Mechanics*, **32**, 269-294 (1989).
9. M. D. Chilcott and J. M. Rallison, *J. Non-Newtonian Fluid Mechanics*, **29**, 381-432 (1988).
10. L. E. Wedgewood, D. N. Ostrov, and R. B. Bird, *J. Non-Newtonian Fluid Mechanics*, **40**, 119-139 (1991); **48**, 211 (1993).
11. B. H. A. van den Brule, *J. Non-Newtonian Fluid Mechanics*, **47**, 357-378 (1993).
12. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, Wiley, New York, 2<sup>nd</sup> Revised Edition (2007), Section 8.6.

## NOTICE

The **Nominating Committee** for the 2007 elections has been formed. The members are John Dealy (chair), Wesley Burghardt, and Morton Denn. The committee will report on their nominations in the spring, in time for announcement to the membership by 5 May 2007 (145 days before the annual meeting per the SOR Constitution). Members interested in serving or in suggesting names to the committee are encouraged to contact John Dealy, [john.dealy@mcgill.ca](mailto:john.dealy@mcgill.ca).

$$\eta = \frac{d\tau}{d\dot{\gamma}}$$

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# Questions About Relaxation Spectra Submitted by a Reader

Kevin Penfield of Uniqema has submitted the following questions to the *Bulletin*:

*"I have a vague sense of what relaxation spectra are, as a distribution of (Maxwell?) elements over a continuum of relaxation times. Could you provide me with a better definition, conceptually? What is a more accurate definition of the ordinate? And what pitfalls might there be in using frequency-sweep data covering finite frequency range to calculate a relaxation spectrum (especially, might the points at either end do weird things)?"*

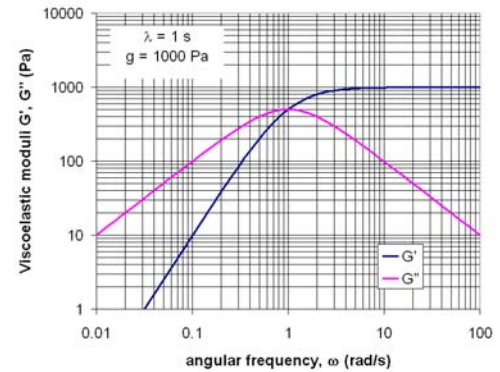
**SOR member Professor John Dealy has provided the following answers.**

These are very important questions that deal with the most fundamental aspects of the practical use of linear-viscoelastic material functions to describe the behavior of polymeric materials. I will deal with these under several headings in response to the issues raised by Kevin Penfield. A more detailed discussion of these subjects can be found in Ref. [1].

In brief, the *discrete relaxation-time spectrum* is a convenient artifice with no physical meaning. It can be calculated easily, but should only be used in a very limited way to interrelate linear-viscoelastic functions. The discrete spectra obtained from such curve-fitting are not unique.

The *continuous relaxation spectrum function*  $H(\tau)$  is a true representation of linear-viscoelastic material properties. It cannot be calculated easily, but in the last two decades good techniques have been developed for calculating the continuous spectrum function from experimental data. The accurate calculation of  $H(\tau)$  from experimental data requires choosing a data-inversion technique that properly accounts for the effect of experimental error. The continuous spectrum function obtained from these methods is unique, within the set of assumptions made about regularization parameters and about the distribution of errors.

$G'$ ,  $G''$  for a single relaxation-time Maxwell model.



Finally, lack of information, especially at long relaxation times, compromises all calculations of linear-viscoelastic properties. Long relaxation-time information, such as is contained in accurate creep compliance data, is required to address this issue. Accurate techniques exist for combining  $G'$ ,  $G''$  and  $J(t)$  data in a way that allows for accurate calculation of the relaxation spectrum function.

## The Discrete Relaxation Spectrum

The material function commonly used as the basis for discussing linear viscoelastic behavior is the relaxation modulus  $G(t)$ , although Don Plazek argues that the creep compliance is a better starting point [2]. In practice it is not possible to measure with good precision the relaxation modulus over the entire range of time from zero to infinity, but we wish to make the best use of the available data to arrive at an analytic function providing the truest possible representation of  $G(t)$  within the limits imposed by the range, accuracy and precision of the data.

It is common practice to describe the relaxation moduli of polymers using a sum of exponentials, referred to as the generalized (multi-mode) Maxwell model.

$$G(t) = \sum_{i=1}^N G_i e^{-t/\tau_i} \quad (1)$$

The set of constant,  $\{\tau_i, G_i\}$ , are said to constitute a *discrete relaxation spectrum*. While these empirical parameters have no physical significance, in the limit of large  $N$ , the sum should, in principle, approach the underlying function  $G(t)$  that is a material property. The discrete spectrum lends itself to the conversion of one response functional into another, for example  $G(t)$  to  $J(t)$  or  $G'(\omega), G''(\omega)$ , and can be inferred from data in such a way that it describes these data with a precision limited only by that of the data themselves.

It is important to note that this choice of a sum of exponentials is arbitrary and does not have a solid foundation in polymer physics. It is thus an empirical description; there is no unique discrete spectrum, and

the fitting parameters  $\{\tau_i, G_i\}$  have no physical significance. It is true that there are theories of polymer behavior that lead to relaxation moduli of the form of Eq 1, and this seems to imply that there is a basis at the molecular level for the use of a sum of exponentials. These theories, however, are based on a much simplified picture in which the molecule is replaced by a chain of  $N$  beads connected by  $N-1$  connecting springs [3, p. 157]. Unlike the actual molecule, this chain is freely-jointed, which dramatically reduces the mathematical complexity of the model. The number of springs is much less than the number of backbone bonds, is arbitrary within certain limits, and thus has no physical significance. For example, the Rouse-Bueche model for an unentangled melt predicts that

$$G(t) = \frac{\rho RT}{M} \sum_{p=1}^N e^{-t^2/\tau_p} \tau_p = \frac{6\eta_0 M}{\pi^2 \rho RT} \quad (2)$$

The Doi-Edwards model for an entangled chain is also based on the freely-jointed chain picture and predicts the following relaxation modulus for an entangled, monodisperse melt in the plateau and terminal zones.

$$G(t) = \frac{8}{\pi^2} G_N^0 \sum_{i, \text{odd}} \frac{1}{i^2} e^{-i^2 t/\tau_d} \quad (3)$$

where  $\tau_d$  is the reptation or disengagement time. The upper limit of the summation is generally not indicated, because it converges very rapidly, but the empirical picture of the freely-jointed chain still lurks in the background.

We conclude that there is little basis at the level of molecular physics for the use of a sum of exponentials to describe the relaxation modulus. Thus, the use of a discrete spectrum should be seen as a convenient empirical representation of experimental data.

#### Continuous relaxation spectrum functions

If the number of elements in the generalized Maxwell model is increased toward infinity, one arrives at the continuous spectrum function,  $F(\tau)$ , where  $F(\tau)d\tau$  is the contribution to  $G(t)$  due to Maxwell elements having relaxation times between  $\tau$  and  $\tau+d\tau$ . The relaxation modulus is related to the spectrum function as shown by Eq 4.

$$G(t) = \int_0^{\infty} F(\tau) [\exp(-t/\tau)] d\tau \quad (4)$$

However, because of the concentration of relaxation information at very short times, it is generally preferable to work with a logarithmic time scale. This leads to a relaxation spectrum function,  $H(\tau)$ , which is a time-weighted spectrum function defined as  $F\tau$ , so that the relaxation modulus is given by:

$$G(t) = \int_{-\infty}^{\infty} H(\tau) [\exp(-t/\tau)] d(\ln \tau) \quad (5)$$

Relationships between the various material functions describing linear behavior and methods for converting among them are discussed by Ferry [4]. The continuous functions  $F(\tau)$  and  $H(\tau)$  are not empirical fittings as is the discrete spectrum, as they are integral transforms that contain all the information that is in the modulus itself.

