### **RHEOLOGY BULLETIN**

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### RONALD G. LARSON 2002 BINGHAM MEDALIST

The Bingham medal of the Society for 2002 will be awarded at the Minneapolis meeting to Professor Ronald G. Larson of the University of Michigan; Ron is a past President of the Society. A write-up appears inside this issue of the Bulletin.

### 74<sup>th</sup> ANNUAL MEETING MINNEAPOLIS, MN OCTOBER 13 – 17, 2002

The 2002 annual meeting of the Society of Rheology will be held at the Radisson Metrodome Hotel on the campus of the University of Minnesota in Minneapolis. The Twin Cities of Minneapolis and St. Paul, situated near the confluence of the Minnesota and Mississippi rivers, offer a remarkable blend of readily accessible cultural, gastronomic, athletic, and shopping opportunities. Mid-October usually coincides with the peak of fall colors, and the many urban lakes and parks provide beautiful settings for walking, jogging, and biking.

A welcoming reception will be held on Sunday evening in the Radisson Hotel. The Society reception will be held on Monday evening at the Frederick R. Weisman Art Museum, a stunning Frank Gehry edifice overlooking the Mississippi river and downtown Minneapolis and just three blocks from the hotel. The meeting banquet on Tuesday evening will be located in the McNamara Alumni Center, immediately adjacent to the Radisson. The meeting organizers are from the University of Minnesota:

Technical Program:

Timothy P. Lodge (612) 625-0877; Fax: (612) 624-1589 e-mail: lodge@chem.umn.edu

Local Arrangements:

Christopher W. Macosko (612) 625-0092; Fax: (612) 626-1686 e-mail: macosko@cems.umn.edu

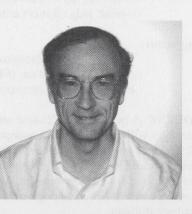
**SHORT COURSE** A two-day short course on Microfluidics and Microrheology will be offered in Minneapolis, October 12-13, 2002. The instructors are Dr. Andrea Chow of Caliper Technologies Corp. and Professor Steve Granick of the University of Illinois at Urbana-Champaign. Additional details about the meeting and short course are given in inserts to this . issue of Rheology Bulletin. RHEOLOGY BULLETIN Rakesh K. Gupta, Editor Department of Chemical Engineering West Virginia University P.O. Box 6102 Morgantown, WV 26506 (304) 293-2111 Ext. 2427 Fax: (304) 293-4139 E-mail: Rakesh.Gupta@mail.wvu.edu

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### 2002 BINGHAM MEDAL GOES TO RON LARSON

The extraordinary ability of Ronald G. Larson was recognized early on by his undergraduate mentors at the University of Minnesota. Contrary to normal departmental practice, they retained Ron at Minnesota for all three of his degrees, BS in 1975, MS in 1977, and Ph.D. in 1980. Upon graduation, he assumed a position at the Bell Laboratories, and, in time, became a Distinguished Member of the Technical Staff. After a remarkably productive period there, he left in 1996 to join the faculty of the University of Michigan and in 2000 became the Granger Brown Professor and Head of the Department of Chemical Engineering.

At a relatively early age, Ron has become one of the world's preeminent authorities across a broad range of rheology subspecialties. Throughout his career, he has been a careful and prolific author, contributing to both the research and educational literature of the field. Inspection of his publication list demonstrates convincingly that he has advanced in central ways most of the important branches of current rheological research, a remarkable accomplishment for one whose Ph.D. thesis only twenty-plus years ago dealt with flow through porous media.



Professor Ron Larson

Ron is a "Renaissance Man" of rheology, excelling in molecular and continuum theory, molecular simulation, and experiment. Consider, for example, three of the many areas with which he is identified:

Constitutive Theories This is an area that established his reputation as a heavyweight in rheology. This is all the more remarkable since, as most know, the field is notoriously "messy" and very difficult to comprehend in a unified way. That is precisely what Ron did. Throughout his research in the mid-80s on distributions of relaxation times and the influence thereof on constitutive behavior, he revealed a relationship between molecular and continuum approaches that was not previously appreciated. This culminated in his book, Constitutive Equations for Polymer Melts and Solutions (Butterworths, 1988). Many veteran rheologists have learned much from this important book. His contributions to constitutive theory continued to the present. A recent example is his work with Mead and Doi (1998-present) on constraintrelease theories. These results permit one to apply the Doi-Edwards theory to highly nonlinear flows, an extremely important generalization. Likewise, his work with McLeish (1996-present) has explained extensional hardening and shear thinning for classes of branched polymers. Their 1997 theoretical paper won a Journal of Rheology Publication Award and has had a major impact.

Liquid Crystal Polymers Ron's emergence as an authority in this area is the result of his presence in the stimulating surroundings of Bell Laboratories in the 1980s and early 90s. The essence of his work has been to elucidate microstructure in LCPs due to flow. In particular, his studies of arrested tumbling during shear (1990) and the importance of "textured domains" (1991) with Doi are the basis for much of the present state of knowledge of the dependence of LCP structure on imposed flow fields. Here his work also continues, as evidenced by his 1999 paper with Huang and Magda in *Journal of Rheology*.

