



# Rheology Bulletin

## Inside:

McKenna 2009 Bingham Medalist

Another view on Pressure - Huilgol

Time-Temperature Superposition - Dealy and Plazek

AIP's Dylla on the SOR, and . . .

## SOR Announces First Metzner Early Career Award Recipient



## *Executive Committee*

(2007-2009)

*President*  
Robert K. Prud'homme

*Vice President*  
Faith A. Morrison

*Secretary*  
A. Jeffrey Giacomini

*Treasurer*  
Montgomery T. Shaw

*Editor*  
John F. Brady

*Past-President*  
Andrew M. Kraynik

*Members-at-Large*  
Marie-Claude Heuzey  
Daniel J. Klingenberg  
Norman J. Wagner

# Table of Contents

Greg McKenna is 2009 Bingham Medalist	4
Jonathan Rothstein is Inaugural <i>The Arthur B. Metzner Early Career Awardee</i>	6
<i>Extending the SOR's Reach Through the AIP Umbrella</i> , by AIP Executive Director Fred Dylla	8
81 <sup>st</sup> Annual Meeting of The Society of Rheology: Madison 2009	11
<i>On the Definition of Pressure in Rheology</i> , by Raja Huilgol	12
<i>Time Temperature Superposition – a Users Guide</i> , by John Dealy and Don Plazek	16
Society News/Business Officer elections, new postdoc poster award, travel grants, other news, ExCom minutes, Treasurer's report	22
Calendar of Events	32

**Cover photo shows** participants in the 12<sup>th</sup> Annual Tiger-Hen-Hawk Rheology Symposium, held at Lehigh University on 9 May 2009. The symposium highlights graduate research from Princeton University (Tigers), University of Delaware (Hens) and Lehigh University (Hawks) and included 10 oral and 31 poster contributions presented to approximately 60 attendees. Professor Jeffrey Morris from the Levich Institute, City College of New York, offered a plenary lecture on "Fluid mechanics of suspensions: A consideration of pressure and inertia." The meeting was sponsored by Anton-Paar and TA Instruments. Photo by Pisist Kumnorkaew.

# Standing Committees

## *Membership Committee (2007-2009)*

Shelley L. Anna, chair  
Patrick D. Anderson  
Saad Khan  
Charles P. Lusignan  
Chris White  
H. Henning Winter

## *Education Committee (2007-2009)*

Michael J. Solomon, chair  
Robert J. Butera  
Anne M. Grillet  
Anthony J. McHugh  
Patrick Spicer

## *Bingham Award Committee*

Ole Hassager (2006-2009), chair  
Timothy Lodge (2007-2010)  
Christopher Macosko (2008-2011)  
Kalman Migler (2008-2011)  
Susan J. Muller (2007-2010)  
Michael Rubinstein (2008-2011)  
Norman Wagner (2006-2009)

## *Metzner Award Committee*

Lynn Walker (2008-2011), chair  
John Brady, JOR Editor  
Charles P. Lusignan (2008-2010)  
Michael J. Solomon (2008-2010)  
Jan Vermant (2008-2009)

## *Meetings Policy Committee*

Faith Morrison, Chair  
Albert Co  
Andrew Kraynik  
Gerald Fuller (2008 Local)  
Ralph Colby (2008 Program)  
Gary Leal (2008 Program)  
Jeffrey Giacomini (2009 Local)  
Jeff Morris (2009 Program)  
Srini Raghavan (2009 Program)

## *Webmaster*

*Editor, Rheology Bulletin*

*Associate Editor for Business, Journal of Rheology*

*Representative to AIP*

*Representative to AIP Committee on Public Policy*

*Representative to and Chair AIP Publications Services Subcommittee*

*Rep. to AIP Liaison Committee for Under-Represented Minorities*

*Rep. to U.S. National Committee on Theoretical and Applied Mechanics*

*Delegate to International Committee on Rheology*

Albert Co

Faith A. Morrison

A. Jeffrey Giacomini

Morton M. Denn

Kalman Migler

A. Jeffrey Giacomini

Willie E. (Skip) Rochefort

Michael D. Graham

Andrew M. Kraynik

The Rheology Bulletin is the news and information publication of The Society of Rheology (SOR) and is published twice yearly in January and July. Subscription is free on membership in The Society of Rheology. Change of address or letters to the editor: [rheology@aip.org](mailto:rheology@aip.org).

The Rheology Bulletin is archived on the SOR website at [www.rheology.org/sor/publications/rheology\\_b/issues.htm](http://www.rheology.org/sor/publications/rheology_b/issues.htm)





# Greg McKenna 2009 Bingham Medalist

Gregory B. McKenna is the 2009 Bingham Medalist of The Society of Rheology.

Greg McKenna is the Paul Whitfield Horn Professor in the Department of Chemical Engineering at Texas Tech University where he served as chair of the Department from 2001-2004. From 1977-1992 he was a Physical Scientist at the National Bureau of Standards (NBS) in the Polymer Division, where he served as Group Leader in the Structure and Mechanics Group. His academic training came from the US Air Force Academy (B.S. 1970), Massachusetts Institute of Technology (S.M. 1971), and the University of Utah (PhD. 1976 in Material Science and Engineering). In awarding him the 2009 Bingham Medal, the committee cited McKenna's development of novel rheological experiments and methods to interrogate the physics of polymers and complex fluids. Greg's contributions to rheology have been made in four areas: (1) nanorheology and surface rheological methods, (2) nonlinear viscoelasticity and rejuvenation of polymer glasses, (3) molecular rheology and rheological characterization of polymer heterogeneity, and (4) mechanics and thermodynamics of cross-linked rubbers.

In the area of nanorheological measurements, McKenna's miniaturization of the classical membrane inflation experiment involved the application of an AFM instrument to measure the creep compliance of 1-5 micron diameter polymer membranes with thicknesses as small as 27 nm. The measurements were the first absolute determinations of creep compliance of ultrathin free standing films, and they provided direct information about the glass transition and chain dynamics of polymers in confinement.

In the area of the rejuvenation of polymer glasses by mechanical deformation, McKenna applied a novel torsional dilatometer to study the volume relaxation of glasses. In his research Greg demonstrated that the rate of relaxation was unaffected by the magnitude of a large mechanical deformation – contrary to the rejuvena-



tion hypothesis. Previous workers had interpreted data obtained from experiments where small strains were superimposed on large strain deformations in terms of change in the thermodynamic state of the polymer glass. McKenna and co-workers showed how the rejuvenation phenomenon could be explained with a nonlinear constitutive model without invoking a change in thermodynamic state.

McKenna's contributions to molecular rheology were collaborations with A.J. Kovacs and D.J. Plazek in which the viscosity and viscoelastic properties of cyclic polystyrene molecules were measured as a function of molecular weight and the concentration of linear chains in blends of rings and chains. Their work was the first observation that even small amounts of linear chain contamination can lead to dramatic increase in the viscosity of rings. A novel rheological technique,



Greg and spouse Sindee Simon prepare first class aviation for Horatio, their dog, to go to West Virginia.

Mechanical Spectroscopic Hole Burning (MSHB) was used to study the dynamic heterogeneity of materials. When applied to small molecule glass formers, they showed that *m*-toluidine, glycerol, and sucrose benzoate exhibit the same type of dynamic mechanical behavior as do polymer glass-formers. The glass-formers exhibit strong deviations from classical VFT or WLF temperature dependence of the viscosity, i.e., the viscosity does



McKenna and Simon and other participants celebrate their good showings in a 2007 tennis tournament in Plonéour-Lanvern, Bretagne, France.

not diverge as  $T_g$  is approached. The work provides important insights into the strength of the temperature singularity of glassy dynamics that were not previously known.

Finally, in the area of the mechanics and thermodynamics of cross-linked rubbers, McKenna showed that the fundamental assumption of the Flory-Rehner hypothesis of separability of the mixing and elastic contributions to the free energy function is essentially correct. Studies on isotropically swollen elastomers showed that the apparent discrepancies previously reported in the Flory-Rehner hypothesis were due to a simplifying assumption that the mixing contribution to the free energy for a crosslinked and uncrosslinked polymer are the same.

However, this is not the case since the cross-linked rubber behaves as if it were less soluble than the uncrosslinked material, implying that the Flory-Huggins interaction parameter  $\chi$  depends on crosslink density. The work relied upon the use of torque and normal force to obtain the strain energy function for the rubber. McKenna's work to understand the thermodynamics and mechanism of crosslinked networks has had a substantial impact on current research in this area because of the insights provided by his use of continuum concepts to fully explore the consequences of the Flory-Rehner molecular approach to rubber elasticity.

Greg McKenna was born in Pittsburgh, PA and was exposed to science through youth programs at the Buhl Planetarium on Pittsburgh's North Side, as well as through the magnificent dinosaur collection at the Carnegie Museum in Oakland. Greg was athletic in school and participated in cross country, swimming, and track in high school, boxed both during and after college, and currently plays a mean game of tennis. Between his junior and senior years of high school Greg used money saved from his work as a caddy to go on an exchange trip to Paris, France for six weeks. This trip initiated his strong appreciation and affection for France that continues to this day. In 2006 Greg and spouse Sindee Simon purchased a "pied à terre" (small apartment) in France that they enthusiastically visit both for vacation and to work and collaborate with French colleagues. Greg has two children, Stacey, who is now in a Ph.D. program at the University of Colorado, Denver in Anthropology, and Lucas who is finishing high school.

# Jonathan Rothstein Honored with First Arthur B. Metzner Early Career Award

Jonathan P. Rothstein of the University of Massachusetts, Amherst, has been named the first recipient of The Society of Rheology's Arthur B. Metzner Early Career Award.

Jonathan Rothstein is an associate professor in the Department of Mechanical and Industrial Engineering at the University of Massachusetts, Amherst, where he has taught since 2001, and where he oversees a large group working in different aspects complex fluids rheology. In the past several years, Rothstein has been able to use his extensive expertise in fluid mechanics and rheology to make significant contributions in the areas of flow-microstructure coupling in polymer and micelle solutions, rheology and microrheology, flow transitions, and drag reduction. Members of the award selection committee, chaired by Lynn Walker, report that they were impressed by the rigor of Rothstein's work and that his work dealt with the most challenging rheological questions in areas of great importance. Letters of support pointed out that Rothstein's research group is equally well versed in experimental and computational techniques, a capability vital to tackling modern rheological problems. In fact, in the past several years, Rothstein has been able to use his versatility to elucidate many phenomena that would not have been uncovered by a purely experimental and/or theoretical/computational approach. Indeed this balanced approach is what makes



Rothstein's papers of such high impact and demonstrates the potential of the field of rheology. The committee was also impressed by the strong support from Rothstein's former and current students, indicating that he is passing on his expertise, rigor, and passion to a new group of young rheologists.

The Metzner Award Committee received ten nominations for the inaugural Arthur B. Metzner Early Career Award. The award is given to a member of The Society who is younger than 35 (on January 15<sup>th</sup> of the year the award is to be given) and who has distinguished him/herself in rheological research, rheological practice, or service to rheology. The SOR has several awards, but

the Metzner Award is the first SOR award targeted at practitioners early in their careers. The Metzner Award is seen as an opportunity to signal to the wider world that the individual so named is a rheologist of high promise.

The Arthur B. Metzner Early Career Award is named after the distinguished rheologist, university professor, *JOR* editor, Bingham medalist, and mentor Art Metzner from the University of Delaware USA. Art Metzner taught at the University of Delaware from 1953 until his retirement in 1993. Metzner was born

in Saskatchewan Canada, receiving his technical degrees from the University of Alberta and the Massachusetts Institute of Technology. In his long career, Metzner contributed to the advancement of understanding of, among other topics, turbulent drag reduction, shear normal stresses, dilute polymer solutions flowing through porous media, and extensional flow of fiber suspensions. Art Metzner was active in The Society of Rheology, serving as editor of the *Journal of Rheology* for 10 years. The Metzner Early Career Award is described in detail on the Society web pages ([www.rheology.org/sor/awards/Metzner/](http://www.rheology.org/sor/awards/Metzner/)).