The degree to which a discrete spectrum approaches the continuous spectrum that is a true material characteristic depends on the density of data points and the technique used to infer the set of spectrum parameters  $\{\tau_i, G_i\}$ . Obviously, the greater the density of data points the better the characterization, but the method used to infer the parameters is also of crucial importance.

#### Methods of Inferring a Discrete Spectrum From Experimental Data

Whether using a discrete or a continuous spectrum function to represent  $G(t)$ , the practical problem is how to use experimental data to determine it. We must first recognize that it is not possible to determine the relaxation modulus with good precision and accuracy over the entire range of relevant times, which may run from microseconds to hours or days. Furthermore, the classical step strain experiment is not a popular method for determining  $G(t)$  because of the difficulties involved in generating an instantaneous deformation and tracking the very rapid initial decay of the stress following the strain. The experiment most often used to characterize linear behavior is small amplitude oscillatory shear. Oscillatory shear data are usually reported as a table of the storage and loss moduli at a series of frequencies, *i.e.*, the set  $\{G'_k, G''_k, \omega_k\}$ . Using the Boltzmann superposition principle, one can show that these are Fourier transforms of the relaxation modulus:

$$G'(\omega) = \omega \int_0^{\infty} G(s) \sin(\omega s) ds \quad (6a)$$

$$G''(\omega) = \omega \int_0^{\infty} G(s) \cos(\omega s) ds \quad (6b)$$

These transforms can, in principle, be inverted to give  $G(s)$ , given the storage and loss moduli [4, p.68]. However, to carry out the inversion in a precise way, these moduli must be known as continuous functions of frequency over the range of frequencies from zero to a value at which they have reached their high-frequency limiting behaviors, whereas what is available are  $G'$  and  $G''$  values at discrete frequencies whose range is limited by the capabilities of the instrument used.

The conversion of a data set  $\{G'_k, G''_k, \omega_k\}$  into a relaxation modulus function is usually carried out by representing  $G(t)$  in terms of a discrete relaxation spectrum  $\{G_i, \tau_i\}$ . This requires the inversion of the summations:

$$G'(\omega) = \sum_{i=1}^N \frac{G_i (\omega \tau_i)^2}{[1 + (\omega \tau_i)^2]} \quad (7a)$$

$$G''(\omega) = \sum_{i=1}^N \frac{G_i (\omega \tau_i)}{[1 + (\omega \tau_i)^2]} \quad (7b)$$

It is very important to note that the success of this transformation is limited by the following inevitable features of oscillatory shear data.

1. Data are obtained only at a certain number of discrete frequencies.
2. Data are available only between maximum and minimum frequencies that are imposed by the capabilities of the instruments used. This range of frequencies is called the "experimental window".
3. There is always some imprecision (called scatter or noise) in the data.

There may also be systematic error (bias) in the data, but there is no way of correcting for this if it cannot be modeled explicitly. As a result of these nonidealities, the inference of a discrete spectrum using Eqs. 7a,b is an ill-posed problem. Although a set of parameters can be found that provides an approximate description of the rheological behavior that is suitable for some purposes, there is no unique discrete spectrum corresponding to a given set of data.

There are two approaches to this problem, depending on one's objectives. If one wants only an empirical equation that fits the data, it is a relatively simple matter of curve fitting. The most straightforward method for accomplishing this is linear regression, an example of which is the work of Laun [5]. Laun started by selecting one relaxation time parameter  $\tau$

per decade and determined the  $G_i$  values corresponding to them by linear regression based on both  $G'$  and  $G''$ . When Laun used the resulting discrete spectrum to recalculate the storage and loss moduli, he found that spurious oscillations were present. It is also possible using this technique to arrive at a parameter set that includes one or more negative values of  $G_i$ , which is obviously nonphysical. Of course, the number  $N$  of empirical constants fitted should not exceed the number of data points available. Furthermore, in this approach, one ends up modeling the scatter in the data along with the underlying "true" values of the moduli.

A more sophisticated approach to this curve fitting is that of Baumgaertel and Winter [6]. Using nonlinear regression, they developed an algorithm that converges to a "parsimonious" spectrum, *i.e.*, one having the fewest possible Maxwell modes consistent with the level of random error in the data. They do not smooth or filter the data. In other words, they are careful not to model the error. A commercial software package, IRIS [7], is based on their method. This technique yields the simplest possible fitting of the data but contains much less information than was in the data set and has very little if any relationship to the "true" relaxation spectrum.

The second approach to the problem of inferring a spectral function from dynamic data is directed at establishing as accurately as possible the spectrum that is a material property of the material under study rather than simply fitting experimental data. To accomplish this, it is necessary to overcome the ill-posedness of the problem by providing information in addition to the experimental data. A general approach to the problem of arriving at a spectrum that approximates a true material property is the use of regularization. Here the additional information introduced is the specification that the spectrum be a smooth function of time and an estimate of the error in the data. Honerkamp and Weese [8] accomplished this by assuming that the spectrum and its first and second derivatives are continuous and that the second derivative is small. To avoid modeling the noise (random error) in the data, they employ Tikhonov regularization. Provencher [9] has described an algorithm for treating data using this technique, and a commercial version of this code, CONTIN, is available [10]. Tikhonov regularization requires the selection of a value for the regularization parameter, and Honerkamp and Weese [11] have proposed a reliable method for doing this. They use regularization with linear regression to arrive at a spectrum that converges to a unique material function as the number of terms in the discrete spectrum,  $N$ ,

(continues page 30)





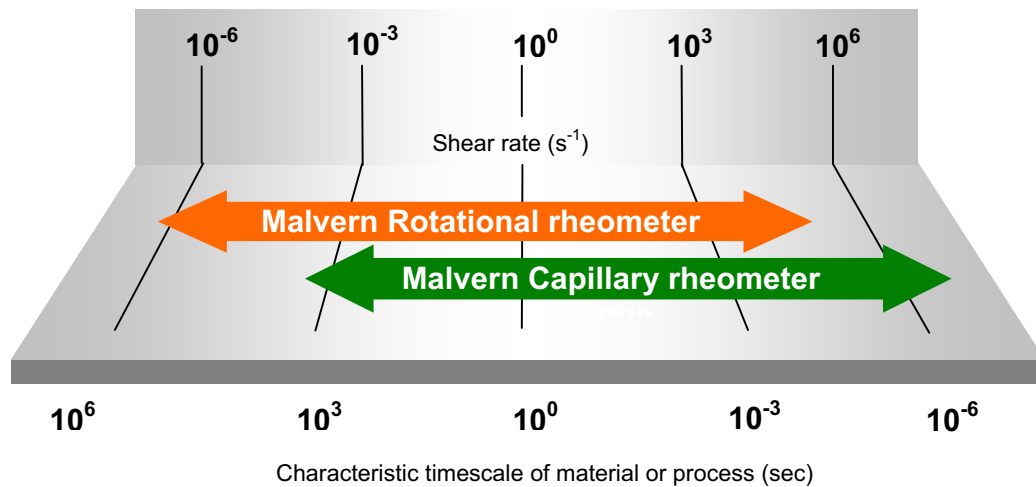
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# Report from Portland

The 78<sup>th</sup> Annual Meeting of The Society of Rheology took place in Portland, Maine USA 8-12 October 2006 amid beautiful fall colors and pleasant temperatures. There were 354 meeting registrants, 235 oral presentations and 72 posters.