Individual Molecule Behavior Ron's recent collaborations with Chu and others on observations of DNA molecules in shearing fields has, along with related studies by others, been nothing short of astounding. Thanks to these multidisciplinary endeavors, we can now see what macromolecules do in welldefined flow fields. Larson and his coworkers reveal to us the unraveling dynamics in shear and extensional flow that give rise to the macroscopic effects we wish to explain. A key paper in this series is a 1995 publication in *Science* with Perkins, Smith, and Chu. His 1999 paper on molecular stretching in dilute DNA solutions with Chu's group, in which Ron did the molecular simulation, was put forward by members of the Publication Award Committee for the 2000 Award, only to be disqualified when Ron was appointed to the Committee. His list of achievements includes other "firsts" as well, such as his discovery (together with Muller and Shaqfeh) of a new viscoelastic instability in Taylor-Couette flow. Suffice it to say that there is hardly any aspect of the rheology of complex liquids that Ron has not addressed during the past two decades, with important contributions as the result. His recent book, *The Structure and Rheology of Complex Fluids* (Oxford, 1999), should become at least as influential as his earlier one. Thus one has to wonder if anyone has had greater impact across the spectrum of rheology during the past three or four decades.

In addition to being prolific in research, Ron has been generous with his time and talent. He served effectively as president of the Society and has been an influential mentor to younger rheologists, including Eric Shaqfeh, Lynden Archer, Jaye Magda, David Mead, Susan Muller, Karen Winey, Saad Khan, and Faith Morrison. In short, he is not only deserving of the Bingham Medal for his research accomplishments, but he is the epitome of the type of person whom we want to represent rheology to the public.

### MINUTES OF THE EXECUTIVE COMMITTEE MEETING April 14, 2002

Bill Russel called the meeting to order at 8:45 a.m. in Room 2016 of the Hilton Chicago O'Hare Airport hotel. Committee members in attendance were Susan Muller, Lisa Mondy, Monty Shaw, Jeffrey Giacomin, Gerry Fuller, Mort Denn, Bill Russel, and Bob Powell. Invited guests were Andy Kraynik, Chris Macosko, Janis Bennett and Faith Morrison. The minutes of the previous meeting were read and approved, amending the dates for the Lubbock meeting to February 13-17, 2005.

Faith Morrison reports that as of March 2002 we have 1535 members (1267 regular, and 195 student, 38 retired, 12 of record and 23 Society of Physics Students (High School)). We expect to exceed our end of 2001 total of 1703.

Mort Denn, Editor, reported that the Journal of Rheology is healthy. Articles over the period April 12, 2001 – April 11, 2002: 120 submitted, 40 accepted, 38 rejected and 42 pending. Mean time for acceptance: 152, mean time for rejections 43.

Treasurer, Monty Shaw, presented a statement for the Bethesda meeting including a \$12,000 profit for the Society. A motion passed unanimously to congratulate Carl Schultheisz and his committee for their complete success, accomplished under unimaginably challenging circumstances. Shaw then presented the Statement of Revenues and Expenses for The Society of Rheology and for its Journal of Rheology. The financial position of the Society is sound. The Executive Committee passed a motion to accept these reports. A motion was passed to change the Student Travel Grant category of allowable expenses from "public transportation" to accommodation in the meeting hotel for up to 3 nights. Susan Muller, for Education Committee Chair Norm Wagner, reported on the Education Committee. The Minneapolis short course "Microfluidics and Microrheometry" is expected to be successful. The Bethesda short course on "Polymer Melt Shear Rheology and Molecular Structural Applications" attracted 11 students and was profitable. Short courses on Food Rheology, Biorheology, Interfacial Rheology and other subjects are being considered for upcoming meetings. Prospective participants should contact Norm Wagner with suggestions.

Giacomin, Editor for Business, reported that as of April 12, 2002 library subscriptions are down to 367 (2002 year to date) from 377 (2001) and from 401 (2000). This is our slightest percentage decline in institutional subscriptions in over a decade, with still eight months more to work on new sales and subscription recovery.

Andy Kraynik, Chair, Ad-Hoc Committee on the ICR 2008, reported on plans for the 2008 International Congress on Rheology. By the new ICR rules, this meeting must take place in North America. Andy Kraynik presented a bid on Bob Armstrong's behalf to host the meeting in Boston, Gerry Fuller presented a proposal to host the meeting in Monterey or San Francisco. Jeffrey Giacomin discussed the proposal that he is developing for a Madison meeting.

Chris Macosko, for Timothy Lodge, Program Chair, presented the technical program plans for the Minnesota meeting. Chris Macosko, Chair of Local Arrangements, reported on the meeting to be held in the Radisson Hotel Metrodome (surrounded by the University of Minnesota Campus), 615 Washington Ave. SE, Minneapolis, Minnesota (October 13-17, 2002). Everything is shaping up nicely.

On behalf of Savvas Hatzikiriakos, Gerry Fuller led a discussion about having the October 16-20, 2005 meeting of The Society of Rheology in Vancouver, Canada. The Executive Committee unanimously approved this proposal.

Susan Muller proposed guidelines and policy for preparing proposals to host Annual Meetings of the Society. Historical data on meeting attendance and budgets will be made available at www.rheology.org.

The meeting was adjourned at 4:53 p.m. In the subsequent Executive Session, the Bingham Award Committee recommendation to award the Bingham Medal to Ronald Larson was approved unanimously. The Executive Session was adjourned at 5:12 p.m.