# TA INSTRUMENTS

IT'S NOT A RHEOMETER... IT'S THE NEW ARES-G2.



## NEW ARES-G2

- Unique separate motor and transducer technology
- New Force Rebalance Transducer with 5,000,000:1 dynamic range
- New high torque, friction free brushless DC motor with high resolution optical encoder
- Inertia free dynamic measurements to 100 Hz
- New advanced strain and stress control
- New touch screen with intuitive graphical interface
- New Force Convection Oven with Camera Viewer
- New Smart Swap™ Peltier Plate with Solvent Trap
- New TRIOS Software

WWW.TAINSTRUMENTS.COM

# Extending The SOR's Reach Through the AIP Umbrella



**H. Frederick Dylla**  
Executive Director and CEO  
American Institute of Physics

After my attendance at last summer's XV<sup>th</sup> International Congress on Rheology, I was very pleased with the invitation to submit an article for the *Rheology Bulletin*.

Being two years into the job as the

Executive Director and CEO of the American Institute of Physics (AIP), I am still learning about the heart and soul of the Institute—the Member Societies that make up the umbrella. To gain a better understanding of all the communities represented within AIP, I became a member of all 10 Member Societies shortly after my arrival in the spring of 2007. I am growing to understand The SOR's culture and appreciate the organization's forward thinking and worldview. And despite its small size, the SOR membership base has shown unparalleled commitment. Indeed, few communities can boast such high levels of



AIP is headquartered at the American Center for Physics (ACP) in College Park, MD (inside the Washington, DC, Capital Beltway). AIP shares the building with APS, AAPT, and the American Association of Physicists in Medicine.

member activity—from strong meeting participation to the running of the society itself.

The SOR was one of the first societies with the foresight to recognize what it stood to gain by aligning itself with like scientific associations. In 1931, The SOR joined the American Physical Society (APS), the Optical Society of America, the Acoustical Society of America, and the American Association of Physics Teachers (AAPT) to form the American Institute of Physics. In doing so, The SOR made available to itself a new pool of resources and opened up opportunities to advance its mission on a scale it would otherwise not attain. Since then, the partnership has continued to grow in size and scope, to 10 Member Societies and 24 Affiliated Societies. Over 127,000 scientists are represented within AIP's Member Societies alone. Where the Member Societies serve individual members, AIP serves its Member Societies. Each society contracts AIP services to a varying degree depending on its needs. From the individual's standpoint, perhaps the most visible benefit of this relationship is *Physics Today* magazine, but AIP services run the gamut from publishing to exhibits, from society administration to promoting science through a suite of resources, such as career and statistical services. The Member Societies also partner with each other to effectively leverage the combined resources of the umbrella.

So, how does this partnership work today, and what tangible value does it bring?

AIP provides The SOR and its other publishing partners with essential services at competitive prices and delivers additional value by continuously evolving and developing our online platform, by representing partner interests on trade association boards, and by engaging in public-policy advocacy on behalf of our collective publishing interests. AIP is proud to have assisted The SOR in publication of the *Journal of Rheology (JOR)* over the past 18 years. The SOR takes full advantage of the suite of services offered by AIP Publishing. In addition to journal production, XML composition, and copyediting, AIP provides services to streamline the user experience, from author to researcher. Prospective authors for *JOR* use the AIP Peer X-Press system for easy online submission and review of manuscripts. The system allows Chinese, Japanese, and Korean authors to print their names in their native languages. Current issues and the entire backfile of *JOR* are hosted on AIP's online publishing platform, Scitation—host to over 1.6 million documents from scholarly journals, magazines, conference proceedings, and other special publications in fields that include rheology, engineering, and the physical sciences. Last year, AIP worked with *JOR* to enhance its constituency's Scitation user experience by



# Rheometry Focusing on Solutions.



**Anton Paar**

## Looking to build on your current rheometer?

### **Perform structural investigations simultaneous with rheometry:**

The MCR rheometer series offers a wide range of special accessories for microscopy, Small Angle Light Scattering (SALS), birefringence, dichroism, dielectric spectroscopy and many more.

## Looking for a quick start with rheometry?

### **Benefit from Anton Paar's Academic Advantage Program:**

A custom program for your guaranteed and affordable quick start with the world-renowned MCR rheometer series.

Find out more about our special accessories and the Academic Advantage Program at [www.anton-paar.com](http://www.anton-paar.com)



**Anton Paar**® USA

800-722-7556  
[info.us@anton-paar.com](mailto:info.us@anton-paar.com)  
[www.anton-paar.com](http://www.anton-paar.com)



The AIP Publishing Center is based in Melville, NY.

launching a new article page format in August 2008. The design expanded user functionality and simplified navigation, and also incorporated Web 2.0 features such as social bookmarking, code that allows bloggers to plug directly into a journal's blog, and a mobile device view. Also included is a research toolkit with links to valuable online workflow tools such as Zotero and Google Notebook. Check these new features out yourself at [scitation.aip.org/](http://scitation.aip.org/). In February 2009, we introduced online advertising for *JOR* online. In terms of administration, The SOR has also contracted with AIP to provide subscription management, marketing services, and membership management. Administrative support services are provided to the Society's leadership and members through Janis Bennett's office, within AIP's Editorial Operations group. Janis ably serves as a liaison between the Society and various service providers within AIP.

Another key advantage of belonging to AIP is effectiveness in advocacy. Because an umbrella organization represents the broad and diverse interests of its member organizations, it carries more weight in its interactions with the community and with the federal government. AIP has been very vocal in the issue of open access and the movement's potential impact on the publishing community and the entire enterprise of peer-reviewed journals. A number of other multi-society initiatives spearheaded by AIP involve issues such as renewed commitments to science education and energy research. AIP monitors science policy developments in Washington and publishes regular *FYI* news bulletins informing the physical sciences community of opportunities for science and funding decisions that affect them. Furthermore, the relationship allows all the partners to take advantage of each other's competencies. For example, with 40% of current SOR members residing outside the United

States, The SOR is particularly interested in visa issues, and APS pays close attention to visa requirements and restrictions as part of their international affairs efforts. For the past several years AIP has been working with The SOR to cover rheology-related research news items, with the goal of increasing the general public's awareness and appreciation of the science. We have two main vehicles for promoting science in the news. Inside Science News Service targets news reporters who do not usually cover science. Stories are drawn from current events and from research published in scientific journals, and several stories each year involve rheology. *Discoveries and Breakthroughs Inside Science* is a syndicated science and engineering news service for local television newscasts. Last year, eight rheology-related stories were produced, including "Detecting Turbulence" and "Edible Antifreeze Saves Ice Cream."

The SOR takes advantage of other services within the AIP Physics Resources Center. The Center for History of Physics and Niels Bohr Library & Archives work with

The SOR to preserve the history of the organization and have archived its historical documents and copies of the very first issues of *Transactions*. Over 70 photographs of SOR presidents and members are stored in the Emilio Segrè Visual Archives, all of which are available for download. Through the Society of Physics Students' (SPS) joint-membership program, The

SOR offers free membership to undergraduate student members of SPS and gains the opportunity to interest the next generation in the study of rheology.

Over our 78-year history, The SOR has used AIP resources in several ways to manage or advance various aspects of the Society, for a short time or for an extended period. Likewise, AIP depends on its Member Societies for continuous support, mainly through annual dues and publishing partnerships. AIP's advisory committees absorb advice from Member Society volunteers, which lends clarity and direction to our goals and program objectives. The SOR representatives serve on several of these committees, and the advice is quite helpful. The success of the partnership is manifested in this healthy relationship. Together, we are greater than the sum of our parts.

Best regards,

**Several AIP outreach products and services are available to AIP Member Society members free of charge. To access the AIP Products & Services Quick Guide, visit: [www.aip.org/aip/](http://www.aip.org/aip/).**

**For the fourth time in the 80 years** since its founding in 1929, The Society of Rheology will hold its annual meeting in Madison, Wisconsin, USA. Please join us in Madison for the 81<sup>st</sup> Annual Meeting of The Society of Rheology during the week of 18-22 October 2009. The venue for the meeting is the Frank Lloyd Wright-designed Monona Terrace Community and Convention Center in Madison. Hosting the meeting is the Rheology Research Center at the University of Wisconsin, Madison, led by Jeffrey Giacomin, director.

Five parallel sessions have been organized by Jeff Morris and Srini Raghavan and will take place Monday 19 October through Thursday 22 October. The Annual Meeting will have eleven thematic sessions and a poster session, which includes the annual student paper competition and a new poster competition for post-docs (see p22). In addition to the lecture of the 2009 Bingham medalist Gregory B. McKenna (Texas Tech University, Department of Chemical Engineering), two plenary lectures will be presented, one by Ajay K. Sood (Indian Institute of Science, Department of Physics) and a second by Norman J. Wagner (University of Delaware, Department of Chemical Engineering).

The short course for the Madison meeting will be given by the team of Mike Graham of the University of Wisconsin-Madison and Juan Pablo Hernández-Ortiz of Universidad Nacional de Colombia on the topic "Mesoscopic Simulation of Dynamics in Complex Fluids." The course will run 17-18 October 2009. This course provides an introduction to physical, mathematical and computational aspects of Brownian motion and mesoscopic dynamic simulation of complex fluids, through a mix of lectures and programming sessions. For more on the short course please see [www.rheology.org/sor/short\\_course/2009Oct/](http://www.rheology.org/sor/short_course/2009Oct/).

The Madison meeting includes an extensive social program scheduled throughout the week. The meeting kicks off with a new event, an Industry / Faculty / Student Mixer, which will be held on Sunday, 18 October, from 4 pm to 6 pm in the Monona Terrace Ballroom A. The Mixer is sponsored by a generous

contribution from the Industrial Outreach Program of the American Institute of Physics. The Welcoming Reception will be held on Sunday, 18 October, from 7 pm to 10 pm in the Grand Terrace - West, and is sponsored by a generous contribution from Malvern Instruments.

On Monday there will be a Society Luncheon at noon and an evening Society Reception in the Grand Terrace from 7 pm to 9 pm. The Bingham Award Reception honoring Greg McKenna as the 2009 Bingham medalist will start at 7 pm on Tuesday, 10 October in Grand Terrace - East. This will be followed by the Bingham Award Banquet at 8 pm in the Madison Ballroom A-B. There is no charge for entry to the reception; tickets for the Banquet can be purchased with the meeting registration ([www.rheology.org/sor/annual\\_meeting/2009Oct/](http://www.rheology.org/sor/annual_meeting/2009Oct/)). The Bingham Award Reception is sponsored by a generous contribution from Xpansion Instruments.

The poster session and reception will be held from 6 pm to 8 pm on Wednesday, 21 October in the Grand Terrace. The reception at the Poster Session is sponsored by a generous contribution from Anton Paar USA.

Madison can be accessed conveniently with direct flights to Dane County Regional Airport (airport code MSN) from a number of cities. Airlines serving MSN include Northwest, United Express, American Eagle, Midwest Connect, Continental Express, and Delta Connection. Madison is 2 hours 20 min by car from Chicago O'Hare Airport and 1 hour 30 minutes from Milwaukee Mitchell International Airport. Travel grants to support the cost of attending the meeting are available to any graduate student who is a member in good standing of the Society as of 15 July 2009, and whose faculty advisor is also a member as of that date. See the meeting website for details.

The Wisconsin countryside offers a wide variety of outdoor activities, and Madison is a cosmopolitan city with a wide variety of restaurants and shops. Please join us for an enjoyable and stimulating week of rheology this October.