Three and a half days of technical talks (four parallel sessions) and a full social program were arranged by local arrangements co-chairs Albert Co and Doug Bousfield and technical program co-chairs Antony Beris and Eric Furst. The social program included a welcoming reception at the Holiday Inn, a Society luncheon on Monday, and the Society reception held at the Portland Museum of Art (see photo at right). The collections at the Portland Museum of Art are world class and were much appreciated by meeting attendees.

On Tuesday 10 October the 2006 Bingham Medal lecture was presented by Bob Armstrong on the topic "Rheology and Energy." At the Tuesday evening Awards Banquet, Armstrong was thoroughly roasted by Susan Muller and Jeff Giacomini. Armstrong and his wife Debbie took the ribbing with good humor (photo at right).

The 79<sup>th</sup> Annual Meeting of The Society of Rheology is scheduled for 7-11 October 2007 in Salt Lake City, Utah USA, hosted by Jaye Magda and Andy Kraynik. The technical program for Salt Lake City is listed on the next page. Utah is known for its many National Parks and striking geological formations. Details on the Salt Lake City meeting arrangements will be printed in the July 2007 Bulletin and will appear on the web in spring 2007 ([www.rheology.org](http://www.rheology.org)).



Portland was the location for a reunion of the authors of the classic rheology text, *Dynamics of Polymeric Fluids*, (2nd ed, 1986, Wiley, NY) Bob Armstrong, Ole Hassager, and Bob Bird.



Bingham medalists present in Portland included (back row) Mort Denn, Ron Larson, Kurt Wissbrun, John Dealy, Gerry Fuller, Jan Mewis, (front row) Bob Bird, Bob Armstrong (2006 medalist) and Andy Acrivos.

# SLC 2007

## Technical Program for the 79th Annual Meeting of The Society of Rheology

7-11 October 2007  
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## Application for Membership in The Society of Rheology

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signature: \_\_\_\_\_ date: \_\_\_\_\_

Please enclose remittance in US dollars drawn on a US bank payable to “The Society of Rheology” and mail to Janis Bennett at AIP, Suite 1NO1, 2 Huntington Quadrangle, Melville, NY 11747-4502, 516-576-2403, 516-576-2223 (fax). A member subscription to the *Journal of Rheology* is only for your personal use. By your signature below, you agree not to loan or give any issues of this journal to a library or other lending institution without written permission from The Society of Rheology.

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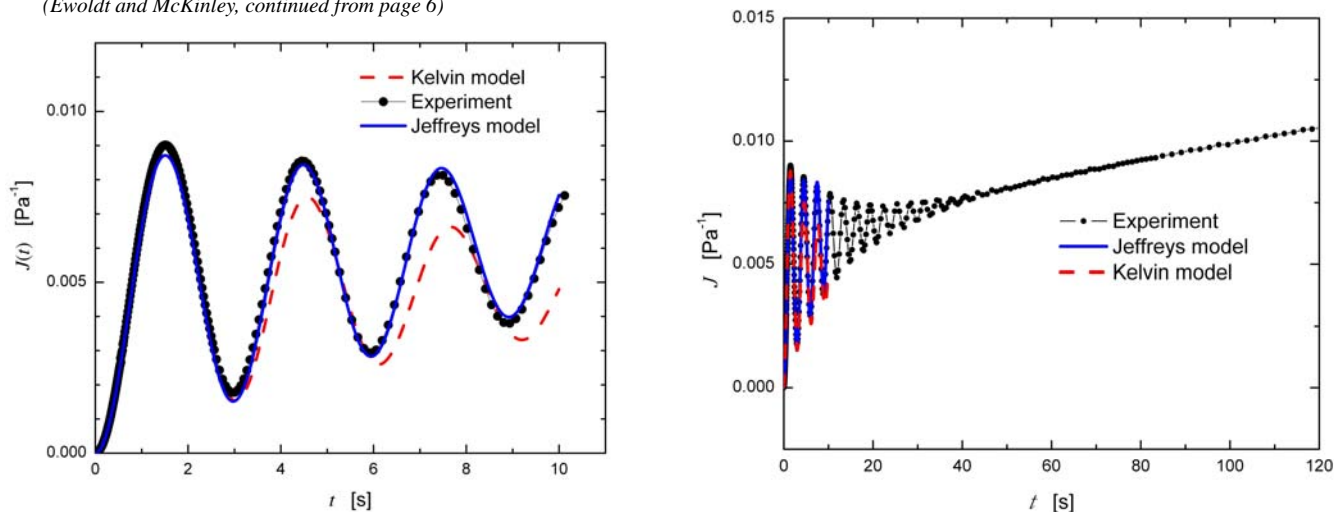


Figure 3: Creep test of native pedal mucus from the terrestrial gastropod *Helix aspera*; inertio-elastic ringing fit to both a Kelvin-Voigt and Jeffreys model (AR-G2,  $D=0.8$  cm plate with sandpaper,  $1000\mu\text{m}$  gap,  $T=22^\circ\text{C}$ ,  $\tau_0 = 5 \text{ Pa} \ll \tau_y$ ).

any instantaneous (or ‘glassy’) elastic response, then at time  $t = 0^+$  the sample stress resisting the acceleration of the rheometer fixture can be ignored, and the resulting second order differential equation is  $(I/b)\ddot{\gamma} = \tau_0$ , which can be readily integrated to give  $\gamma(t) = \frac{1}{2}(\tau_0 b/I) t^2 + \dots$  for *any* constitutive model. As the shear strain and the shear rate build up in the material, the viscous or viscoelastic stress will retard the acceleration of the fixture. The next order correction to the short time solution is also given in Table 1 for the Kelvin-Voigt and Jeffreys models.

It is clear from the asymptotic expression above that all controlled-stress rheometers undergoing a step-stress loading will exhibit a quadratic response at short times. It is interesting to note that the degree to which this response is actually resolved will vary with the temporal sampling rate of the data acquisition system and the minimum angular displacement (or strain) that can be resolved by the rheometer. As angular resolution and temporal sampling rates increase, inertio-elastic oscillations will become increasingly apparent in short-time creep data.

As a further illustration of the creep ringing technique, Figure 3 shows real data from a creep test on pedal mucus (a biopolymer gel) from the terrestrial gastropod *Helix aspera* (also known as the common garden snail). This protein-polysaccharide gel exhibits an apparent yield stress on the order of  $100\text{Pa}$  [9] but is dominated by elasticity below the yield stress. The ringing frequency is approximately  $\omega_* = 2.14 \text{ rad/s}$  ( $f_* = 0.34 \text{ Hz}$ ), and the slow decay in the oscillations indicates weak damping. The underdamped oscillatory response for the two-parameter Kelvin-Voigt model and three-parameter Jeffreys model (Table 1) were fitted to the experimental data using a nonlinear fitting routine in MATLAB. Once the model parameters are determined they can be converted into values of  $G'$  and  $G''$  (see formulae in

Table 1) and compared with the values extracted from the approximate analysis of Struik, which are *model-independent* and use only the ringing frequency  $\omega_*$  and logarithmic decrement  $\Delta$ . Here the logarithmic decrement was determined from the first two cycles, using the four-point calculation (Figure 2(c)) to account for the finite flow in the response. Table 2 shows the comparative results, using all three techniques.

The Jeffreys model achieves a satisfying fit to the data especially at short times before any finite flow effects are observed, and will therefore be used as a benchmark for comparing the results. It is interesting that the approximation, based on frequency and logarithmic decrement, does as well or better than the Kelvin-Voigt model at determining the moduli. Here the logarithmic decrement is small ( $\Delta \approx 0.25 \ll 2\pi$ ), which satisfies the low-loss criteria for using the approximation. In addition to achieving a better fit to the data, another benefit of assuming a rheological model is the opportunity to extend the measured result from free oscillations (which are inherently limited to the single frequency,  $\omega_*$ ) to frequencies above and below the ringing frequency. The precision of this extrapolation certainly depends on the quality of the model fit, but at a minimum allows one to estimate the trends in frequency-dependence within a small range of the ringing frequency.