### **CHANGE OF ADDRESS**

If you are moving, please inform Janis Bennett by phone at (516) 576-2403 or by fax at (516) 576-2223. You may also write to her at:

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**BOHLIN INSTRUMENTS** 

### **RHEOLOGY OF SILICATE GLASSES**

#### Jesper deClaville Christiansen\* and Aleksey D. Drozdov

Center for Nanotechnology, Aalborg University Fibigerstraede 16, DK-9220 Aalborg East, Denmark \*E-mail: i9ictus@iprod.auc.dk

Silicate glasses show a very intricate rheological behavior, where the complex mechanical response is strongly affected by structural relaxation. This paper is concerned with modeling the viscoelastic behavior of silicates together with the evolution of their structural state. Conventional phenomenological equations for structural recovery (Adam-Gibbs, Tool-Narayanaswamy, etc.) are discussed, and some unresolved problems are formulated.

### Introduction

Rheology was a key parameter in the birth of our planet where geological silicates were melted and solidified in a process that is still ongoing today. The importance of this field to mankind is evident from phenomena such as explosive volcanism and earthquakes. It is estimated that about a billion people live under the shadow of active geological processes. The field of rheology of silicates is also of great importance for industrial applications ranging from production of rock wool and glasses for automobiles, windows and bottles to applications of vitreous silica in wave-guides and semiconductor wafers. A number of excellent studies have been conducted in this field in the past two decades. However, the interaction between the specialists in rheology and those in the fields of geology, chemistry and physics of silicates has been rather weak. In the present work, we focus on the inclusion of structural parameters into constitutive models, because viscosity and elastic moduli of silicates depend not only on temperature and pressure, but also of the structural state of the material.

### Silicates

This paper is concerned with the rheology of silicates in the melt state, the state of supercooled liquid, and the glassy state. Most features of the melt are preserved in all the three states, in spite of significant differences in their physical properties. The structure of silicates is rather complex, and it strongly depends on the chemical composition: natural melts contain a number of different oxides that noticeably affect their response. For example, the mechanical behavior of a viscous silica-rich "granitic" melt differs substantially from that of a "basaltic" melt which is silica poor.

### Structural relaxation

The term "structural relaxation" (and its synonyms, structural recovery and physical aging) is conventionally employed to describe slow changes in the internal structure of a glass with time [1,2]. Here, the adjective "slow" means that the rate of structure alteration is smaller than the characteristic rates of other time-dependent phenomena (such as the viscoelastic response observed in creep and relaxation tests, the viscoplastic effects revealed in tensile tests with various strain rates, the mass-transport rates measured in diffusion tests, and so on.).

It is presumed that above the glass transition temperature, the internal structure of a supercooled liquid changes so rapidly with temperature that the equilibrium state of a material is reached practically immediately (within the experimental time-scale). This means that a supercooled liquid may be treated as an equilibrated medium at any instant.

Below the glass transition temperature, the rate of change of the internal structure decreases severely, which implies that the time necessary for reaching an equilibrium state after a step change in temperature noticeably exceeds the time-scale of standard tests. Structural recovery is conventionally thought of as development of the internal structure of a glass with time driven by changes in temperature or pressure.

An excellent review on structural relaxation in silicates is provided by Stebbins et al. [3] where a number of complex phenomena are described. Previous work on silicate rheology focused mainly on characterizing systems in thermal equilibrium and extrapolating the effect of temperature on moduli and viscosities by means of the Arrhenius or WLF equation. The mechanical relaxation is traditionally represented using Maxwell models with a single relaxation time or a series of relaxation times. By analogy with this approach, structural relaxation (evolution of the internal structure to a new equilibrium state driven by a step change in temperature, pressure or chemical composition) is described by the function

$$\phi(t) = \exp\left(-\frac{t}{\tau}\right) \tag{1}$$

where  $\tau$  is a structural relaxation rime. At small departures from equilibrium, the temperature dependence of  $\tau$  is approximated by an Arrhenius relationship

$$\tau = \tau_0 \exp\left(\frac{\Delta H^*}{RT}\right) \tag{2}$$

where  $\tau_0$  is a constant,  $\Delta H^*$  is the activation enthalpy, R is the gas constant and T is the absolute temperature. As Equation (2) is not very good at quantitatively describing observations in a one-step thermal test, more sophisticated

phenomenological equations are often used. According to the Tool concept [4], the relaxation process depends not only upon the current temperature, but also on a fictive temperature,  $T_f$ , that characterizes the internal structure of a silicate.  $T_f$  is conventionally thought of as a temperature at which the current internal structure of a glass is in equilibrium. As the current state of an amorphous material depends on the history of its treatment, the fictive temperature is a function of the entire thermal pre-history. With reference to the Narayanaswamy [5] equation, we write

$$\tau = \tau_0 \exp\left(\frac{x\Delta H^*}{RT} + \frac{(1-x)\Delta H^*}{RT_f}\right) \qquad (3)$$

where the parameter x lies between 0 and 1. Another conventional model for structural relaxation is provided by the Adam-Gibbs equation [6],

$$\tau = \tau_0 \exp\left(\frac{B}{TS_c(T_f)}\right) \tag{4}$$

where B is a constant and  $S_c(T_f)$  is the configurational entropy. An important advantage of Eq. (4) is that the configurational entropy can be found experimentally, for example, from calorimetric experiments [7] and FTIR (Fourier transform infrared spectroscopy) measurements [8]. The configurational entropy is expressed in terms of the fictive temperature as:

$$S_{c}(T_{f}) = \Delta C_{p} \ln \left(\frac{T_{f}}{T_{k}}\right)$$
(5)

where  $\Delta C_p$  is the difference between the liquid and the glass heat capacities in regions close to  $T_g$  and  $T_k$  is the Kauzmann temperature (the temperature at which the configurational entropy vanishes in equilibrium). Several experimental studies have proven that Eq. (1) describes the isothermal relaxation rather poorly. To improve the quality of data fitting, a model with a distribution of relaxation times can be employed [9]

$$\phi(t) = \sum_{i} g_{i} \exp\left(-\int_{0}^{t} \frac{dt'}{\tau_{i}}\right)$$
(6)

where  $g_i$  are temperature-independent coefficients that satisfy the condition  $\Sigma g_i=1$ . Despite the advantage of Eq. (6) compared to Eq. (1) in the approximation of experimental data, the description of the micro-mechanisms corresponding to various relaxation times for structural relaxation in Eq. (6) still remains a challenge for researchers. For transient experiments, where temperature varies with time, the above equations can be used in combination with the Boltzmann superposition principle.

At  $T_g$  the viscosity for all glasses is in the range of  $10^{12}$  Pa s and the typical shear modulus is of order of 30 GPa. The characteristic time for mechanical relaxation is, consequently, around 100 s, and the structural relaxation time is of order of 200 s [6], while a significant part of structural changes occur after 400 s [1]. These estimates reveal that structural relaxation times are quite long compared to the time-scale of many industrial processes in the vicinity of  $T_g$ .

### Viscosity functions accounting for structural relaxation

To take into account structural changes in a rheological model, we combine Eqs. (4) and (5)

$$\eta = A_e \exp\left(\frac{B_e}{TS_c}\right) = A_e \exp\left(\frac{B_e}{T\Delta C_p \ln\left(\frac{T_f}{T_k}\right)}\right)$$
(7)

Here  $A_e$  is a pre-exponential coefficient and the constant  $B_e$  is proportional to the free energy. Eq. (7) was tested by several authors and was found to be acceptable for the analysis of Newtonian fluids. For a non-Newtonian flow, one can combine the Adam-Gibbs formula (4) with e.g. a Carreau type [11] model for shear viscosity to obtain

$$\eta = \eta_0^* \left( 1 + \lambda^2 \dot{\gamma}^2 \right)^{-N} \exp\left(\frac{B_e}{T \Delta C_p \ln\left(\frac{T_f}{T_k}\right)}\right) (8)$$

where  $\lambda$  is a characteristic time, and the viscosity plateau at high shear rates is neglected. Equation (8) is proposed here for the first time, and it has to be further evaluated in viscosity tests on non-Newtonian fluids.

#### Rheometry

High temperatures and very corrosive melts combined with large variations in viscosity (typically more than 10 decades from  $T_g$  to the temperatures above liquidus) make rheometry of stone a challenge. Due to crystallization of melts, viscosity can be directly measured above the liquidus temperature and in some limited range above Tg (for rapidly quenched melts) only, whereas in the interval between these temperatures it has to be extrapolated. Several methods exist for determining viscosities of silicate melts and glasses. In our laboratory, the concentric cylinder method is commonly used. Adopting the

DIN standard geometry for spindle heads, the crucible is chosen to provide a medium gap size

 $(0.5 < R_{spindel}/R_{crucible} < 0.99)$ . The spindle shaft is extended to reach out of an oven and is connected to a Paar-Physica MC1 rheometer. Both crucible and spindle are made of 80% Platinum and 20% Rhodium by weight. The oven can reach temperatures of over 1900 K. Some data obtained by this method are plotted in Figure 1. Other methods that have been used include capillary rheometry [12, 13] at temperatures above 1500 K in a graphite rheometer under inert gas. At lower temperatures near T<sub>g</sub>, available methods are ball indentation, biaxial compression and solid bar oscillatory rheometry. Fiber elongation is used to measure the response in tensile tests. The high-frequency behavior is analyzed by ultrasonic methods.

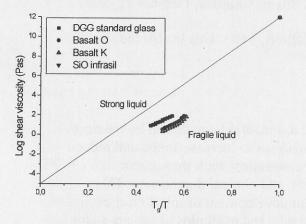


Figure 1. Viscosity versus the inverse normalized (with  $T_g$ ) temperature. DGG is a German standard glass (wt%: 71.7 SiO<sub>2</sub>, 1.2 Al<sub>2</sub>O<sub>3</sub>, 0.1 TiO<sub>2</sub>, 0.2 FeO, 6.7 CaO, 4.2 MgO, 15.0 Na<sub>2</sub>O, 0.4 K<sub>2</sub>O, 0.4 SO<sub>3</sub>), Basalt O (wt%: 49.3 SiO<sub>2</sub>, 15.6 Al<sub>2</sub>O<sub>3</sub>, 1.8 TiO<sub>2</sub>, 11.7 FeO, 10.4 CaO, 6.6 MgO, 3.9 Na<sub>2</sub>O, 0.7 K<sub>2</sub>O), Basalt K (wt%: 48,9 SiO<sub>2</sub>, 14.0 Al<sub>2</sub>O<sub>3</sub>, 2.0 TiO<sub>2</sub>, 11.9 FeO, 7.0 CaO, 10.0 MgO, 2.9 Na<sub>2</sub>O, 1.0 K<sub>2</sub>O, 0.6 P<sub>2</sub>O<sub>5</sub>). SiO<sub>2</sub> data are taken from [3]. Data in the entire temperature range should reach the same end point at 10<sup>12</sup> Pas at Tg/T=1. For all measurements T=T<sub>f</sub>.