## 81<sup>st</sup> Annual Meeting of The Society of Rheology, Madison, Wisconsin USA 18-22 October 2009





# On the Definition of Pressure in Rheology

Raja R. Huilgol

*School of Computer Science,  
Engineering and Mathematics  
Flinders University of South Australia*

## Abstract

A detailed examination of the definition of pressure in the deformation and flow of incompressible materials is made. It is shown that requiring the indeterminate part of the stress tensor to produce zero stress power in divergence-free motions leads to a definition of pressure which is ambiguous. Currently, almost all of the constitutive equations, whether derived from continuum mechanics or molecular models, suffer from this defect. However, a more careful application of the theory behind constraint and non-constraint forces in Lagrangian mechanics leads to a unique definition of pressure, which is the negative of the mean normal stress. Such a definition is in accord with the constitutive equations of viscoplastic fluids as well. Given this unique definition of pressure, Lagrangian mechanics shows that material functions can be defined to depend on it. However, this dependence raises a number of questions regarding the rheometry of fluids with pressure-dependent viscosity and normal stress differences.

## Introduction

In a recent article in the *Rheology Bulletin*, Dealy [1] is concerned about the effect of “pressure” on rheological properties, because it cannot be measured in experiments; he points out that in experiments intended to show the effect of “pressure” on rheological properties, the quantity measured is one component of the total stress tensor, not the pressure. Hence, the reporting of data intended to show the effect of “pressure” can lead to errors. This raises the following questions. What is the true meaning of “pressure” in the rheology of incompressible materials, whether they be elastic solids, or viscoelastic fluids or viscoplastic substances? Can it be defined uniquely? Further, can pressure be incorporated into a constitutive equation? The answers to the above questions are found in Lagrangian mechanics, as applied to rigid bodies.

To begin, let us follow [1] and consider the following decomposition of the total stress tensor  $\sigma_{ij}$  in an incompressible fluid:

$$\sigma_{ij} = \tau_{ij} + \pi\delta_{ij}, \quad (1)$$

where  $\tau_{ij}$  is the extra stress tensor, defined through a constitutive relation, and  $\pi$  is the pressure. If one wishes to include  $\pi$  in the equations defining material functions, such as viscosity, normal stress differences and extensional viscosity, it is necessary to show that the pressure  $\pi$  at any point in an incompressible fluid can be defined uniquely and that it has permanent significance. While Dealy [1] says that this cannot be done, in this article we use the techniques of continuum mechanics to show that:

1. The pressure at any point in an incompressible fluid can be defined uniquely, and it has a permanent significance.
2. A uniquely defined pressure imposes a restriction on the trace of the extra stress tensor in every deformation.
3. Just because the density of an incompressible fluid is not affected by pressure, it is not true that “pressure has no effect on rheological properties [1].” In fact, there exists a fully developed theory to incorporate this dependence [2].

We shall now turn to Lagrangian mechanics to demonstrate its relevance to rheology and its use in establishing the above three claims.

## The Meaning of Pressure

In Lagrangian mechanics, the forces acting on a rigid body are split into two classes: those forces which arise due to externally imposed constraints and the rest, usually described as given forces. This decomposition, along with the associated kinematics, is sufficient to understand the definition of pressure in an incompressible body. Here is an example from dynamics which has a direct correspondence with continuum mechanics.

1. Assume that a rigid box is dragged along a rough horizontal surface; this is the kinematical constraint on the motion.
2. In turn, the surface of constraint exerts a normal reaction  $N$  on the body. All that can be said, at this point, is that this force  $N$  is parallel to the normal to the surface. Subsequently, the equations of motion reveal that the force  $N$  opposes the weight of the body. Clearly,  $N$  does no work in this motion.

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

© 2008 Thermo Fisher Scientific. All rights reserved.

## Get the Full Picture – Combine Rheology with Microscopy.

The easy-to-use Rheoscope module for the Thermo Scientific HAAKE MARS rheometer platform allows you to simultaneously record rheological properties and changes to the microscopic structures of complex fluids.

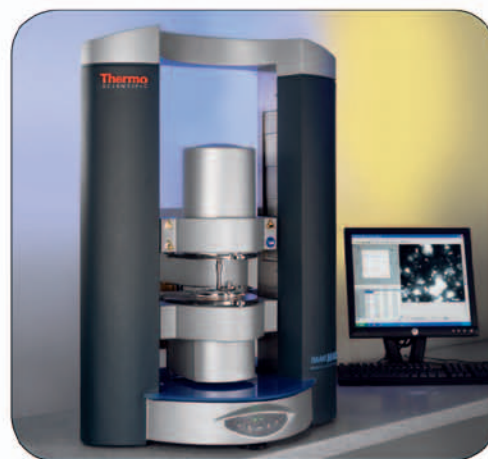
Get the full picture and visualize the interaction between the rheological and structural changes – understand how your products work.

Advantages of the combined method:

- A sophisticated rheometer combined with a powerful visualization technique.
- Ease of use: Both the rheometer and camera are controlled via the HAAKE RheoWin software. Link the structural image to flow characterization.

Visit [www.thermo.com/mars](http://www.thermo.com/mars) to download a video of the product in action.

Thermo Fisher Scientific  
Karlsruhe/Germany · [www.thermo.com/mc](http://www.thermo.com/mc)  
Tel. +49 (0) 721 4 09 44 44 · [info.mc.de@thermofisher.com](mailto:info.mc.de@thermofisher.com)



### Get the benefit of 2 instruments in 1

Shear rate, rheological results and visual structure at the same time and same place.

3. The body is acted on by a force which lies along the surface of constraint. This force  $F$ , due to friction, has to be defined by an equation. Typically,  $F$  is assumed to be that of the Coulomb type, i.e.,  $F = \mu N$ , or it is proportional to the force of constraint. The frictional force is part of the non-constraint forces.
4. The dragging force  $D$  and the weight of the body also form part of the non-constraint forces.

We shall now make the connection between the motion of a rigid body, as described above, and the continuum mechanics of an incompressible body transparent [2].

1. The kinematical constraint on the motion is given by the requirement that the velocity field  $\mathbf{v}$  has zero divergence everywhere, i.e.,  $\nabla \cdot \mathbf{v} = 0$ .
2. The surface of constraint exerts a stress on the body, given by  $C_{ij}$ , which is parallel to the normal to the surface. At this point, it is not obvious whether this tensor is of the ‘compressive’ or ‘tensile’ type.
3. The extra stress tensor is defined to lie along the surface of constraint; it is defined through a constitutive relation.
4. The body is acted upon by surface tractions and body forces.

Thus, the first question is this: can one define the constraint tensor of an incompressible material? Is this unique?

One approach, used extensively in continuum mechanics, is based on an extension of the fact that the reaction  $N$  does no work when the rigid body slides along the surface. So, one demands that the total stress tensor  $\sigma_{ij}$  be determined to within a stress tensor  $\pi_{ij}$  which produces zero stress power in any motion meeting the kinematical constraint. So, let the total stress tensor  $\sigma_{ij}$  be decomposed into two parts:

$$\sigma_{ij} = \tau_{ij} + \pi_{ij}. \quad (2)$$

Let  $A_{ij}^1$  be the first Rivlin-Ericksen tensor [3] defined through

$$A_{ij}^1 = v_{i,j} + v_{j,i}. \quad (3)$$

This tensor is the same as the rate of tensor [4],  $\dot{\gamma}$ , since

$$\mathbf{A}^1 = \nabla \mathbf{v} + (\nabla \mathbf{v})^T = \dot{\gamma}. \quad (4)$$

Now, the stress power [2] of  $\pi_{ij}$  is given by  $(1/2)\pi_{ij}A_{ij}^1 = (1/2)\boldsymbol{\pi} : \dot{\gamma}$ . Since  $v_{i,i} = \nabla \cdot \mathbf{v} = 0$

is the same as  $A_{ii}^1 = 0$ , the condition that  $\pi_{ij}$  produces zero stress power in any motion meeting the latter constraint is that

$$\pi_{ij}A_{ij}^1 = 0 \text{ for all } A_{ii}^1 = 0. \quad (5)$$

The solution for  $\pi_{ij}$  in Eq (5) is well known. It is

$$\pi_{ij} = \pi \delta_{ij}. \quad (6)$$

Unfortunately, as remarked by Rajagopal and Srinivasa [2], one can add a multiple of the Kronecker delta to  $\tau_{ij}$  in Eq. (2) and subtract it from  $\pi_{ij}$  without affecting the requirement of zero stress power. So, this method does not lead to a unique definition of  $\pi$ , as also noted through different arguments by Dealy [1]. In fact, this non-uniqueness has led to a general feeling that what one calls as the ‘‘pressure’’ is not very important, when one is dealing with incompressible materials. Just about every part of the stress proportional to the Kronecker delta is dumped into the pressure term. It is obvious that this practice causes no difficulties when the material functions are independent of pressure; however, when one assumes that they are pressure-dependent, it behooves us to define the latter precisely. It is this matter to which we turn next.

Once again, let us decompose the total stress tensor into two parts [2]:

$$\sigma_{ij} = \tau_{ij} + C_{ij}, \quad (7)$$

where the stress tensor  $C_{ij}$  arises due to the incompressibility constraint  $A_{ii}^1 = 0$ . Let us write the latter as defining the ‘‘surface of constraint’’

$$\phi(\mathbf{A}^1) = A_{ii}^1 = 0. \quad (8)$$

Just as the level surface  $f(x, y, z) = 0$  has a normal defined through  $\nabla f$ , we can define a normal  $\mathbf{N}$ , which is a symmetric second order tensor, to the surface of constraint through [2]

$$\mathbf{N} = \frac{\partial \phi}{\partial \mathbf{A}^1}, \quad N_{ij} = \frac{\partial N}{\partial A_{ij}^1}. \quad (9)$$

Then, any motion of an incompressible material occurs on ‘‘the surface of constraint,’’ and the constitutive equation for the extra stress tensor defines it on this surface [2].

Since the tensor  $C_{ij}$  must be parallel to the normal  $N_{ij}$ , we have the unique decomposition of the total stress tensor  $\sigma_{ij}$ , with  $C_{ij} = \lambda N_{ij}$ :

$$\sigma_{ij} = \tau_{ij} + \lambda N_{ij}, \quad \tau_{ij}N_{ij} = 0. \quad (10)$$

Hence, the Lagrange multiplier  $\lambda$  is given by

$$\lambda = \frac{\sigma_{ij}N_{ij}}{N_{kl}N_{kl}}. \quad (11)$$



Obviously, the tensor  $N_{ij} = \delta_{ij}$  so that we obtain:

$$\sigma_{ij} = \tau_{ij} + \lambda \delta_{ij}, \quad (12)$$

$$\tau_{ij} \delta_{ij} = \tau_{ii} = 0, \quad (13)$$

$$\lambda = \frac{1}{3} \sigma_{ii}. \quad (14)$$

So,  $\lambda$  exists and is uniquely defined through Lagrangian mechanics. Usually, one replaces  $\lambda$  by  $-p$ , and calls  $p$ , the pressure.

In conclusion, the pressure  $p$ , now defined as the negative of the mean normal stress through Eq. (14), has a fundamental significance. It arises as a unique response due to the kinematic constraint on the velocity field in an incompressible material. So, we arrive at the following unambiguous decomposition of the total stress tensor in all incompressible bodies, including rubber elasticity:

$$\sigma_{ij} = \tau_{ij} - p \delta_{ij}, \quad \tau_{ii} = 0. \quad (15)$$

Thus, we have a unique, working definition of *pressure*. It is common to call

$$p = -\frac{1}{3} \sigma_{ii} \quad (16)$$

as the ‘mechanical pressure.’ We note that as a consequence of the decomposition described above, the trace of the extra stress tensor  $\tau_{ij}$  is zero in all motions of an incompressible body.

### Dependence of Material Functions on the Pressure

We have shown that Eq. (16) is a unique and meaningful definition of pressure. We now turn to the dependence of material functions on pressure. Naturally, this can only arise through the extra stress tensor  $\tau_{ij}$ . Once again, Lagrangian mechanics shows the way. As already remarked, the Coulomb frictional force  $F$ , a non-constraint force acting on a body sliding on a rough surface, is given by  $F = \mu N$ , where  $N$  is the force of constraint. This can be generalized further: for a theoretical treatment of “given forces which are (linear) functions of constraint forces,” see Rosenberg [5], Sec. 9.10. For a full examination of the relationships between constraint and non-constraint forces in dynamics, see O’Reilly and Srinivasa [6].