## Conclusions

This short note has hopefully clarified some of the key features of inertio-elastic creep oscillations that can often be discerned in the high resolution data obtained with state-of-the-art rheometers. We remind the reader that when the effects of inertia are negligible (at ‘long’ times  $t \gg \{1/A_J, 1/A_K\}$  respectively from Table 1), the frequency-dependent linear viscoelastic moduli can be determined directly from the creep compliance  $J(t)$  [4], although the

Table 1: Creep ringing solutions for a Kelvin-Voigt model (viscoelastic solid) and a Jeffreys model (viscoelastic fluid) each coupled with an inertial mass.

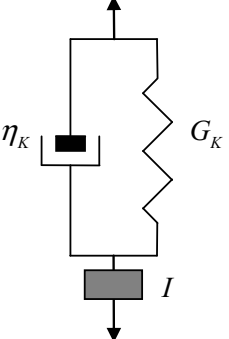
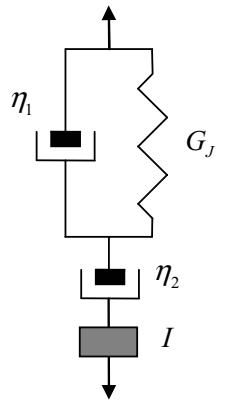
<p style="text-align: center;"><b>Kelvin-Voigt</b></p> 	<p>for ringing : <math>G_K &gt; G_{critical} = \frac{\eta_K^2 b}{4I}</math></p> $\gamma(t) = \gamma_K \left\{ 1 - e^{-A_K t} \left[ \cos(\omega_K t) + \frac{A_K}{\omega_K} \sin(\omega_K t) \right] \right\}$ <p>where: <math>\gamma_K = \frac{\tau_0}{G_K}</math>    <math>A_K = \frac{\eta_K b}{2I}</math>    <math>\omega_K = \sqrt{\frac{G_K b}{I} - A_K^2}</math></p> <p>with short time response: <math>\gamma(t) \cong \frac{\tau_0}{I/b} \left[ \frac{1}{2} (\delta t)^2 - \frac{1}{6} \frac{\eta_K}{I/b} (\delta t)^3 + \dots \right]</math></p> <p style="text-align: center;"><math>G' = G_K</math>    <math>G'' = \eta_K \omega</math>    <math>\lambda_K = \frac{\eta_K}{G_K}</math></p>
<p style="text-align: center;"><b>Jeffreys</b></p> 	<p>for ringing : <math>G_J &gt; G_{critical} = A_J^2 \frac{I}{b} (1 + \eta_1 / \eta_2)</math></p> $\gamma(t) = \dot{\gamma}_J t - B_J - e^{-A_J t} \left[ B_J \cos(\omega_J t) + \frac{A_J}{\omega_J} \left( B_J - \frac{\dot{\gamma}_J}{A_J} \right) \sin(\omega_J t) \right]$ <p>where: <math>\gamma_J = \frac{\tau_0}{\eta_2}</math>    <math>\omega_J = \sqrt{\frac{G_J b}{I} \frac{\eta_2}{(\eta_1 + \eta_2)} - A_J^2}</math></p> $A_J = \frac{G_J + \eta_1 \eta_2 b / I}{2(\eta_1 + \eta_2)} \quad B_J = \frac{\tau_0 (\eta_1 + \eta_2)}{G_J \eta_2} \left( \frac{2A_J I}{\eta_2 b} - 1 \right)$ <p>with short time response: <math>\gamma(t) \cong \frac{\tau_0}{I/b} \left[ \frac{1}{2} (\delta t)^2 - \frac{1}{6} \frac{1}{I/b} \frac{\eta_1 \eta_2}{\eta_1 + \eta_2} (\delta t)^3 + \dots \right]</math></p> <p style="text-align: center;"><math>G' = G_J \frac{(\lambda_2 \omega)^2}{1 + (\lambda_1 \omega)^2}</math>    <math>G'' = G_J \frac{(\lambda_2 \omega) [1 + (\lambda_1^2 - \lambda_1 \lambda_2) \omega^2]}{1 + (\lambda_1 \omega)^2}</math></p> <p style="text-align: center;"><math>\lambda_1 = (\eta_1 + \eta_2) / G_J</math>    <math>\lambda_2 = \eta_2 / G_J</math></p>

Table 2: Viscoelastic moduli determined from inertio-elastic creep ringing shown in Figure 3 using three different methods: the approximate relation using frequency and logarithmic decrement, and fitting two assumed constitutive models: Kelvin-Voigt and Jeffreys.

	$\omega_*$ [rad/s]	$G'$ [Pa]	$G''$ [Pa]	$\tan \delta$
Approximation	2.14	231	18.2	0.08
Kelvin-Voigt	2.03	210	25.9	0.12
Jeffreys	2.11	223	17.0	0.08

frequency range and accuracy will still be limited by the rate of data acquisition and length of measurement. However, the presence of inertia limits the high frequency projection, since the short time response of any real creep test is dominated by inertia, and therefore the sample stress is not actually a step function,  $\tau_s \neq H(t)\tau_0$ , but instead  $\tau_s = H(t)\tau_0 - I\ddot{\gamma}$ . The creep compliance is not well defined for these short times. Of course, one way to nearly eliminate instrument inertia is to perform a step *strain* experiment and measure instead the relaxation modulus  $G(t)$ , in which case it is only the response time of the instrument and sample inertia that become the limiting factors.

As we noted earlier, one reported experimental benefit of inertio-elastic ringing is the ability to achieve higher frequencies than forced oscillations. Note, however, that the ability to resolve this frequency is important, and this depends on the rate of data acquisition of the rheometer. The ringing frequency, to first order, depends on the instrumental parameters and sample elasticity as  $\omega_r \sim \sqrt{bG'/I}$ . For a given material, the limiting frequency is maximized by increasing  $\sqrt{b/I}$ . If the inertia of the geometry is much less than the inertia of the instrument, then the choice of geometry should be made to increase  $b$ . For a cone-plate  $b_{c-p} \sim R^3/\theta$ , where  $R$  is the radius and  $\theta$  is the cone angle, while for a plate-plate  $b_{p-p} \sim R^4/h$ , where  $h$  is the gap height. Thus, assuming that the total inertia is primarily from the instrument, large diameters with small gaps maximize the ringing frequency by increasing the ‘stiffness’ of the system. Higher ringing frequencies will also decrease the total timescale of the ringing, since higher frequencies will increase the rate of dissipation in the viscoelastic material (note also in Table 1 that increasing  $b/I$  increases the damping rates  $A_K$  and  $A_J$ , respectively). Decreasing the total ringing time will also improve the approximation of a step-sample-stress,  $\tau_s(t) \approx H(t)\tau_0$  (with progressively higher frequency oscillations that are dissipated increasingly rapidly and which can only be observed for short times  $t < \{A_J, A_K\}$  respectively). Shifting the ringing frequency to higher values is thus useful for observing creep compliance in viscoelastic materials at shorter timescales.