The advantages of the plot in Figure 1 were first discussed by Angell, see also [14]. The straight line corresponds to a strong liquid (whose behavior follows the Arrhenius law), whereas curved lines reflect the response of fragile (non-Arrhenius) liquids. In terms of the Adam-Gibbs equation (7), a strong liquid has a small  $\Delta C_p$ , whereas a fragile liquid possesses a large  $\Delta C_p$ . Figure 2 presents experimental data in a torsional oscillatory test at 760 °C and their approximation by a model derived in [15]. Fair agreement is shown between the observations for the storage and loss moduli and the results of numerical simulation. The model treats a stone melt (glass) as an ensemble of relaxing units with various activation energies for rearrangement. The effect of thermal treatment is accounted for in terms of the fictive temperature.

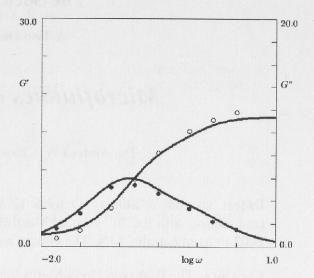


Figure 2. The storage modulus G' in GPa (unfilled circles) and the loss modulus G'' GPa (filled circles) versus frequency  $\omega$  rad/s. Symbols: experimental data. Solid lines: numerical simulation.

#### Structural relaxation, background and future

Three main approaches are conventionally employed to describe transformation of the internal structure of a glass. The first was proposed about half a century ago, see [2] and the references therein, and it is based on the introduction of a structural parameter (or several structural parameters) whose evolution reflects changes in the microstructure. Traditionally, the free volume (the difference between the total volume and the volume occupied by molecules) and the fictive temperature (the temperature at which the current microstructure would be in the equilibrium state) are used as structural variables. According to common practice, the kinetics of their development is described by phenomenological differential (the KAHR relation [16] for the free volume, the Tool formula [4] for fictive temperature) or integral (the Moynihan concept [9]) equations.

To reduce the number of material constants, first-order kinetics are conventionally postulated to derive differential models that are determined by only one parameter (the characteristic time for structural relaxation,  $\tau_s$ ). To account for the nonlinearity and the non-exponentiality of structural transformations,  $\tau_s$  is treated as a function of a structural variable or variables (as an example, we refer to the Narayanaswamy equation, Eq. (3), where an analog of the Arrhenius formula is applied to describe the effect of fictive temperature on  $\tau_s$ ).

The other approach is grounded in the energy-landscape concept [17]. The energy landscape is a hypersurface in the phase space that corresponds to a constant free energy of an

(Continued on Page 11)

### The Society of Rheology Presents A Two-Day Short Course on

### Microfluidics and Microrheology

By Dr. Andrea W. Chow and Professor Steve Granick

**Dates:** Saturday & Sunday, October 12 &13, 2002. The short course is held in conjunction with the 74<sup>th</sup> Annual Meeting of the Society of Rheology, October 13-17, 2002 in Minneapolis, MN. The course will begin at 8:30am, Saturday, October 12, 2002.

Location: The Radisson Hotel Metrodome, in Minneapolis, MN. This is also the site of the Annual Society of Rheology Meeting.

### **Course Description**

The development of microfluidics technology has mainly been driven by the need to miniaturize, integrate, and automate biochemical analyses to increase speed and reduce costs. Interesting applications include analytical instrumentation, high throughput screening of pharmaceutical targets, genomics analysis, and clinical diagnostics. This course will provide an overview of some of the current development of microfluidics, the science of interfacial rheology, microrheological methods, and examples of lab-on-a-chip applications. A laboratory demonstration of macromolecular sizing on-chip will also be performed.

### **Topics**

- Fluid control in microchannels
- Transport phenomena in microchips
- Dynamics of polymers and particulates in confined geometries
- Separation techniques in microchannels
- Microfabrication technologies
- Polymer-surface dynamics and interfacial rheology
- Instrumental methods for the study of polymer interfaces
- Microviscometers and microrheometers
- Lab-on-a-chip applications in life sciences

### About the instructors:

**Dr. Andrea W. Chow** is currently the Director of Microfluidics at Caliper Technologies Corp. in Mountain View, California, U.S.A. Since joining Caliper in 1997, she has been involved in microfluidics analysis, chip design, assay development, system integration, and product development activities for many lab-on-the-chip applications including high throughput screening

### MEETING INFORMATION The Society of Rheology 74th Annual Meeting October 13-17, 2002, Minneapolis, MN

**For more information:** Details about the meeting, associated short course, lodging, registration, and travel (and registration forms) can be found on the Society of Rheology website at http://www.rheology.org under Meeting announcements.