Given the above situation, it is possible to incorporate the pressure  $p$  into the determinate part of the constitutive equation for the stress tensor  $\tau_{ij}$ . That is, we can let [2]

$$\tau_{ij} = \tau_{ij}(\mathcal{S}, p), \quad (17)$$

where  $\mathcal{S}$  is a history of the states experienced by the particle; this history may be based on kinematics or the temperature or both, for instance.

At this stage, it is worth emphasizing that there is no theoretical justification to include an arbitrary “pressure,” such as  $\pi$  in Eq. (1), into the constitutive relation for  $\tau_{ij}$ . Only, the pressure  $p$ , which is derived from  $p = -(1/3)\sigma_{ii}$  will do.

### Viscoplastic Fluids

In viscoelastic fluids, the definitions of various material functions such as viscosity, normal stress differences, dynamic moduli and elongational viscosities do not depend on the exact definition of the pressure  $p$ . However, in Bingham and other viscoplastic fluids, the exact definition of pressure matters since the fluids possess a yield stress  $\tau_y$ . The total stress tensor is decomposed into

$$\sigma_{ij} = -p \delta_{ij} + \tau_{ij}, \quad (18)$$

with the following restrictions:

$$A_{ij} = 0, \quad II(\tau_{ij}) \leq \tau_y, \quad (19)$$

$$\tau_{ij} = \eta A_{ij} + \frac{\tau_y}{II(A_{ij})} A_{ij}, \quad \tau_y < II(\tau_{ij}) \quad (20)$$

The former states essentially that the fluid is either at rest or undergoes a rigid motion in the unyielded zone, while the latter defines a constitutive relation in the yielded zone. Here, the second invariant  $II$  for any symmetric tensor  $M_{ij}$  is defined through  $II(M_{ij}) = (1/2)M_{kl}M_{kl}$ . Because the decomposition in Eq. (18) determines  $\tau_{ij}$  and the invariant  $II(\tau_{ij})$  appears in Eqs. (19) - (20), the decomposition of the total stress into the pressure term and the remainder is crucial. Moreover, the definition of the pressure term in the yielded region must be a function which can be extended continuously into the unyielded zone.

Since Eq. (20) shows that  $\tau_{ii} = 0$  in the yielded domain of the flow, the pressure  $p = -(1/3)\sigma_{ii}$  there. In the unyielded region, there is no constitutive relation for the extra stress tensor. Given this situation, the only unambiguous way of defining the pressure  $p$  in this domain is through  $p = -(1/3)\sigma_{ii}$ , or through  $\tau_{ii} = 0$  again; see [7] for additional comments on this matter.

### Concluding Remarks

It has been argued here that if one wishes to include pressure in the rheological material functions, then one has to accept the consequences of incompressibility in continuum mechanics. Overlooking this would mean that the experimental results lack a theoretical basis. It is also worth noting that when viscosity depends on the pressure  $p$ , a rectilinear flow in a channel, for example, is unlikely [8, 9]; in addition, a normal stress effect appears [9]

(continues page 29)

# Time-Temperature Superposition - A Users Guide

John Dealy

*McGill University, Montreal Quebec Canada*  
and

Don Plazek

*University of Pittsburgh, Pennsylvania USA*

## Abstract

Time-temperature superposition is a valuable tool for describing the viscoelastic behavior of linear polymers over a broad range of times or frequencies by shifting data obtained at several temperatures to a common reference temperature. This technique involves the use of temperature-dependent shift factors for the magnitudes of measured stresses (vertical shift factor) and for time or frequency (horizontal shift factor) on log-log plots of material functions such as the relaxation modulus, the storage and loss moduli, and the creep compliance. The temperature-dependent, vertical shift factor  $b_T$  is usually defined so that it multiplies a stress determined at temperature  $T$  to yield a “reduced stress” that is the value at a “reference temperature,”  $T_0$ ; it is normally very close to unity. The temperature-dependent horizontal shift factor  $a_T$  multiplies a frequency or divides a time to yield a reduced value equal to  $a_T\omega$  or  $t/a_T$ . If time-temperature superposition is obeyed, the use of shift factors will yield a “master curve” showing viscoelastic behavior over a much larger range of times or frequencies than could be studied using a single rheometer at one temperature. However, a shift factor valid in the plateau and terminal zones is not expected to be applicable in the transition zone. And the success of superposition should not be judged on the basis of a small log-log plot or imprecise data.

## Introduction

A single rheometer operated at a single temperature can usually provide data only over a range of three or four decades of frequency or time, and this is inadequate to track viscoelastic behavior from the high-frequency end of the plateau zone into the low-frequency terminal zone. By obtaining data at several temperatures, time-temperature superposition can be used to generate a “master curve” showing the behavior at a “reference temperature” that covers many decades of time or frequency. A material to which this technique is applicable is said to be “thermorheologically simple.”

In preparing master curves, variables having units of time (or reciprocal time) are subject to horizontal shift, while those having units of stress (or reciprocal stress) are subject to vertical shift. For example, in preparing a compliance “master curve,” the variable plotted on the vertical axis is  $J(t)/b_T$ , and that plotted on the horizontal axis is  $t/a_T$  where both  $a_T$  and  $b_T$  are shift factors that depend on temperature.

Thermorheological simplicity obtains when all contributing retardation or relaxation mechanisms of the material have the same temperature dependence and when stress magnitudes at all times or frequencies have the same temperature dependence. This implies that when viscoelastic functions, such as the relaxation modulus  $G(t)$  or the creep compliance  $J(t)$ , are shown on a double-logarithmic plot, data at various temperatures can be shifted horizontally by a constant (independent of time) distance identified as  $\log(a_T)$  and vertically by another constant distance identified as  $b_T$  to obtain a single master curve bringing together all the data. The master curve displays data over a wide range of frequencies or times “reduced” to a reference temperature,  $T_0$ . A thorough discussion of time-temperature superposition can be found in the book by Ferry [1, Section 11-C], who also discusses the shifting of data obtained at several pressures.

We can summarize the above discussion by saying that a master curve of the frequency-dependent storage modulus, based on data obtained at various temperatures  $T$  is obtained by plotting:

$$b_T G'(T) \text{ versus } \omega a_T \quad (1)$$

using logarithmic scales for both axes. While it is not indicated explicitly,  $b_T$  and  $a_T$  are functions of temperature, although the  $b_T$  dependence is quite weak.

The quantity on the left is called the “reduced storage modulus,” sometimes given the symbol  $G'_r$ , while the reduced frequency is  $\omega_r$ . Using these variables, the master curve is a plot of  $G'_r$  versus  $\omega_r$ . And the temperature dependence is usually reported by means of a plot of  $\log(a_T)$  versus  $T$ .

Likewise, for the time-dependent stress relaxation modulus a master curve is obtained by plotting

$$b_T G(T) \text{ versus } t/a_T \quad (2)$$

again using logarithmic scales. This can be written in terms of reduced variables as  $G_r$  versus  $t_r$ . However, the reader should be aware that an alternative definition of  $b_T$  has been used, particularly in the earlier publications of Graessley and his colleagues and in the recent book by

# THE BIG IDEA IN RHEOLOGY

We haven't just redesigned a rheometer.

We've redefined the way it interacts with you.



kinexus<sup>®</sup>  
More rheology, less effort





Rubinstein and Colby [2]. In these publications the reduced modulus is  $(1/b_T)G(t)$ .

The concept of time-temperature superposition can be expressed in terms of an equation relating the property at the reference temperature  $T_0$  to that measured at a temperature  $T$  and then shifted to  $T_0$ :

$$b_T G'(T, \omega a_T) = G'(T_0, \omega) \quad (3)$$

or:

$$G'_r(T, \omega_r) = G'(T_0, \omega)$$

However, some authors write the equality in a different way, which can cause confusion.

Viscosity, which involves both stress and time, requires the application of both shift factors. For example, a master curve of the absolute value of the complex viscosity is constructed by means of a double-logarithmic plot of

$$\frac{b_T}{a_T} |\eta^*|(T) \quad \text{versus} \quad \omega a_T \quad (4)$$

where

$$|\eta^*| = \sqrt{G'^2 + G''^2} / \omega$$

A special case is the zero-shear viscosity.

$$\frac{b_T(T)}{a_T(T)} \eta_0(T) = \eta_0(T_0) \quad (5)$$

If the vertical shift factor is taken to be unity, the horizontal shift factor can be inferred from the zero-shear viscosity.

$$a_T(T) = \frac{\eta_0(T)}{\eta_0(T_0)}$$

Since viscosity is then proportional to the shift factor, the viscosity ratio or even the viscosity itself  $\eta_0(T)$  is often used as a horizontal shift factor.

One can determine the horizontal shift factor without making any assumption about  $b_T(T)$  by plotting as a function of frequency a quantity that is not affected by  $b_T$ , such as the loss angle or its tangent, which is equal to  $G''/G'$ .

Controlled strain rheometers are best suited for measurements at moderate and high frequencies, while controlled torque (stress) instruments are more useful at lower frequencies. However, it often happens that neither oscillatory shear method can provide data in the terminal zone, and creep and creep recovery are used to provide the missing information. The combination of data from these two techniques to produce a single master curve requires a method for conversion of one material function, for example the creep compliance, into another, for example the storage modulus. One approach to this conversion was proposed by He *et al.* [3]. It is important to note that while creep recovery is the most accurate method for determining the steady-state compliance, often called the steady-state recoverable compliance for this reason, is a challenge. In air-bearing instruments, residual torque prevents the reduction of the stress to zero. Either this must be corrected for using a model or a magnetic suspension used in place of an air bearing.

In the case of crystallizable melts, the useful temperature range extends only from the crystallization temperature, on the low end, to the degradation temperature, at the high end, and this limits the applicability of superposition to these polymers.

The compilation of data obtained at several temperatures inevitably adds noise into the resulting master curve. And this noise can interfere with the use of a master curve to determine the molecular weight distribution [4] by the differentiation of  $|\eta^*|$  with respect to frequency.

## Theoretical basis for time-temperature superposition

### Vertical shift factor

The Bueche-Rouse theories of the linear viscoelasticity of unentangled polymer melts and solutions [5,6] assumes that stress magnitudes, *e.g.*,  $G(t)$ ,  $G'(\omega)$  and  $G''(\omega)$ , are proportional to the product of the density and temperature. This implies that the vertical shift factor  $b_T(T)$  is:

$$b_T = T_0 \rho_0 / T \rho \quad (6)$$

For entangled polymer systems, the molecular models most widely used are based on the theory of Doi and Edwards [7], which predicts that the magnitude of the relaxation modulus of an entangled melt is proportional to the factor  $\rho T$  that appears in the Rouse prediction multiplied by a new factor that depends very weakly on temperature. Thus the vertical shift factor is predicted to be slightly different from the  $\rho T$  ratio, but data are rarely if ever precise enough to reveal this difference.

Rather than using Eq. 6, the vertical shift factor is sometimes determined directly from the variation with temperature of a distinctive value of the modulus or

compliance, such as a maximum or minimum in the loss modulus. The plateau in the relaxation modulus  $G(t)$ , the creep compliance  $J(t)$ , the storage modulus  $G'(\omega)$  or the storage compliance  $J'(\omega)$  is also sometimes used. However, since true plateaus with zero slopes are not actually observed, the values at the associated maxima or minima provide more reliable bases for  $b_T(T)$ . Although its precise measurement poses challenges, the steady-state compliance provides a reliable basis for finding  $b_T(T)$ , as demonstrated by Resch *et al.* [8] and Plazek [9]. Another way to determine the vertical (stress) shift factor that is independent of the time or frequency shift is to find the horizontal shift of loss angle data required to obtain superposition on a plot of loss angle versus  $\log |G^*|$ , which is called a Van Gurp-Palmen plot [10].