When analyzing inertio-elastic ringing, the Struik approximation using frequency  $\omega_*$  and logarithmic decrement  $\Delta$  can be used as a very rapid manual self-consistency check to compare with forced oscillation tests. If better precision is desired, the higher order terms given by Struick could be used (which require data at multiple frequencies). Alternatively, a rheological constitutive model can be assumed *a priori*, and the ringing response can be fit to this model. At least one commercial software package for

rheological analysis includes a routine to fit creep ringing to mechanical models such as those in Table 1 (TA Instruments, New Castle, DE). In this particular software the user is still required to manually convert the fitted model parameters to the viscoelastic moduli  $G'(\omega_*)$  and  $G''(\omega_*)$ . Being aware of the existence of inertio-elastic creep ringing and the quadratic short time response of any material to a step stress loading in a rheometer enables the practicing rheologist to extract useful information from data that is often obscured or ignored.

## References

1. Markovitz, H., Free vibration experiment in the theory of linear viscoelasticity. *J. Appl. Phys.*, 1963. 34(1): p. 21-25.
2. Walters, K., *Rheometry*. 1975, New York: Wiley.
3. Struick, L.C.E., Free damped vibrations of linear viscoelastic materials. *Rheol. Acta*, 1967. 6(2): p. 119-129.
4. Ferry, J.D., *Viscoelastic properties of polymers*. 3d ed. 1980: Wiley.
5. Zölzer, U. and H.F. Eicke, Free oscillatory shear measurements - an interesting application of constant stress rheometers in the creep mode. *Rheol. Acta*, 1993. 32(1): p. 104-107.
6. Arigo, M.T. and G.H. McKinley, The effects of viscoelasticity on the transient motion of a sphere in a shear-thinning fluid. *J. Rheol.*, 1997. 41(1): p. 103-128.
7. Baravian, C. and D. Quemada, Using instrumental inertia in controlled stress rheometry. *Rheol. Acta*, 1998. 37(3): p. 223-233.
8. Tschoegl, N.W., *The phenomenological theory of linear viscoelastic behavior: an introduction*. 1989, New York: Springer-Verlag.
9. Ewoldt, R.H., A.E. Hosoi, and G.H. McKinley, Rheological fingerprinting of gastropod pedal mucus and bioinspired complex fluids for adhesive locomotion. *Soft Matter*, (submitted).



The 2006 Student Poster Competition Award was given to Jin Li of the University of Virginia by Poster Session Chair Matthew Liberatore. The award was for his poster “Rheology and Microstructure of Organoclay dispersions,” coauthored with Jim Oberhauser.





## NEWS

### Local Section News

For the second year in a row, the Chicago Society of Rheology fielded a triathlon relay team to compete in the Accenture Chicago Triathlon on 28 August 2006. Over the 1.5k swim, 40k bike and 10k run legs, team 'Everything Flows' improved its time over its 2005 effort, placing 32nd out of 179 relay teams.

Coincidentally, team members Dave Venerus (swim), Jay Schieber (bike) and Wes Burghardt (run) constitute the executive committee of the CSOR, which, until its recent activities in multi-sport, has been primarily known for its annual business meeting at Wrigley Field. CSOR welcomes new members, who should however be aware of the initiation fee, payable to vendors at the next business meeting.

Rumors are swirling about a 'smackdown challenge' between CSOR and rheologists from

Wisconsin at the 2007 Chicago Triathlon...

### Nominations Invited for the 2007 Bingham Award

The Society's Bingham Medal has been awarded annually since 1948 to an individual who has made an outstanding contribution to the science of rheology or who has performed particularly meritorious service to The Society. Nominations for the Bingham Medalist should be submitted before 15 January 2007 to the chair of the 2007 Bingham Award Committee, Andrea Chow, [andrea.chow@caliperls.com](mailto:andrea.chow@caliperls.com). Rules and some selected guidelines governing the Bingham Award are available on the web at [www.rheology.org/sor/awards/binham/nom2007.htm](http://www.rheology.org/sor/awards/binham/nom2007.htm).

### Minutes of the ExCom Meeting

Sunday 8 October 2006  
Portland, Maine USA

Andy Kraynik called the meeting to order at 8:27 a.m. in the Somerset Room of the Holiday Inn By the Bay in Portland, Maine. Attending committee members were Susan Muller, John Brady, Monty Shaw, Jeffrey Giacomini, Bob Prud'homme, Dan Klingenberg, Lynn Walker and Timothy Lodge. Invited guests were Janis Bennett (AIP Liaison), Antony Beris (Technical Program Co-Chair, Portland Meeting), Doug Bousfield (Co-Chair, Local Arrangements, Portland Meeting), Marc Brodsky (AIP, Chief Executive Officer), Albert Co (SOR Webmaster and Chair, Local Arrangements, Portland meeting), Gerry Fuller (Chair, Local Arrangements, ICR 2008), Faith Morrison (Editor, *Rheology Bulletin*), Jaye Magda (Chair, Local Arrangements, Salt Lake City Meeting), Pat Mather (Chair, Membership Committee) and Mike Solomon (Chair, Education Committee). The minutes of the previous meeting were read and approved.

Monty Shaw presented the Statement of



Revenues and Expenses for The Society of Rheology and for its *Journal of Rheology*. The financial position of the Society is sound. A healthy surplus is projected for 2006. In view of the additional liabilities associated with putting on an ICR, the Annual Meeting Reserve will be temporarily increased from \$200,000 to \$300,000. The Executive Committee passed a motion to accept these reports.

John Brady, Editor, reported that the *Journal of Rheology* is healthy. Over the past 10-years, 1610 articles have been submitted. The journal now receives between 10 and 17 paper submissions per month. Over the past 12 months, 151 were submitted from 36 countries, and the average time from receipt to first decision is 87 days. The *Journal of Rheology*'s ISI Impact Factor for 2005 is very healthy relative to competing journals. Brady reported that his biggest editorial problem is the submission of Figures with substandard graphics. Timothy Lodge proposed abolishing the charges for publishing in the *Journal of Rheology* in color. We resolved to table this till the next meeting, and to discuss it at the Portland business meeting. Giacomini pointed out that *JOR* authors can already insert movies into the pdf of a *JOR* article, though none have yet taken advantage of this.

Giacomini, Editor for Business, reported on the *Journal of Rheology On-Line (JOROL)*. Usage remains strong. More and more usage comes through consortium licensees versus classical institutional subscriptions. Giacomini also reported that our electronic submission system is not yet offering open access to authors at submission time. Open access means that the electronic version of the article becomes freely available to anyone if the author opts to pay \$2,500 to The Society of Rheology. Giacomini also gave an on-line demonstration of journal usage statistics provided to the Society at [www.scitation.org](http://www.scitation.org) (password protection). Tom Butkevich's team is still working out the kinks in this system.

Gerry Fuller (Co-Chair, Local Arrangements) reported on plans for the 2008 International Congress on Rheology in Monterey. An open wireless area will be arranged near the conference sessions. A very productive and enjoyable meeting is planned. Rheologists should plan on bringing their families and their graduate students to Monterey. Gerry Fuller led a discussion on foregoing printing proceedings for the ICR.

Antony Beris, Technical Program Committee

Co-Chair, reported on the Portland meeting program. The Society will welcome 235 oral presentations, and 72 posters. Increasingly, Beris reports, rheologists request an invitation from the Technical Program Chair to help them with their travel visa application.

Chair of the Education Committee, Mike Solomon led a discussion about future short courses. On October 7 and 8, 2006 (Saturday and Sunday), the weekend preceding the Portland meeting, the two-day short course "Rheology of High-Interface Systems" taught by Gerry Fuller, Jan Vermant and Andy Kraynik attracted 42 registrants. Solomon moved to offer "Beginning Rheology" (an update of the 2004 Lubbock Meeting offering by Morrison and Giacomini, 2-day) in parallel with "Microfluidics for rheologists" (Squires, Anna and Doyle, 1-day) on the weekend preceding the Salt Lake meeting (6-7 October 2007). This motion passed [Giacomini abstained]. Solomon also reported that the committee is closely considering "Introduction to Rheology of Colloidal Suspensions" (Wagner and Mewis, 2-day) in parallel with "Surfactant rheology, self-assembly and microstructure dynamics" (Spicer, 1-day). The committee is actively soliciting proposals for future meetings.