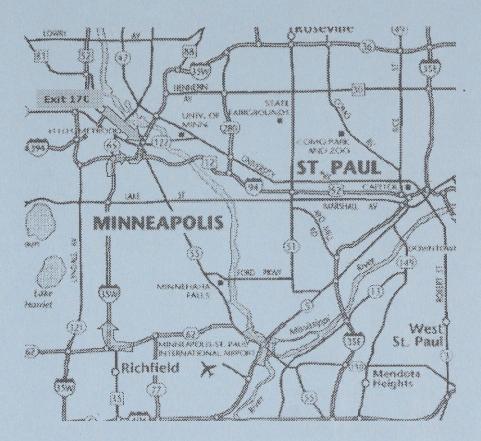
**Location:** The meeting will be held at the Radisson Hotel Metrodome on the campus of the University of Minnesota in Minneapolis. The Twin Cities of Minneapolis and St. Paul, situated near the confluence of the Minnesota and Mississippi rivers, offer a remarkable blend of readily accessible cultural, gastronomic, athletic, and shopping opportunities. Mid-October usually coincides with the peak of fall colors, and the many urban lakes and parks provide beautiful settings for walking, jogging, and biking.

**Transportation:** Direct flights to the Minneapolis-St Paul International Airport are conveniently available from most cities in North America. The airport is 30 minutes from the Radisson by car or taxi; two can travel by taxi (\$27-\$28) for about the same as by one-way shuttle. Parking is expensive on campus, and some would find a car to be an inconvenience.

**Short Course:** The short course held in conjunction with the meeting (Saturday and Sunday before the meeting, October 12 and 13) is on Microfluidics and Microrheology. The University Homecoming Game is also on Saturday. Be advised that you should book your hotel early!

**Social Program:** A welcoming reception will be held Sunday evening in the University Ballroom of the Radisson Hotel Metrodome. A Society Reception will be held Monday evening in the Frederick R. Weisman Art Museum, a stunning Frank Gehry edifice overlooking the Mississippi river and downtown Minneapolis and just three blocks from the hotel. Members are encouraged to attend the annual business meeting Tuesday evening, October 15. The Bingham Award reception will be held, after the business meeting, at 7 PM in the McNamara Alumni Center, immediately adjacent to the Radisson. The Bingham Award Banquet (tickets are extra) will begin at 8 PM. A reception in conjunction with the Poster Session will be held on Wednesday evening in the Humphrey Room of the Radisson Hotel Metrodome.

**Exhibits:** Vendors will demonstrate their products in the lobby outside the main meeting rooms, where the coffee breaks will be also be held.



### To the Radisson Hotel Metrodome...

*from north of campus:* go south on I-35W to exit 17C (U of M exit). Go east on Washington Ave SE across the Washington Ave bridge. The Radisson will be on your left after Harvard St (the third light after you cross the bridge).

*from south of campus:* go north on I-35W to exit 17C (U of M exit). Follow the East Bank signs. You will join Washington Ave, which takes you across the river to the East Bank. The Radisson will be on your left after Harvard St (the third light after you cross the bridge).

*from east or west:* get on I-94 going towards campus. Take the East Bank U of M exit. You will be on Huron Blvd; take Huron to Washington Ave SE and turn left. The Radisson is four blocks down on the right side of the street. (If you get to the river, you've gone too far.)

### Do you want to park?

If you are staying at the Radisson, parking is available behind the hotel for an extra fee. If you are not staying at the Hotel, parking is available in the Washington Ave ramp, across Harvard St from the hotel. *Warning! Parking is generally in short supply and you will pay accordingly.* 

### If you're coming from the MSP International Airport...

Take the Minneapolis exit going north on Hwy 5. Take Hwy 62 west to I-35W north. Follow I-35W north to the U of M East Bank exit, 17C. Continue east over the Washington Ave Bridge. The Radisson will be on your left after Harvard St (the third light after you cross the bridge).

for pharmaceutical targets, research instrumentation applications, genomics analysis, and diagnostics. Her research group is responsible for designing and developing new microchips for the Caliper LabChip® platform products. She has published over 30 referred papers in technical journals and has been a co-inventor in over 10 patents/patent applications. She has also been invited to speak at numerous conferences and seminars on microfluidics, and co-chaired several symposia on microfluidics and electrokinetics. She is a member of the American Institute of Chemical Engineers, the American Chemical Society, the American Association for the Advancement of Science, and the Society of Rheology. She is an editorial board member for the Lab-on-a-Chip Journal. Prior to joining Caliper, Andrea Chow received her B.S. degree in Chemical Engineering from the University of Southern California in 1980, and M.S. and Ph.D. degrees in Chemical Engineering from Stanford University in 1981 and 1984, respectively. After a year of postdoctoral study at the University of Bristol at the U.K., she joined SRI International (formerly Stanford Research Institute), and in 1989, accepted a position at the Lockheed Palo Alto Research Laboratories.

Prof. Steve Granick is currently Founder Professor of Materials Science and Engineering, as well as Professor of Chemistry, Physics, and Chemical Engineering at the University of Illinois at Urbana-Champaign. Professor Granick received his B.A. cum laude from Princeton University in 1978 and his Ph.D. from the University of Wisconsin-Madison in 1982. He joined the faculty of the University of Illinois in 1985 following postdoctoral research at the Collège de France with P.-G. de Gennes and at the University of Minnesota with Matthew Tirrell. His honors include: Beckman Research Board Award, 1985; election to ASME Research Committee on Tribology, 1989; Fellow in the Center for Advanced Study of UIUC, 1990; Fellow, American Physical Society, 1992; Senior Xerox Award, UIUC, 1993; NSF Award for Special Creativity, 1993; Sabbatical Professor, Kyoto University, Japan, 1994; University Scholar, UIUC, 1997; plenary lecture, Society of Rheology, 1998; named as Founder Professor of Engineering, 1999; Chair Paris-Sciences, 2001. He has authored or co-authored over 140 refereed publications and has served on numerous editorial boards. His research interests are in the areas of polymers, complex fluids, and biomaterials. He is especially interested in structured liquids at surfaces; with focus on the nanodynamics of confined liquid films. He has devised a new device, a molecular tribometer, to measure dynamical responses over a wide range of excitation frequency and shear rate.