The vertical shift factor is sometimes used as a fitting parameter for an entire set of data, and the data are shifted both vertically and horizontally in an attempt to achieve a superposition that “looks OK”. This empirical procedure can help to disguise the failure of superposition by averaging the discrepancy over the entire frequency range. Systematic deviations of  $b_T(T)$  from its expected behavior (Eq. 6) can also result from experimental errors. Finally, if both shifts are carried out by fitting, neither factor has any physical significance. For these reasons, such results are questionable.

#### Horizontal shift factor

What do molecular models tell us about the horizontal shift factor? The relaxation times of the Rouse model and those appearing in tube models for the plateau and terminal zones, all depend on temperature in the same way; they are proportional to the ratio  $\zeta/T$ , where  $\zeta$  is the monomeric friction coefficient. If the friction coefficient does not depend on stress or deformation, and if its dependence  $T$  were known *a priori*, a single shift factor would be applicable from the early portion of the transition zone dominated by Rouse relaxations into the terminal zone, and  $a_T(T)$  could be calculated from theory. However, this observation does not allow the prediction of the shift factor, because the monomeric friction coefficient is an empirical parameter in the freely-jointed chain model, and its value can only be inferred from rheological data. Thus, while all the theories mentioned above predict thermorheological simplicity over the time or frequency range of their applicability, in the plateau and terminal zones, they do not lead to a prediction of  $a_T(T)$ .

It is important to note that the Rouse-Bueche model for unentangled polymers and tube models for entangled molecules are based on the freely-jointed chain model, in which the actual molecule is replaced by a much simpler structure that makes it possible to make

quantitative predictions of viscoelastic behavior. This picture has been found to work very well in describing behavior in the plateau and terminal zones and in the longest-time (lowest-frequency) portion of the transition zone. But at shorter times, relaxation modes involving parts of molecules smaller than the segments of the freely-jointed chain come into play, and these are not described by the models discussed above. As a result, a value of  $a_T$  obtained using data in the terminal and plateau zones will not serve to superpose data obtained at significantly shorter times (higher frequencies). Plazek and his coworkers [11-13] have reported exceptionally precise and accurate creep data over many decades of time for several amorphous polymers and have used these to demonstrate the failure of time-temperature superposition (occurrence of thermorheological complexity) when one tries to place all the data on a single master curve using a single value of  $a_T$  at a given temperature. Sometimes, reasonable superposition can be obtained over very wide time/frequency ranges by using two or more horizontal shift factors [14,15] for different time/frequency zones. For polydisperse samples, there is a gradual transition from one zone to another, so one must examine the data carefully to detect the beginnings of thermorheological complexity as the frequency is increased. It is also important to note that short-time relaxation mechanisms will come into play at longer times as the temperature is lowered. One must therefore be on the alert for complexity not only at short times (high frequencies) but also at low temperatures.

Since  $a_T$  cannot be predicted, horizontal shifting is carried out by shifting data until they appear to superpose. Honerkamp and Weese [16] have described a procedure for doing this in an objective manner, and software for this procedure is part of the IRIS package [17].

How does  $a_T$  depend on temperature? Early observations of the dependence of liquid viscosity on temperature led to the empirical Arrhenius relationship that can be expressed in terms of  $a_T$  as follows:

$$a_T(T) = \exp \left[ \frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (7)$$

And this relationship has been found to fit data for linear polymers in the plateau and terminal zones as long as the temperature is well above  $T_g$ . By analogy with reaction rate theory, the constant  $E_a$  has come to be called the activation energy for flow. However, the activation energy concept is often used to characterize polymers even when rheological data do not superpose, and this results in ambiguity as to the meaning of  $E_a$ . For

example,  $E_a$  is sometimes reported to vary with frequency or time or modulus. Various approaches have been proposed for identifying a meaningful activation energy when data do not superpose. One example is a value based on  $\eta_0$ . Several ways of defining  $E_a$  values in the absence of superposition have been compared by Wood-Adams and Costeux [18], and Keßner *et al.* [19] have recently discussed this issue in detail. It is clear that in reporting activation energies for flow, it is essential to explain in detail how these were determined. And one must not compare values obtained in different ways. In any event, when data do not superpose, the use of an activation energy to characterize a polymer is somewhat questionable.

For temperatures closer to  $T_g$ , the fractional or relative free volume concept of Doolittle provided the basis for the WLF (Williams, Landel, Ferry) equation (Eq. 8), a complete discussion of which can be found in Ferry [1, Sections 11-B,C].

$$\log a_T = \frac{-c_1(T - T_0)}{c_2 + (T - T_0)} \quad (8)$$

where  $c_1$  and  $c_2$  are empirical constants.

### Judging the success of superposition

The degree to which superposition is successful is rarely judged on the basis of an objective criterion. And one should not rely on software to make this judgment. Most often one simply looks at the shifted data and declares that time-temperature was successful or unsuccessful. This is particularly true for a portion of a curve that has a slope much less than one, where a significant failure of horizontal superposition results in a shifted data point that is close to the trend line but is actually far from where it should be. Wood-Adams and Costeux [18] proposed the use of linear rather than logarithmic scales to detect complexity. Figure 1 shows data for a metallocene polyethylene homopolymer with a very low level of long-chain branching. On this log-log plot the data appear to superpose well, but the linear plot shown in Figure 2 shows clearly that this material is not thermorheologically simple. In this example, the detection of complexity

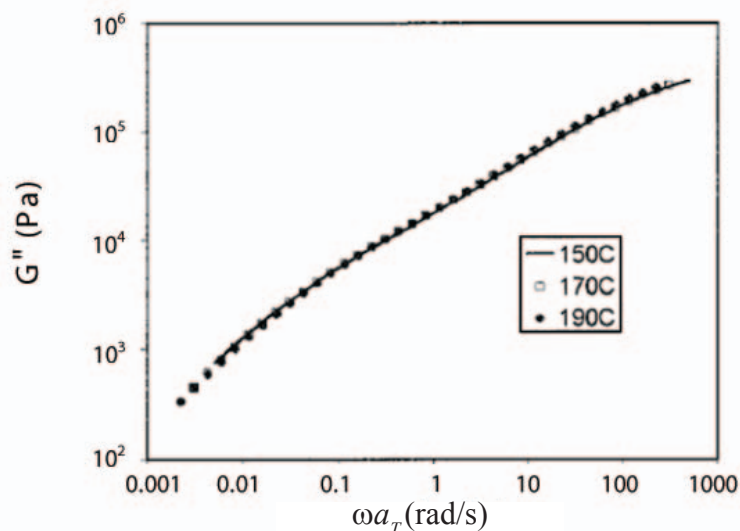


Figure 1: Master curve of loss modulus of a lightly-branched metallocene polyethylene [18]. Logarithmic scales are used for both axes. Note that the vertical shift factor is taken to be unity.

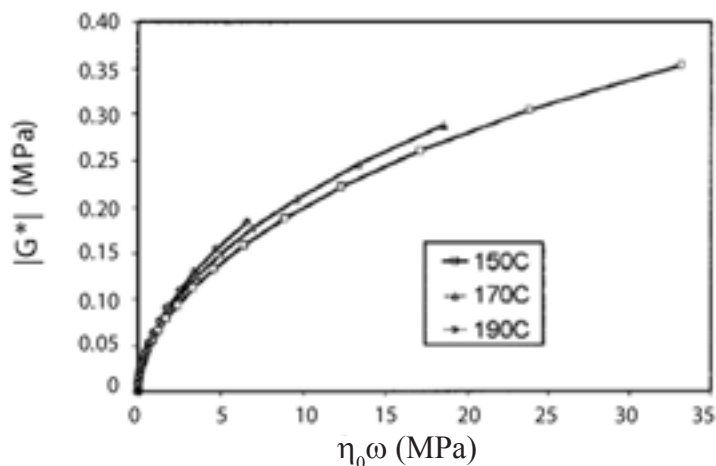


Figure 2: Master curve of absolute value of the complex modulus of the polymer of Fig. 1 [18]. Linear scales are used for both axes. The vertical shift factor is taken to be unity, and the zero-shear viscosity is used as the horizontal shift factor.

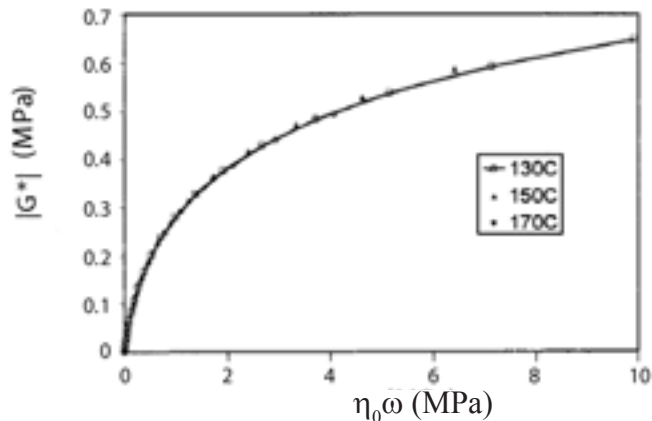


Figure 3: Master curve of absolute value of the complex modulus of a linear polyethylene/octene copolymer [18]. Linear scales are used for both axes. The vertical shift factor is taken to be unity, and the zero-shear viscosity is used as the horizontal shift factor.



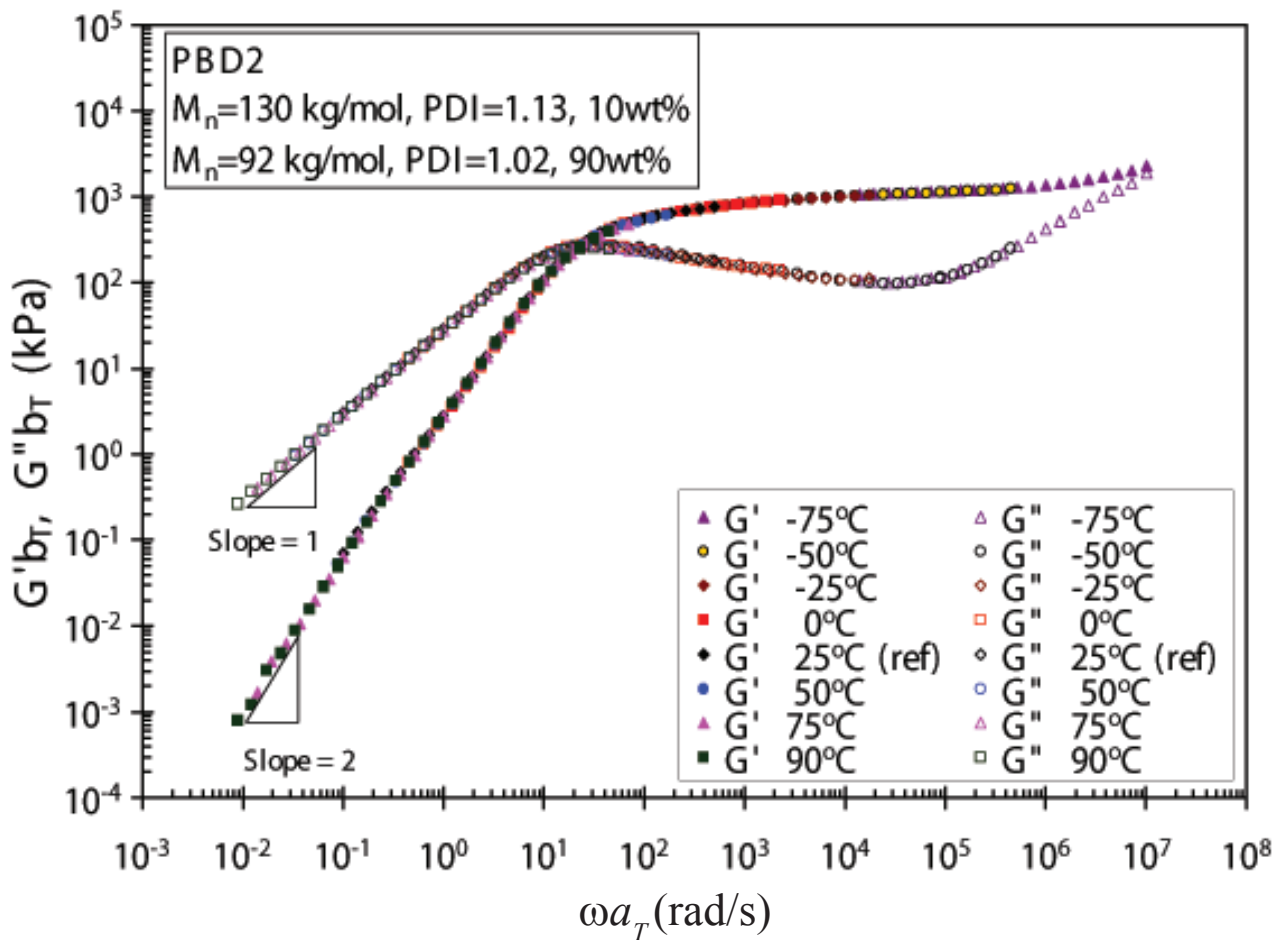


Figure 4: Master curves of storage and loss moduli of a polybutadiene blend based on data obtained at eight temperatures. These data superpose well. (Data of Michelle Li and Hee Eon Park measured at McGill University)

is important, as it provides evidence of long-chain branching. Figure 3 shows the master curve using linear scales for a linear ethylene/butene copolymer that exhibits excellent superposability. Note that the zero-shear viscosity has been used as the horizontal shift factor, while the vertical shift factor is taken to be unity. Sometimes it is claimed that data superposed, but no plot is shown; such a statement must be considered doubtful.