Albert Co (Webmaster and Chair, Local Arrangements) reported that there were 303 early registrants, and that as of Sunday afternoon we had 338 registrants in all, buying 196 banquet tickets: very healthy numbers for Sunday afternoon. Co led an on-line demonstration of the Society's online meeting registration system, and through its online meeting statistics displays.

Mark Brodsky (AIP, Chief Executive Officer) reported on our umbrella organization, the American Institute of Physics. Janis Bennett (AIP Liaison) reported on the individual member electronic journal access that will be implemented with our next membership renewal (beginning week of October 16th). Brodsky also reported that Mort Denn, appointed by President Kraynik, has succeeded Art Metzner as SOR representative to the AIP Executive Committee. Denn participated in his first such committee meeting in Portland in October.

Faith Morrison (Editor, *Rheology Bulletin*) led a discussion on selecting the authors of the Bingham



medal announcement and the corresponding medalist's profile. Shaw moved that we allow advertising in the *Bulletin* to those not yet advertising in the *Journal of Rheology*, while still providing our discount to those who do advertise in the *Journal of Rheology*. This issue was then tabled. Kraynik moved to give one free advertisement to the AIP on their fellowship program. With enthusiasm, this passed.

Kraynik, on behalf of Gary Leal (Technical Program Chair, 2008 ICR, Monterey) presented Leal's written report of 27 September 2006 on the Monterey program. A committee of Kornfield, Brady, Kraynik, Pine, Hyun, James, Cooper-White, McLeish, Vermont, Vlassopoulos, Mendes, Watanabe, and Colby has been selected. Leal's report was accepted.

Jaye Magda (Local Arrangements Chair) reported on the 7-11 October 2007 meeting in Salt Lake City, Utah. Magda moved to appoint Kraynik Co-Chair of Local Arrangements. The motion passed. Everything is falling nicely into place for our next meeting.

Pat Mather reported on the 2011 meeting (9-13 October) at the Intercontinental Hotel and Conference Center in Cleveland, Ohio.

Pat Mather, Chair of the Membership Committee, reports that as of 30 April 2006, we now have 1578 members (including 1361 regular and 194 student). Mather is actively recruiting new student members. If you supervise graduate students, encourage them to join!

Shaw reported that an insurance company has been misusing the SOR logo to market itself to SOR members.

Kraynik discussed a questionnaire on current issues to be distributed at the Society Luncheon. Kraynik also proposed having the next Spring meeting of the EC at the AIP Publishing Center in Melville, New York.

Kraynik moved to clarify the following item from the previous minutes: "A motion was passed to extend free electronic access to retired members. A motion was also passed to extend electronic access to individual members of the Society for \$40/year starting in 2007." By "retired members" we mean "retired members (and not members of record)," and by "individual members" we mean "regular members (and not members of record)." The motion to clarify passed.

Giacomin proposed that the papers winning the *Journal of Rheology* Publication Award (past and

future) be made open access. This motion passed with enthusiasm.

At 5:01 p.m. Andy Kraynik moved the meeting into a brief Executive session. President Kraynik proposed a gift to Albert Co to recognize his dedicated service.

The meeting was adjourned at 5:10 pm.

## Minutes of the Business Meeting

Tuesday, 10 October 2006  
Portland, Maine

Andy Kraynik called the meeting to order at 6:15 p.m. in the Massachusetts room of the Holiday Inn By the Bay in Portland, Maine. A motion was passed to waive reading of the minutes of the previous business meeting in Vancouver.

Each officer report and each committee report presented at the Executive Committee meeting (see above) was presented and accepted at the business meeting. Andy Kraynik reported on the questionnaires circulated at the Society Luncheon. The meeting was adjourned at 6:32 p.m.



## Treasurer's Report

To the membership,

The Treasurer's report for the January *Bulletin* is traditionally that presented to the Membership at the Annual Meeting in October. As such, the most important item is the Budget for next year, which is the left-most column of numbers in the attached tables. Please examine this carefully. In the Receipts category, Dues and *Journal* income are expected to remain at previous levels, although a new income stream from on-membership *JOROL* access could improve *Journal* income somewhat. The Interest income entry is a conservative estimate reflecting the uncertainty surrounding returns on short- to mid-term bonds and money market securities. As for expenses, we are budgeting for moderate increases in *Journal* production costs in

Treasurer's  
Report

anticipation of a higher page count for 2007.

An important change was approved for the Balance sheet—the meeting reserve was increased to \$300,000. This figure is roughly 1/2 of our potential liability for the 2008 International Con-

gress on Rheology in case of cancellation and depending upon the date and cause of the cancellation. While we fully anticipate a successful meeting, it is appropriate to be careful at this time.

Respectfully submitted,

Montgomery Shaw, Treasurer

# Treasurer's Report

## The Society of Rheology

### Receipts and Disbursements

(all amounts, USD)

	2007 Budget	2006 Projection	2006 August	2006 Budget	2005 Year End
<b>RECEIPTS</b>					
Dues	55,000	55,408	54,310	55,000	56,780
Interest	53,000	57,105	34,203	35,000	29,823
Journal of Rheology	262,600	271,794	245,151	259,500	270,107
Mailing List Sales	0	0	0	1,000	0
Bulletin Advertising	10,000	5,728	2,430	7,000	17,820
Annual Meeting (net)	0	2,344	23,439	0	7,709
Short Course (net)	0	623	6,231	0	-2,225
<b>TOTAL RECEIPTS</b>	<b>380,600</b>	<b>393,002</b>	<b>365,764</b>	<b>357,500</b>	<b>380,014</b>
<b>DISBURSEMENTS</b>					
AIP Dues Bill & Collect.	11,000	10,446	6,675	12,000	10,503
AIP Adm. Services	9,500	9,526	6,344	9,500	9,511
AIP Mem. Soc. Dues	7,700	7,936	5,291	7,600	7,706
Contributions and Prizes	1,900	1,731	31	1,900	2,033
Journal of Rheology	214,533	168,913	107,443	191,420	218,437
Bulletin	9,000	9,991	9,991	9,000	8,745
Bingham Award	7,000	5,000	0	7,000	10,000
Executive Cmt. Meetings	8,000	7,212	6,012	13,000	6,326
Pres. Discretionary Fund	1,500	0	0	1,500	0
Treas. Discr. Fund	1,500	400	0	1,500	556
Bulletin Editor Discr. Fund	1,500	0	0	0	0
Progr. Chm. Discr. Fund	3,000	4,000	0	3,000	2,637
Webmaster Discr. Fund	3,000	1,800	0	3,000	503
Office Expenses	4,000	4,103	1,806	4,000	2,880
Banking Services	100	40	20	300	39
Liability Insurance	7,500	5,654	0	7,500	4,349
Membership Broch. & Appl.	500	300	276	500	0
Accountant	2,200	1,925	1,925	2,200	1,925
Student member travel	12,000	12,754	0	12,000	3,566
Annual meetings, future	9,000	10,377	7,173	7,000	2,108
Website	1,000	300	0	1,000	637
Miscellaneous	500	0	0	1,000	0
<b>TOTAL DISBURSEMENTS</b>	<b>315,933</b>	<b>262,408</b>	<b>152,987</b>	<b>295,920</b>	<b>292,459</b>
<b>Net</b>	<b>64,667</b>	<b>130,595</b>	<b>212,777</b>	<b>61,580</b>	<b>87,555</b>