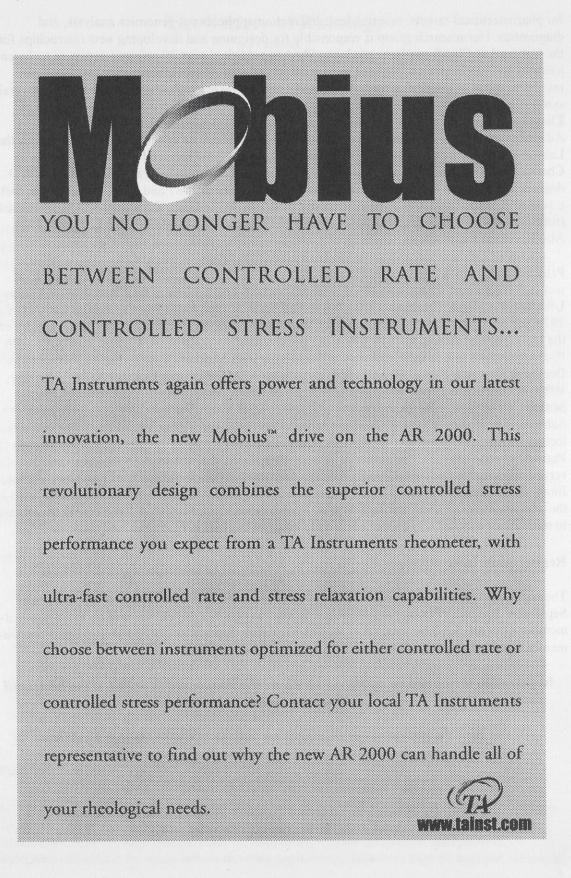
### **Registration Information:**

The registration fee for the two-day course is \$450 for members who registered not later than September 20, 2002. For members registering after September 20, the fee will be \$550. Student-member rates are \$250 by September 20 and \$325 after September 20. Registration fees for non-members are listed on the short course registration form.

## Registration forms and complete registration information are available at the Society of Rheology website, at:

http://www.rheology.org/sor/short\_course/2002Oct/default.htm

Questions can be directed to Professor Norman Wagner, *chair of the education committee*, at Wagner@che.udel.edu.



### **RHEOLOGY OF SILICATE GLASSES (CONTINUED)**

amorphous medium. It is presumed that this surface has a relatively simple shape when the temperature, T, exceeds the glass transition temperature Tg (which means that the surface possesses only a few points of minima), whereas below T<sub>g</sub>, the topological structure of the hypersurface becomes more and more complicated when temperature drops [18]. Given a temperature,  $T < T_g$ , the energy landscape is treated as a surface with a large number of minima (potential wells) separated by barriers. The points of local minima are gathered into groups (that correspond to the same valley), while valleys, in turn, are assumed to be separated by barriers with larger heights (compared to the energy of thermal fluctuations). Structural evolution of a glass is treated as motion of a point (its position characterizes the current state of the internal structure) that hops from one potential well to another over barriers (searching for a global minimum corresponding to the equilibrium state), as well as from one valley to another (this motion becomes available when the point reaches a saddle point that separates two contiguous valleys). Hops over barriers are assumed to be driven by thermal excitations and are described by the theory of thermally activated processes. Transition from one valley to another is attributed either to reaching a saddle point between the existing valleys, or to changes in the shape of a hypersurface. The latter transformations are associated with a dependence of the energy landscape on the current state of a glass, which implies that new valleys arise (become available for the travelling point) when it reaches some local minima. The current state of the energy landscape is determined by a configurational entropy that is associated with the number of local minima (inherent structures) available for a glass in a non-equilibrium state. The topology of an energy landscape has been adequately described only in the past several years [19], whereas the dynamics of motion along the free-energy hypersurface have not vet been unambiguously determined. A convenient approach was proposed by Bouchaud [20], who treated a glass as a set of points located in potential wells with various depths and described the hopping process by a distribution function for occupied wells. The evolution of the distribution function is attributed to jumps to new potential wells, when the points reach some reference level in their hops.

According to the third approach, the glass transition temperature is associated with changes in the time-dependent behavior of some basic elements from which a glass is composed. It is assumed that the response of these basic elements (whose physical meaning is determined by the chemical composition of a glass) is not affected by their interactions above the glass transition temperature. Below  $T_g$ , these elements are organized into flow units: cooperatively rearranging regions (CRR) which relax when all elements in a group change their positions with respect to each other simultaneously [6]. Cooperative organization of the basic elements (a few tetrahedra in silicate glasses or several nearby strands in polymer glasses) is induced by a severe reduction (with a decrease in temperature) in the volume available for rearrangement.