A simple and direct technique for detecting complexity is the use of a van Gorp-Palmen plot [10] of loss angle versus  $\log|G^*|$ . If the effect of  $b_T$  on the magnitude of the complex modulus is negligible, the data will superpose without shifting if the material is thermorheologically simple.

The degree of thermorheological complexity may not have serious consequences if only a general trend is of

interest, but when one wishes to infer structural features from data, it becomes very important. For a highly-entangled polymer, molecular structure is revealed by behavior in the plateau and terminal zones, and data in the transition zone and at even shorter times are not of interest for this application. In fact, rheological behavior is more sensitive to the presence of small quantities of large molecules than chromatography.

#### How well does it work?

Figure 4 is master curve of data obtained at eight temperatures for a blend of two linear polybutadienes. Each point is an average of three measurements, and the vertical shift factor was calculated using Eq. 6. Careful inspection reveals a few small deviations from superposition but, taking into account the precision obtainable in this type of measurement, the superposition is deemed to be acceptable.

(continues page 30)



## NEWS

### New Poster Competition: Postdoctoral Associates

The Madison meeting will feature an inaugural poster competition for post-doctoral researchers. The competition is intended to encourage and identify excellence in young researchers at an early point in their careers, and will run alongside the longstanding student competition, with an award presented to the top candidate in each section. Details of the competition are available from the Madison meeting webpage ([www.rheology.org/sor/annual\\_meeting/2009Oct/](http://www.rheology.org/sor/annual_meeting/2009Oct/)) or from the program chairs for the poster session.

Program Chairs Poster Session Madison:

Chinedum Osuji  
Dept. of Chemical Engineering  
Yale University  
PO Box 208286  
New Haven, CT 06511  
Phone (203) 432-4357  
[chinedum.osuji@yale.edu](mailto:chinedum.osuji@yale.edu)

Danilo Pozzo  
Dept of Chemical Engineering  
University of Washington  
Benson Hall  
Box 351750  
Seattle, WA 98195-1750  
(206) 543-2250  
[dpozzo@u.washington.edu](mailto:dpozzo@u.washington.edu)



### 2009 Officer Elections:

This year is an election year in The Society of Rheology, and our Constitution/Rules spell out the procedure. The Nominating Committee reported on their nominations, and the membership was informed on 18 November 2008 of their selections, as outlined below.

*President:* Faith A. Morrison  
*Vice-President:* A. Jeffrey Giacomin  
Gregory B. McKenna  
*Secretary:* Albert Co  
*Treasurer:* Montgomery T. Shaw  
*Editor:* John F. Brady  
*Members-at-Large:*  
Ole Hassager  
Marie-Claude Heuzey  
Kalman Migler  
Michael J. Solomon  
Norman J. Wagner  
Hiroshi Watanabe

Balloting will take place electronically; members in good standing will receive instructions on how to cast their ballots by email. The Constitution specifies that balloting will begin at least 80 days before the annual meeting, and thus for 2009, balloting will begin 1 August 2009 and will end 20 September 2009.

### Help Wanted in Search for Errata

Readers of *Molecular Structure and Rheology of Molten Polymers* by John M. Dealy and Ronald G. Larson (Hanser Gardner Publishers, 2006) are asked to report errors that they may have found in the book. In return they will receive the list of errors detected to date along with the corrections. In fact, anyone who requests it can receive this list. To report errors or request the list of corrections, please send a message to [john.dealy@mcgill.ca](mailto:john.dealy@mcgill.ca) (Even if you are in doubt as to whether something is incorrect, please report it.)

## Travel Grants Available for Madison 2009

The Society of Rheology is again offering grants to partially support the cost of attending the Annual Meeting of the Society. These grants are available to any graduate student who is a member of the Society as of 15 July 2009 and whose faculty advisor is also a member as of that date. We anticipate that each grant will cover up to a maximum of four days of lodging at the conference rate. Only students who have never before received an SOR travel grant are eligible. To apply, the student must write a letter requesting the grant. The student's faculty advisor should add a letter of support, certifying that both the advisor and the student are members of The Society of Rheology. Only one application per faculty advisor will be accepted for each meeting. Letters from the student and advisor should be emailed before 15 July 2009 to:

**Daniel J. Klingenberg**  
Department of Chemical Engineering  
University of Wisconsin  
Madison, WI 53706  
klingen@engr.wisc.edu

## Minutes of the ExCom Meeting

Sunday, April 5, 2009  
Schiller Park, Illinois

Attending: Monty Shaw, Faith Morrison, John Brady, Marie-Claude Heuzey, Bob Prud'homme, Jeffrey Giacomini, Andy Kraynik, Janis Bennett, Gerry Fuller, Norm Wagner, Shelley Anna, Jeff Morris and Michael Mackey (by teleconference).

President Prud'homme called the meeting to order 8:22am in the Tri-State Room of the Four Points Hotel near Chicago O'Hare Airport in Schiller Park, Illinois. The minutes were read and approved with three corrections: (1) "Gerry Fuller" is to be added to the list of attending (p. 17, Col 2), and (2) "of on our AIP position" should be "of our AIP position (p. 18, Col 1).

Gerry Fuller, Local Arrangements Chair for the 2008 ICR in Monterey reported on the success of the meeting that attracted 1029 registrants. Fuller, as President of the International Committee on Rheology (ICR) then led a discussion on the role of the ICR. Beginning in

2000, the host society for the International Congress on Rheology has donated some operating funds to the International Committee on Rheology. A motion passed to authorize giving \$10,000 to the International Committee on Rheology for their operating purposes. As current President of the International Committee on Rheology, Fuller feels he could be effective in developing international communities of rheology. A motion passed to allocate \$5,000 to support Gerry Fuller's proposal to foster the development of international communities (FDIC) of rheology. This will be an SOR budgetary line item for international outreach. Andy Kraynik, Co-Chair of the Organizing Committee for the 2008 International Congress on Rheology in Monterey led a discussion about the ICR program. Treasurer Shaw reported an \$87,000 deficit for the Monterey 2008 ICR. Treasurer Shaw also reported that the overall financial condition of the Society is very good and that the *Journal of Rheology* is financially successful. The Executive Committee accepted each of the Treasurer's reports. The Executive Committee thanked Shaw for outstanding financial stewardship during this extraordinary year for the Society.

John Brady, Editor of the *Journal of Rheology*, reported on the vigor and health of the *Journal*. The *Journal* continues to attract submissions from around the world, though there has been a slight decline in the total number of submissions. The *JOR* impact factor for 2008 is an all-time high of 2.7, placing our journal very well compared to cognate journals. The Editor's report was accepted.

President Prud'homme reported on the AIP Meeting of Society Officers. Journal publication issues remain an important concern for that group. For Mike Solomon, Chair of the Education Committee, Bob Prud'homme reported on short course arrangements for upcoming meetings. The next installment of "Beginning Rheology" by Morrison and Giacomini is planned for Cleveland, but due to the Executive Committee meeting on October 9, the short course is proposed for 7-8 October [Friday-Saturday], 2011 (2 day). The Executive Committee agreed that a Friday-Saturday course could be tried as an experiment; this will be communicated to Education Chair Solomon. For the upcoming Madison meeting short course, "Mesoscopic simulation of dynamics in complex fluids", by Mike Graham and Juan Hernandez-Ortiz (2 day) is proposed on the weekend of 17-18 October 2009. There is currently no short course in the works for Santa Fe and all are invited to send suggestions to Solomon. The education report was accepted.

Bob Prud'homme informed the committee that past-president John Dealy will report on efforts to standardize nomenclature for suspension rheology for The Society of



Rheology at the Madison Executive Committee meeting.

Bob Prud'homme reported for Albert Co that the Webmaster is actively updating the Society's web pages. In June or July the members' site will include minutes of the Executive Committee and Business Meetings. A new server will be brought on line also this summer.

Shelley Anna, Chair of the Membership Committee, reported that the Society membership has declined steadily over the past decade. The committee is working on strategies to increase membership including exploiting our presence on linkedin.com. A motion passed to accept the Membership Chair's report.

Bob Prud'homme announced that the Bingham committee has not completed its selection, and the Executive Committee's vote on the 2009 Bingham Medal will be conducted electronically in about two weeks.

Janis Bennett, SOR Liaison to the AIP, reported on Institute business.

Jeffrey Giacomini, Chair of Local Arrangements, gave a presentation on the next meeting of The Society of Rheology, to be held in Madison, Wisconsin (October 18-22, 2009). Local arrangements are moving along swimmingly. This meeting will feature reasonably priced accommodations for graduate students, so faculty should plan to bring their research groups. The meeting registration website will be brought up in Mid-May ([www.rheology.org](http://www.rheology.org)).



Technical Program Chair Jeff Morris proposed that we host an AIP-sponsored student mixer on Sunday, October 18, to begin at 4:00 p.m. His proposal was warmly received.

The meeting entered Executive Session at 1:00 p.m. The committee approved the recommendation for the inaugural Arthur B. Metzner Award winner. Bob

Prud'homme led a discussion on the Editor's honorarium and an adjustment was made. The Executive Session then closed.

Andy Kraynik, Chair of Local Arrangements, reported on arrangements for the Santa Fe meeting (October 24-27, 2010); all is going well. This report was accepted. With enthusiasm, the Executive Committee approved John Brady's proposal for a spring meeting (10-14 February 2013) in Pasadena, California. Marie-Claude Heuzey, Co-Chair of Local Arrangements with

Paula Wood-Adams, reported on arrangements for the Montreal meeting (13-17 October 2013). A motion passed to accept her report.

Norm Wagner in collaboration with Michael Mackey and the University of Delaware rheology community proposed to host an annual meeting in the Loews Philadelphia Hotel in Philadelphia, Pennsylvania (5-9 October 2014). With enthusiasm, this proposal was approved.

Conflict of interest on the Bingham and Metzner award committees was discussed.

The Society is a small society, and we chose committee members for our award committees from among the most productive members of our Society. It is therefore likely that the members of these committees could be close collaborators or colleagues of a nominee. This has happened on recent committees (for example, in 2006 per Andy Kraynik). Eliminating all conflicts by dismissing committee members with apparent conflict could seriously reduce the quality of the committee.

## An Invitation to Join The Society of Rheology

Dedicated to advancing the science of rheology: the study of deformation and flow of matter.