**Journal of Rheology**  
**Receipts and Disbursements**

	<b>2007 Budget</b>	<b>2006 Projection</b>	<b>2006 August</b>	<b>2006 Budget</b>	<b>2005 Year End</b>
<b>RECEIPTS</b>					
Subscriptions	177,100	179,934	171,729	181,500	180,061
Reprint Sales	13,500	11,181	4,854	7,000	13,791
Ad Sales	35,000	31,057	22,389	35,000	35,107
JORO revenue	36,000	43,379	39,989	35,000	37,610
Miscellaneous	1,000	6,243	6,190	1,000	3,538
<b>TOTAL RECEIPTS</b>	<b>262,600</b>	<b>271,794</b>	<b>245,151</b>	<b>259,500</b>	<b>270,107</b>
<b>DISBURSEMENTS</b>					
Ads	9,500	6,581	4,271	9,000	9,454
Reprints, Single Copy	5,400	1,519	1,292	5,400	5,363
Paper, Printing	28,345	18,289	11,188	24,500	32,656
SOR Editorial	42,000	37,960	24,081	42,000	39,855
Production	55,000	29,242	17,255	43,500	54,985
Fulfillment	6,625	6,402	4,113	7,600	6,560
Distribution	18,663	19,825	12,004	17,020	19,094
Electronic publishing	43,000	43,103	23,004	35,000	42,239
Miscellaneous	6,000	5,991	10,235	7,400	8,231
<b>TOTAL DISBURSEMENTS</b>	<b>214,533</b>	<b>168,913</b>	<b>107,443</b>	<b>191,420</b>	<b>218,437</b>
Net	48,067	102,881	137,708	68,080	51,670

**The Society of Rheology, Inc.**  
**Balance Sheet**

(all amounts, USD)

	<b>2006 August</b>	<b>2005 Year End</b>	<b>2005 August</b>	<b>2004 Year End</b>	<b>2003 Year End</b>
<b>Assets</b>					
Cash in checking account	43,322	12,721	46,161	29,012	2,047
Securities	0	0	0	0	0
Balance in AIP account	1,099,125	1,056,188	982,525	976,655	938,047
<b>Total Assets</b>	<b>1,142,447</b>	<b>1,068,909</b>	<b>1,028,686</b>	<b>1,005,667</b>	<b>940,094</b>
<b>Liabilities and Net Assets</b>					
<b>Liabilities</b>					
Deferred revenue	0	132,396	0	155,969	143,603
<b>Total Liabilities</b>	<b>0</b>	<b>132,396</b>	<b>0</b>	<b>155,969</b>	<b>143,603</b>
<b>Net Assets</b>					
Publication reserve	450,000	450,000	450,000	450,000	450,000
Student travel grant reserve	10,000	10,000	10,000	10,000	10,000
Annual Meeting reserve	300,000	200,000	100,000	100,000	100,000
Operating reserve	100,000	100,000	100,000	100,000	70,000
Unrestricted	282,447	176,513	368,686	189,698	166,491
<b>Total Net Assets</b>	<b>1,142,447</b>	<b>936,513</b>	<b>1,028,686</b>	<b>849,698</b>	<b>796,491</b>
<b>Total liabilities and net assets</b>	<b>1,142,447</b>	<b>1,068,909</b>	<b>1,028,686</b>	<b>1,005,667</b>	<b>940,094</b>

the end

increases. In order to take random errors into account, it is necessary to have a model for the error distribution, and this is usually assumed to be Gaussian. Elster and Honerkamp [12] have addressed this issue in some detail.

One more difficulty that arises in inferring the parameter set  $\{G_i, \tau_i\}$  from the data set  $\{G'_k, G''_k, \omega_k\}$  is that the magnitudes of the storage and loss moduli and of the relaxation strength vary enormously over the range of frequencies and times of interest. Honerkamp and Weese [13] addressed this problem by the use of nonlinear regression, together with regularization, in which it is the logarithm of  $h(\tau)$  that is calculated rather than the spectrum function itself. The algorithm developed for this regression (NLREG) is available commercially [14]. Orbey and Dealy [15] compared discrete spectra calculated in several ways. They found that nonlinear regression with regularization, together with a sufficient density of data points, can yield a discrete spectrum whose parameter values describe very well the continuous spectrum that is characteristic of the material.

#### Danger Lurks Where the Data End

It is often assumed that the spectrum inferred from a set of data is valid between values of  $t$  equal to the reciprocal of the maximum and minimum frequencies of the data set. However, Davies and Anderssen [16] have shown that this gives an overly optimistic estimate. Their analysis indicates that the range of  $t$  over which the relaxation spectrum can be reliably determined is 2.36 decades less than the range of frequencies over which experimental data are available. Anderssen and Davies [17] have proposed a spacing for experimental data that optimizes the quality of the discrete spectrum inferred from them. Jensen [18] proposed a Monte Carlo method called *simulated annealing* to infer a discrete spectrum from data; in this method the range of relaxation times is constrained by the Anderssen and Davies criteria [16].

#### Probing the Terminal Zone

It is often necessary to use more than one measurement technique to probe the widest possible range of times or frequencies. In using rheological data to infer molecular structure, the behavior at very long times (low frequencies) is of special interest. For example, the zero-shear viscosity is very sensitive to molecular weight. However, for a material whose longest relaxation time is quite large, oscillatory shear experiments are of limited usefulness at very low frequencies because the stress is very small and the

experimental time required is very long. It is in this region that creep measurements are most useful. Recent advances in the design of commercial, controlled-torque (controlled-stress) rheometers have made it possible to carry out precise measurements of creep and creep recovery on a routine basis.

However, for very polydisperse materials, particularly those with even a small amount of high-molecular-weight polymer, creep measurements become problematic as a result of the need to measure extremely slow deformations while maintaining the stress at a very low, constant value. In order to reach steady state, so that the steady-state compliance and the zero-shear viscosity can be determined, a large strain will be required, which may take the sample into the regime of nonlinear viscoelasticity. Kraft *et al.* [19] proposed a technique for determining the creep compliance up to the steady-state flow region without moving outside the regime of linear behavior and without the use of a super-sensitive creep meter. During a standard creep experiment at a stress  $\sigma_0$ , they reduce the stress back to zero at a time,  $t_1$ , when the deformation is still within the range of linear behavior, and monitor the resulting recoil. They show how data from the two stages of this experiment can be combined to construct the entire creep curve. Since the preferred technique for characterizing linear viscoelastic behavior at times below (or frequencies above) the terminal zone is oscillatory shear, there remains the problem of combining creep data with storage and loss modulus data to obtain a characterization valid over the broadest possible time range. He *et al.* [20] developed a method for doing this using standard commercial rheometers that appears to work quite well. They calculate continuous retardation spectra using both modulus and creep data and plot these together. The resulting graph shows clearly the zones in which each technique provides reliable data as well as the zone of overlap.

More information on this topic may be found in Ref. [1].

#### References

1. Dealy, J.M. and Larson, R.G., *Structure and Rheology of Molten Polymers*, (2006) Hanser Publishers, Munich; Hanser Garder Publications, Cincinnati.
2. Plazek, D.J., Echeverría, I. Don't cry for me Charlie Brown, or with compliance comes comprehension. *J. Rheol.* (2000) 44, 831-841.
3. Bird, R.B., Hassager, O., Armstrong, R.C., Curtiss, C.F. *Dynamics of Polymeric Liquids*, Vol 2, 2<sup>nd</sup> edition (1987) John Wiley & Sons, New York.
4. Ferry, J.D. *Viscoelastic Properties of Polymers*, 3<sup>rd</sup> edition (1980) John Wiley & Sons, New York.