The Society of Rheology was founded in 1929 to foster the study of the mechanical properties of deformable materials.

SOR is a founding member of the American Institute of Physics.

Visit our website  
[www.rheology.org/sor/](http://www.rheology.org/sor/)

Apply for membership on-line

The Executive Committee discussed this and determined that when a potential conflict of interest is identified, the chair of the award committee should consult with the Society president. The committee chair and the president shall determine a course of action to resolve the conflict.

Bob Prud'homme led a discussion of Society representation on AIP Committees. Prud'homme will circulate the long list of AIP committees to the Executive Committee and committee members will give feedback on which positions the Society should seek to fill.

The meeting was adjourned at 4:45 p.m.

Submitted by Jeffrey Giacomini, Secretary

October. In spite of a loss of over \$80,000 for the Monterey meeting (International Congress of Rheology), the financial position the Society at the end of 2008 remained strong. As for 2009, we are suffering from lower principal and interest rates on our reserves and lagging membership. The budget for 2010 allows for a continuation of these trends, but with a steady income for the *Journal of Rheology* due to the continuing popularity of subscription consortia.



Respectfully submitted,

Montgomery T. Shaw  
Treasurer

## Treasurer's Report

To the Membership,

The tables included here summarized the financial situation for The Society of Rheology at the end of calendar year 2008, along with a proposed budget for 2010. The latter will be presented for the approval of the Membership at The Society's Annual Meeting in Madison in

# Treasurer's Report

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

(all amounts, USD)	2008 Year End	2007 Year End	2006 Year End	2005 Year End	2004 Year End
<b>Assets</b>					
Cash in checking account(s)	10,859	24,466	9,777	12,721	29,012
Securities	0	0	0	0	0
Balance in AIP account	1,342,819	1,292,672	1,185,978	1,056,188	976,655
<b>Total Assets</b>	<b>1,353,678</b>	<b>1,317,138</b>	<b>1,195,755</b>	<b>1,068,909</b>	<b>1,005,667</b>
<b>Liabilities and Net Assets</b>					
<b>Liabilities</b>					
Deferred revenue	87,675	111,995	129,339	132,396	155,969
<b>Total Liabilities</b>	<b>87,675</b>	<b>111,995</b>	<b>129,339</b>	<b>132,396</b>	<b>155,969</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	300,000	200,000	200,000	100,000
Operating reserve	100,000	100,000	100,000	100,000	100,000
<b>Unrestricted</b>	<b>406,003</b>	<b>345,143</b>	<b>306,416</b>	<b>176,513</b>	<b>189,698</b>
<b>Total Net Assets</b>	<b>1,266,003</b>	<b>1,205,143</b>	<b>1,066,416</b>	<b>936,513</b>	<b>849,698</b>
<b>Total liabilities and net assets</b>	<b>1,353,678</b>	<b>1,317,138</b>	<b>1,195,755</b>	<b>1,068,909</b>	<b>1,005,667</b>

# Treasurer's Report

## *Journal of Rheology*

### Receipts and Disbursements (all amounts, USD)

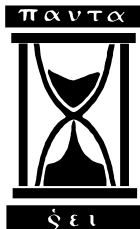
	<b>2010 Budget</b>	<b>2009 Budget</b>	<b>2008 Year End</b>	<b>2008 Budget</b>	<b>2007 Year End</b>
<b>RECEIPTS</b>					
Subscriptions	172,000	171,000	172,338	170,000	171,391
Royalties & Reprint Sales	11,000	23,200	12,736	10,200	17,203
Ad Sales	39,000	34,000	43,582	36,000	33,556
JORO revenue	54,000	54,000	54,612	41,000	51,816
Miscellaneous	1,500	1,000	525	1,000	1,000
<b>TOTAL RECEIPTS</b>	<b>277,500</b>	<b>283,200</b>	<b>283,793</b>	<b>258,200</b>	<b>274,966</b>
<b>DISBURSEMENTS</b>					
Ads	11,000	10,000	10,671	7,000	9,830
Reprints, Single Copy	1,300	1,800	1,255	1,900	1,354
Paper, Printing	22,000	24,000	21,811	20,000	22,480
SOR Editorial	39,000	39,000	37,298	41,000	36,935
Production	41,000	42,000	39,055	30,000	37,125
Fulfillment	5,825	6,425	5,934	6,425	6,025
Distribution	20,800	25,100	20,290	20,100	21,020
Electronic publishing	33,000	34,000	32,570	35,000	33,055
Miscellaneous	7,600	7,300	5,583	4,800	5,896
<b>TOTAL DISBURSEMENTS</b>	<b>181,525</b>	<b>189,625</b>	<b>174,468</b>	<b>166,225</b>	<b>173,720</b>
Net	95,975	93,575	109,325	91,975	101,246



**The Society of Rheology**  
 Receipts and  
 Disbursements  
 (all amounts, USD)

	<b>2010 Budget</b>	<b>2009 Budget</b>	<b>2008 Year End</b>	<b>2008 Budget</b>	<b>2007 Year End</b>
<b>RECEIPTS</b>					
Dues	48,000	52,000	49,955	56,000	52,495
Interest	29,000	52,000	35,734	58,000	62,442
Journal of Rheology	277,500	283,200	283,793	258,200	274,966
Mailing List Sales	100	0	80	0	465
Donations	0	0	0	0	0
Bulletin Advertising	9,000	5,000	11,150	5,000	13,480
Annual Meeting (net)	0	0	-54,096	0	20,338
Short Course (net)	0	0	-8,347	0	1,360
<b>TOTAL RECEIPTS</b>	<b>363,600</b>	<b>392,200</b>	<b>318,269</b>	<b>377,200</b>	<b>425,546</b>
<b>DISBURSEMENTS</b>					
AIP Dues Bill & Collect.	11,000	11,000	10,834	11,000	11,037
AIP Adm. Services	9,000	9,000	9,187	11,000	7,508
AIP Mem. Soc. Dues	8,000	7,600	8,119	8,000	7,909
Contributions and Prizes	12,000	12,000	1,699	1,900	1,910
Journal of Rheology	175,000	189,625	174,468	166,225	173,720
Bulletin	19,000	16,000	18,557	12,000	16,298
Bingham Award	12,000	12,000	5,000	7,000	5,000
Executive Cmt. Meetings	8,500	11,000	8,751	8,000	17,018
Pres. Discretionary Fund	1,500	1,500	750	1,500	0
Treas. Discr. Fund	1,500	1,500	0	1,500	0
Bulletin Editor Discr. Fund	1,500	1,500	1,366	1,500	0
Progr. Chm. Discr. Fund	2,000	2,000	0	2,000	2,805
Webmaster Discr. Fund	3,000	3,000	0	3,000	685
Office Expenses	3,000	3,000	2,196	3,000	3,212
Banking Services	100	66	65	100	0
Liability Insurance	3,900	4,500	3,830	7,500	3,830
Membership Broch. & Appl.	0	500	0	500	0
Accountant	2,000	2,100	1,940	2,100	1,910
Student member travel	26,000	24,000	0	24,000	21,468
Annual meetings, future	9,000	8,000	6,533	4,000	16,932
Website	500	500	420	1,000	484
Miscellaneous	500	500	0	500	0
<b>TOTAL DISBURSEMENTS</b>	<b>309,000</b>	<b>320,891</b>	<b>253,714</b>	<b>277,325</b>	<b>291,724</b>
<b>Net</b>	<b>54,600</b>	<b>71,309</b>	<b>64,555</b>	<b>99,875</b>	<b>133,822</b>

the end



## Application for Membership in The Society of Rheology

Any student, scientist or engineer with an interest in the deformation or flow of matter is invited to join The Society of Rheology. Members receive the *Rheology Bulletin*, the *Journal of Rheology* and *Physics Today*. There are no academic or geographic requirements for membership. Complete and send a copy of this application form to the address below.

I wish to apply for membership in The Society of Rheology dating from January \_\_\_\_\_ (year) **WEB**

last name:																
first name:																
department:																
institution:																
work address:																
city:																
state/province:																
postal code:									(work address appears in the directory)							

mail address:																
city:																
state/province:																
postal code:									(publications sent to the mail address)							

country:																
phone:																
fax:																
e-mail:																

affiliation:      academia       industry       government       (check most appropriate)

annual dues:      regular member (\$40)       student member (\$25)       (include copy of student ID)

credit card:      AMEX       MasterCard       Visa       exp. date: \_\_\_\_\_

card number:																
--------------	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--

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.

signature (required): \_\_\_\_\_ date: \_\_\_\_\_

even in purely viscous fluids. When normal stress differences are included, a complicated consistency relation between  $N_1$ ,  $N_2$  and the pressure  $p$  has to be met [9]. Thus, using a rheometer to study visco-metric flows is problematic, and Dealy [1] is correct to be skeptical of such results.

Appealing to molecular models [10, Chap. 4] is not of any help in resolving the conundrum regarding the meaning of pressure. This is because the extra stress tensor in many of these models does not have a zero trace, or the pressure in these models is not uniquely defined. The only exception seems to be the Doi-Edwards model [11, pp. 71], for the authors state that the extra stress tensor has a zero trace. Whether the Doi-Edwards model can be modified to include the effect of pressure in its constitutive equation remains to be seen.

Compromises between theory and experiments are necessary and will continue to be made. However, it is not possible to argue around the matters raised here by saying that whatever the theory may be, one is restricted by the measurements that are available. A detailed analysis of the role played by pressure in theory and experiment is required to resolve the current uncertainty regarding the reporting of experimental data at elevated “pressures.”

#### Acknowledgements

I wish to thank the Australian Research Council for a Linkage Grant and Modflow Pty Ltd for a matching contribution in support of this research. Secondly, I wish to thank the two reviewers for their comments which led to a significant improvement in the content and wording of the article. Finally, I wish to thank the Editor, Professor Morrison, for a number of important suggestions which have also been incorporated.

#### References

- [1] J.M. Dealy, “Misuse of the Term *Pressure* in Rheology,” *Rheol Bull*, 77 (1) January 2008, 10.
- [2] K.R. Rajagopal and A.R. Srinivasa, “On the nature of constraints for continua undergoing dissipative processes,” *Proc R Soc A Lond* 461 (2005) 2785.
- [3] R.S. Rivlin and J.L. Ericksen, “Stress-deformation relations for isotropic materials,” *J Rational Mech Anal*, 4 (1955) 323.
- [4] R.B. Bird, R.C. Armstrong and O. Hassager, *Dynamics of Polymeric Liquids*, Vol. 1, 2<sup>nd</sup> edition, Wiley & Sons, New York, 1987.
- [5] R.M. Rosenberg, *Analytical Dynamics of Discrete Systems*, Plenum Press, New York, 1977.
- [6] O.M. O’Reilly and A.M. Srinivasa, “On the nature of constraint forces in dynamics,” *Proc R Soc Lond A* 457 (2001) 1307.
- [7] R.R. Huilgol and Z. You, “Prolegomena to variational inequalities and numerical schemes for compressible viscoplastic fluids,” *J Non-Newt Fluid Mech* 158 (2009) 113.
- [8] J. Hron, J. Málek and K.R. Rajagopal, “Simple flows of fluids with pressure-dependent viscosities,” *Proc R Soc Lond A* 457 (2001) 1603.
- [9] R.R. Huilgol and Z. You, “On the importance of the pressure dependence of viscosity in steady non-isothermal shearing flows of compressible and incompressible fluids and in the isothermal fountain flow,” *J Non-Newt Fluid Mech* 136 (2006) 106.
- [10] R.R. Huilgol and N. Phan-Thien, *Fluid Mechanics of Viscoelasticity*, Elsevier, Amsterdam, 1997.
- [11] M. Doi and S.F. Edwards, *The Theory of Polymer Dynamics*, Clarendon Press, Oxford, 1999 (Reprint of the 1988 edition).



A material will exhibit thermorheological simplicity if all of its relaxation times have the same dependence on temperature. As demonstrated above, we expect this to be so in the plateau and terminal zones. And this should continue to be the case as we move into the transition zone, as long as relaxation is governed by Rouse modes. However, it is not possible to say in advance over what portion of the transition zone data will superpose. Molecular models based the freely-jointed chain picture must fail for processes involving portions of the chain smaller than the imaginary “subunit” that makes up this chain. And another complication at high frequencies (short times) is that as the entropy spring modes are damped, the glassy modes of relaxation become dominant [20]. We expect then that shift factors based on data in the plateau and terminal zones will always fail at some point not far beyond (higher frequencies or shorter times) the plateau zone.

### Nonlinear properties

Graessley [21, p. 239] provides a discussion of the application of time-temperature superposition to nonlinear properties, and we provide here only a brief summary. The viscosity function has been reported to obey time-temperature superposition. If the vertical shift factor is neglected, the zero-shear viscosity can be used as the horizontal shift factor to obtain a master curve by plotting

$$\frac{\eta(T, \dot{\gamma})}{\eta_o(T)} \text{ versus } \eta_o(T) \dot{\gamma} \quad (9)$$

The other viscometric functions can also be treated in this manner. But viscometric functions are not functions of time; what about time-dependent properties? Constitutive equations for melts almost universally build on the same spectra of relaxation times that are used to describe linear viscoelasticity. This implies that if time-temperature superposition brings linear data together, it should also work for nonlinear properties using the same shift factors. The fundamental assumption is that the relaxation times are independent of the state of stress. For example, a temperature-invariant representation of the shear stress-growth coefficient is based on the following relationship:

$$\frac{b_T}{a_T} \eta^+(t/a_T, \dot{\gamma} a_T, T) = \eta^+(t, \dot{\gamma}, T_0) \quad (10)$$

Muller and Froelich [22] applied time-temperature superposition to extensional stress-growth data.

### Structural features contributing to complexity

The most successful demonstrations of superposition have involved linear homopolymers, and complexity is often observed in the case of more complex molecules. Variations in the local microstructure of linear polybutadienes resulting from hydrogenation to various extents were found not to result in deviations from simplicity [23], and all the polymers produced in that study were found to have the same horizontal shift factor when the reference temperature was  $T_g + 50^\circ\text{C}$ . As we might have expected, these shift factors did not superpose data obtained at frequencies well above the plateau region [24] because of the prominence of segmental relaxations in this region.

Wood-Adams and Costeux [18] found that the very short branches in ethylene-octene copolymers did not result in thermorheological complexity. The effect of long-chain branching depends on a combination of chain chemistry and molecular architecture. Metallocene polyethylenes containing low levels of long-chain branching have been found to be thermorheologically complex [18, 25]. Polyisoprene stars have the same shift factors as the linear polymer [26]. Kapnistos *et al.* [27] studied a series of polybutadienes having star-like backbones with grafted branches and reported that the shift factors were the same for all the structures that they used. Moreover, these were the same as shift factors reported previously for linear and comb polybutadienes. On the other hand, data for hydrogenated polybutadiene stars were not superposable [28], although their unhydrogenated precursors exhibited simple behavior [29]. This anomalous behavior has been examined by Graessley [30] and a theoretical explanation has been proposed [31].

Low-density polyethylene has a complex structure that involves both long and short branches, and it is known to be thermorheologically complex.

### Acknowledgements

The authors benefited from lengthy discussions with W. W. Graessley, and comments on a draft of the manuscript from Ute Keßner of the University of Erlangen. However, it is not to be inferred that these individuals are in agreement with every statement made in the paper. Michelle Li and Hee Eon Park worked for several weeks to obtain the data shown in Fig. 4 and provided the plot. Jen Shueng Tiang read the “final” manuscript very carefully and found many ways to improve it.

## References

1. J.D. Ferry, *Viscoelastic Properties of Polymers*, 3<sup>rd</sup> ed., John Wiley & Sons, N.Y. 1980.
2. M. Rubinstein and R.H. Colby, *Polymer Physics*, Oxford Univ. Press, Oxford, 2003.
3. C. He, P. Wood-Adams and J.M. Dealy, "Broad frequency range characterization of molten polymers," *J Rheol*, 48, 711-724 (2004).
4. P. Wood-Adams and J.M. Dealy, "Use of rheological measurements to estimate the molecular weight distribution of linear polyethylene," *J Rheol*, 40, 761-778 (1996).
5. P.E. Rouse, "A theory of the linear viscoelastic properties of dilute solutions of coiling polymers," *J Chem Phys*, 21, 1272-1280 (1953).
6. F. Bueche, "Viscosity self-diffusion and allied effect in solid polymers," *J Chem Phys*, 20, 1959-1964 (1952).
7. M. Doi and S.F. Edwards, *The Theory of Polymer Dynamics*, Clarendon Press, Oxford, 1986, Chap. 7.
8. J. A. Resch, F.J. Stadler, J. Kaschta and H. Münstedt, "Temperature dependence of the steady-state recoverable compliance of linear and long-chain branched polyethylenes," *Macromol*, in press, 2009.
9. D.J. Plazek and A.J. Chelko, Jr., "Temperature dependence of the steady state recoverable compliance of amorphous polymer," *Polymer*, 18, 15-18 (1977).
10. M. van Gurp, and J. Palmen, "Time-temperature superposition for polymeric blends," *Rheol Bull*, 67(1), pp.5-8 (Published by the Soc. of Rheol.) (1998).
11. D.J. Plazek, "The temperature dependence of the viscoelastic behavior of poly(vinyl acetate)," *Polym J*, 12, 43-53 (1980).
12. K. L. Ngai and D. J. Plazek, "A quantitative explanation of the difference in time-dependences of the viscoelastic softening and terminal dispersions of linear amorphous polymers," *J Polym Sci B, Polym Phys*, 24, 619-632 (1986).
13. D.J. Plazek, "1995 Bingham Medal address : Oh, thermorheological simplicity, wherefore art thou?" *J Rheol*, 40, 987-1014 (1996).
14. C.G. Robertson and C.M. Rademacher, "Coupling model interpretation of thermorheological complexity in polybutadienes with varied microstructure," *Macromol*, 37, 10009-10017 (2004).
15. D.J. Plazek, "The temperature dependence of the viscoelastic softening and terminal dispersions of linear amorphous polymers," *J Polym Sci, Phys Ed*, 20, 729-742 (1982).
16. J. Honerkamp and J. Weese, "A note on estimating mastercurves," *Rheol Acta*, 32, 57-64 (1993).
17. IRIS software is described at [rheology.tripod.com](http://rheology.tripod.com).
18. P. Wood-Adams and S. Costeux, "Thermorheological behavior of polyethylene: Effects of microstructure and long chain branching," *Macromol*, 34, 6281-6290 (2001).
19. U. Keßner, J. Kaschta and H. Münstedt, "Determination of method-invariant activation energies of long-chain branched low-density polyethylene," *J Rheol*, in press, 2009.
20. K.L. Ngai and D.J. Plazek, "Identification of different modes of molecular motion in polymers that cause thermorheological complexity," *Rubber Chem Tech*, 68, 376-434 (1995).
21. W.W. Graessley, *Polymeric Liquids & Networks: Dynamics and Rheology*, Garland Science, London, N.Y. 2008.
22. R. Muller and D. Froelich, "New extensional rheometer for elongational viscosity and flow birefringence: Some results on polystyrene melts," *Polymer*, 26, 1477-1482 (1985).
23. J.M. Carella, W.W. Graessley and L.J. Fetters, "Effects of chain microstructure on the viscoelastic properties of linear polymer melts: Polybutadienes and hydrogenated polybutadienes," *Macromol*, 17, 2775-2786 (1984).
24. C.G. Robertson and C.M. Rademacher, "Coupling model interpretation of thermorheological complexity in polybutadienes with varied microstructure," *Macromol*, 37, 10009-10017 (2004).
25. F.J. Stadler, J. Kaschta and H. Münstedt, "Thermorheological behavior of various long-chain branched polyethylenes," *Macromol*, 41, 1328-1333 (2008).
26. L.J. Fetters, A.D. Kiss, D.S. Pearson, G.F. Quack and F.J. Vitus, "Rheological behavior of star-shaped polymers," *Macromol*, 26, 647-654 (1993).
27. M. Kapnistos, G. Koutalas, N. Hadjichristidis, J. Roovers, D.J. Lohse and D. Vlassopoulos, "Linear rheology of comb polymers with star-like backbones: Melts and solutions," *Rheol Acta*, 46, 273-286 (2006).
28. V.R. Raju, H. Rachapudy and W.W. Graessley, "Properties of amorphous and crystallizable hydrocarbon polymers. IV. Melt rheology of linear and star branched hydrogenated polybutadiene," *J Polym Sci, Phys Ed*, 17, 1223-1235 (1979).
29. W.E. Rochefort, G.G. Smith, H. Rachapudy, V.R. Raju, and W.W. Graessley, "Properties of amorphous and crystallizable hydrocarbon polymers. II. Rheology of Linear and Star-Branched Polybutadiene," *J Polym Sci-Phys Ed*, 17, 1179-1210 (1979).
30. W.W. Graessley, "Effect of long branches on the temperature dependence of viscoelastic properties in polymeric melts," *Macromol*, 15, 1164-1167 (1982).
31. A.J. Levine and S.T. Milner, "Star polymers and the failure of time-temperature superposition," *Macromol*, 31, 8623-8637 (1998).

# CALENDAR OF RHEOLOGY CONFERENCES AND COURSES

## 2009

*12-15 June 2009*

7<sup>th</sup> International Conference on Clinical Hemorheology, Yaroslavl, Russia, A. V. Muravyov ([www.yspu.yar.ru/ICH/index\\_e.htm](http://www.yspu.yar.ru/ICH/index_e.htm))

*17-21 August 2009*

18<sup>th</sup> Nordic Rheology Conference, Rheo Iceland 2009, Reykjavik, Iceland. [www.rheo.is](http://www.rheo.is)

*17-18 October 2009*

SOR Short Course on Rheology *Mesosopic Simulation of Dynamics in Complex Fluids* by Mike Graham and Juan Hernandez-Ortiz, Madison, WI USA

*18-22 October 2009*

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

## 2010

*7-10 April 2010*

6<sup>th</sup> Annual European Rheology Conference AERC 2010, Goteborg, Sweden, Mats Stading.

*4-7 July 2010*

26<sup>th</sup> Annual Meeting of the Polymer Processing Society, Banff, Canada, U. Sundararaj

*Summer 2010*

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

*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

*Summer 2011*

14<sup>th</sup> International Congress of Biorheology (held every three years), location TBA (last conference: [www.outreach.psu.edu/programs/isbisch/](http://www.outreach.psu.edu/programs/isbisch/))

*June 2011*

27<sup>th</sup> Annual Meeting of the Polymer Processing Society, Marrakesh, Morocco, M. Bousmina

*8-9 October 2011*

SOR Short Course on Rheology (topics 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

*5-10 August 2012*

XVI<sup>th</sup> International Congress on Rheology, Lisbon, Portugal, João M. Lopes Maia (every four years; in 2016 in Asia)

*19-24 August 2012*

XXIII<sup>rd</sup> International Congress of Theoretical and Applied Mechanics ICTAM 2012; Beijing, China (every four years)

## 2013

*9-10 February 2013*

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

*10-14 February 2013*

84<sup>th</sup> Annual Meeting of The Society of Rheology, Pasadena, CA USA, John Brady and Julia Kornfield

*12-13 October 2013*

SOR Short Course on Rheology (topic TBA), Montreal, Quebec, Canada.

*13-17 October 2013*

85<sup>th</sup> Annual Meeting of The Society of Rheology, Montreal Quebec Canada, Marie-Claude Heuzey, Paula Wood-Adams.

## 2014

*4-5 October 2014*

SOR Short Course on Rheology (topic TBA), Philadelphia, PA USA.

*5-9 October 2014*

86<sup>th</sup> Annual Meeting of The Society of Rheology, Philadelphia, PA USA, Michael Mackey and Norm Wagner.