(Meetings, continued from back cover)

## 2010

### Spring 2010

6<sup>th</sup> Annual European Rheology Conference AERC  
2010, location TBA

### 23-24 October 2010

SOR Short Course on Rheology (topic TBA), Santa  
Fe, NM USA

### 24-28 October 2010

82<sup>nd</sup> Annual Meeting of The Society of Rheology,  
Santa Fe, New Mexico USA, Andy Kraynik

## 2011

### Spring 2011

7<sup>th</sup> Annual European Rheology Conference AERC  
2011, location TBA

### 8-9 October 2011

SOR Short Course on Rheology (topic TBA),  
Cleveland, Ohio USA

### 9-13 October 2011

83<sup>rd</sup> Annual Meeting of The Society of Rheology,  
Cleveland, Ohio USA, Pat Mather

## 2012

### Summer 2012

XVI<sup>th</sup> International Congress on Rheology, location  
TBA (every four years; in 2012 in Europe)

### See also:

[www.rheology.org/sor/info/Other\\_Meetings.htm](http://www.rheology.org/sor/info/Other_Meetings.htm)

[www.rheology-esr.org/Meetings.php](http://www.rheology-esr.org/Meetings.php)

[www.appliedrheology.org/](http://www.appliedrheology.org/) (click on conferences)

5. Laun, H.M. Description of the non-linear shear behavior of a low-density polyethylene, *Rheol. Acta* (1978) 17, 1-15.
6. Baumgaertel, M., Winter, H.H. Determination of discrete relaxation and retardation spectra from dynamic mechanical data. *Rheol. Acta* (1989) 28, 511-519.
7. For information on IRIS see the website: <http://members.tripod.com/~Rheology/>.
8. Honerkamp, J., Weese, J. Determination of the relaxation spectrum by a regularization method. *Macromolecules* (1989) 22, 4372-4377.
9. Provencher, S.W. CONTIN: A general purpose constrained regularization program for inverting noisy linear algebraic and integral equations. *Computer Physics Communications* (1982) 27, p. 229.
10. For information on CONTIN see website: <http://s-provencher.com/pages/contin/shtml>.
11. Honerkamp, J., Weese, J. Tikhonov's regularization method for ill-posed problems: A comparison of different methods for determination of the regularization parameter. *Continuum Mech & Thermodyn.* (1990) 2, 17-30.
12. Elster, C., Honerkamp, J. The role of the error model in the determination of the relaxation time spectrum, *J. Rheol.* (1992) 36, 911-927.
13. Honorkamp, J., Weese, J. A nonlinear regularization method for the calculation of relaxation spectra. *Rheol. Acta*, (1993) 32, 65-73.
14. For information on NLREG see: [http://www.fmf.uni-freiburg.de/service/sg\\_info/programs/](http://www.fmf.uni-freiburg.de/service/sg_info/programs/).
15. Orbey, N., Dealy, J.M. Determination of the relaxation spectrum from oscillatory shear data. *J. Rheol.* (1991) 35, 1035-1049.
16. Davies, A.R., Anderssen, R.S. Sampling localization in determining the relaxation spectrum. *J. Non-Newt. Fl. Mech.* (1997) 73, 163-179.
17. Anderssen, R.S., Davies, A.R. Simple moving-average formulae for the direct recovery of the relaxation spectrum. (2001) *J. Rheol.* (2001) 45, 1-27.
18. Jensen, E.A. Determination of discrete relaxation spectra using simulated annealing. *J. Non-Newt. Fl. Mech.* (2002) 107, 1-11.
19. Kraft, M., Meissner, J. Kaschta, J. Linear viscoelastic characterization of polymer melts with long relaxation times. *Macromolecules* (1995) 32, 751-757.
20. He, C., Wood-Adams, P., Dealy, J.M. Broad frequency characterization of molten polymers. *J. Rheol.* (2004) 48, 711-724.



At the Portland meeting Editor John Brady presented the JOR Publication Award to representatives of the winning team: left to right, Brady, Alex Likhman, and Oliver Harlen. The cited paper is JOR 49(2) 501 (2005), and it is designated open access online.

# CALENDAR OF RHEOLOGY CONFERENCES AND COURSES

## 2007

12-14 April 2007

4<sup>th</sup> Annual European Rheology Conference  
AERC 2007, Naples Italy, Nino Grizzuti and  
Pier Luca Maffettone

June 2007

Short Course on *Rheological Measurements*,  
directed by Chris Macosko, University of  
Minnesota, Minneapolis, MN USA  
([www.cems.umn.edu/rheology](http://www.cems.umn.edu/rheology))

11-14 June 2007

IUTAM Symposium on Recent Advances in  
Multiphase Flows: Numerical and Experimental,  
Istanbul, Turkey, Andreas Acrivos and Can  
Delale

June 25-28, 2007

2<sup>nd</sup> International Conference on Advances in  
Petrochemicals and Polymers (ICAPP 2007),  
The Imperial Queen's Park Hotel, Bangkok,  
Thailand; The Petroleum and Petrochemical  
College, Chulalongkorn University, Thailand  
([www.ppc.chula.ac.th/icapp2007.html](http://www.ppc.chula.ac.th/icapp2007.html))

June 2007

Short Course on *Practical Rheology*, by Hemi  
Nae, Hydan Technologies, Inc., Hillsborough,  
NJ USA

6-8 September 2007

IUTAM Symposium on Advances in Micro- and  
Nanofluidics, Dresden, Germany, N.A.  
(Nikolaus) Adams

6-7 October 2007

SOR Short Course on *Beginning Rheology* by  
Faith A. Morrison and A. Jeff Giacomin, Salt  
Lake City, UT USA; may be taken as a one-day  
course followed by the *Microfluidics for  
Rheologists* course, below, on the second day.

7 October 2007

SOR Short Course on *Microfluidics for Rheologists*  
by Todd Squires, Shelley Anna, and Patrick Doyle,  
Salt Lake City, UT USA

7-11 October 2007

79<sup>th</sup> Annual Meeting of The Society of Rheology, Salt  
Lake City, UT USA, Jaye Magda

## 2008

2-3 August 2008

SOR Short Course on Rheology (topic TBA),  
Monterey, CA USA

3-8 August 2008

XV<sup>th</sup> International Congress on Rheology and 80<sup>th</sup>  
Annual Meeting of The Society of Rheology,  
Monterey, CA USA, Gerry Fuller and Bob Powell



24-30 August 2008

XXII International Congress of Theoretical and  
Applied Mechanics ICTAM 2008, Adelaide,  
Australia, [prandtl.maths.adelaide.edu.au/ictam2008/](http://prandtl.maths.adelaide.edu.au/ictam2008/)

Summer 2008

13<sup>th</sup> International Congress of Biorheology, location  
TBA (held every three years, [www.coe.ou.edu/isb](http://www.coe.ou.edu/isb)).

## 2009

February 2009

5<sup>th</sup> International Symposium on Food Rheology and  
Structure - ISFRS 2009, Zurich Switzerland (every 3  
years; [www.isfrs.ethz.ch](http://www.isfrs.ethz.ch))

Spring 2009

5<sup>th</sup> Annual European Rheology Conference AERC  
2009, location TBA

Summer 2009

5<sup>th</sup> Pacific Rim Conference on Rheology, location  
tentatively Hokkaido, Japan, Hiroshi Watanabe (every  
4 years)

17-18 October 2009

SOR Short Course on Rheology (topic TBA),  
Madison, WI USA

18-22 October 2009

81<sup>st</sup> Annual Meeting of The Society of Rheology,  
Madison, WI USA, Jeff Giacomin

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