Two scenarios were suggested for the non-Debye structural relaxation in glasses (that presume organization of flow units in parallel and in sequence). According to the first picture [21], elements with small activation energies relax first preparing a necessary place for rearrangement of elements with higher activation energies. Then, elements with higher potential energies are rearranged, providing new opportunities for the small-energy elements (opening new valleys on the energy landscape for these elements). These multi-step processes (where more and more elements rearrange in sequence) are repeated until an equilibrium state is reached. The other scheme is based on rearrangement of cooperative regions in parallel [22] (which presumes that various regions are characterized by various activation energies, and the higher the activation energy is, the longer a region waits for a rearrangement event). Rearrangement of a CRR does not necessary result in its equilibration (which means that the equilibrium state of a region is reached by an infinite sequence of rearrangement events only). The current state of a CRR is characterized by its configurational entropy that is thought of as a measure of irregularity in mutual positions of basic elements in a group. The higher is this irregularity, the smaller is the activation energy necessary for rearrangement, and the larger the rate of structural recovery is. A simple and convenient formula that accounts for these correlations is provided by the Adam-Gibbs equation.

It is natural to assume that these three different approaches to the description of evolution of the microstructure of a glass should be mutually dependent. Some correlations between them may be easily established by using phenomenological relations. For example, assuming the configurational entropy,  $S_c$ , to be expressed in terms of the fictive temperature,  $T_f$ , by means of a conventional formula that connects entropy and temperature, see Eq. (5), a relation may be developed between the phenomenological approach and the concept of cooperative relaxation. In another example, the configurational entropy of an ensemble (that characterizes topology of an energy landscape) is assumed to coincide with the configurational entropy of a cooperative region. Despite the convenience of these assumptions for applied research, their physical basis is rather questionable, and their justification requires a serious revision of the fundamental concepts.

This brief survey of constitutive models for structural relaxation in glasses leads to several questions that remain to be answered even at the present stage of our knowledge:

1. Our experimental data [23] reveal striking similarity between changes in the configurational entropy (that characterizes an ensemble of relaxing domains with various activation energies) and changes in relaxation times (found by fitting observations in mechanical tests) for several amorphous and semicrystalline materials. It was also found that the graphs of the mechanical relaxation time versus temperature (recalculated using data in rheological tests on equilibrated silicate melts) and of the structural relaxation time versus fictive temperature (obtained from DSC measurements on silicate glasses) plotted on a semi-log scale coincide after their shift along the time-axis. These findings lead to a hypothesis that the short-term response of a glass (measured when its internal structure remains unchanged) and the long-term behavior (observed as structural recovery of a glass) are governed by the same physical mechanism at the micro-level. What the nature of this mechanism is, and in which way experimental data in short-terms tests may be used to predict structural relaxation remain unclear.

- Within the energy-landscape concept (where the 2. configurational entropy is treated as a measure of distribution of cooperatively relaxing units with various activation energies), changes in the ensemble of CRRs driven by mechanical factors should result in alteration of the average rate of structural recovery. Some attempts have been undertaken in the past decade to observe slowing down of structural relaxation (rejuvenation of a glass) induced by loading [24]. Unfortunately, the experimental data on polymeric glasses do not provide an unambiguous answer to whether the equilibration process decelerates. Silicate glasses, where structural recovery occurs in a larger interval of temperatures compared to polymeric glasses, provide excellent opportunity to check the applicability of the energy-landscape theory.
- There are no doubts that the configurational entropy 3. (irrespectively, whether it is defined in terms of the energy-landscape theory or within the concept of . cooperative rearrangement) reflects the evolution of the internal structure of a glass. However, the kinetics of changes in the configurational entropy should noticeably differ for these two approaches. As the configurational entropy in the Adam-Gibbs theory cannot be calculated ab initio, the only way to predict its evolution with time is based on the phenomenological equation (5) and an appropriate (Tool-like) kinetic equation for the fictive temperature. The energy-landscape concept together with physically transparent hypotheses regarding transformations of the free-energy hypersurface ensures additional opportunities that lead to new classes of governing equations. For example, assuming that transformation of the micro-structure is governed by the fragmentation-aggregation mechanism [25, 26] (which means that several CRRs with small activation energies can aggregate to form a region with higher activation energy and a CRR with a large potential energy can be broken into several smaller parts being exited by thermal fluctuations), one can describe in a unified fashion such interesting phenomena as over-shooting of DSC traces on

aged samples and a non-monotonic dependence of elastic moduli and strength of silicate glasses on time and temperature of annealing. We believe that development of constitutive equations for the evolution of the energy landscape (based on this or similar scenarios) and their experimental validation is a challenging task to be performed in the coming years.

### Acknowledgements

We acknowledge the contributions of our research group and Rockwool International A/S, especially Dr. S. Lund Jensen.

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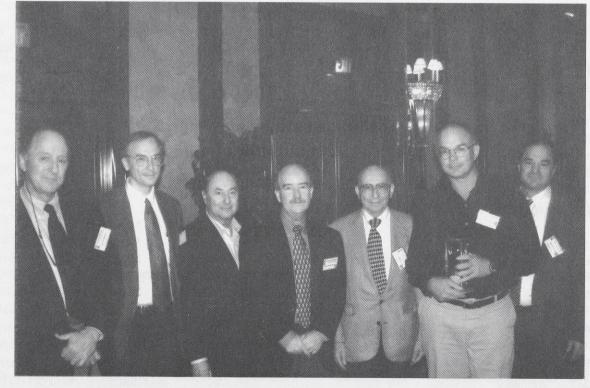
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### FUTURE MEETINGS OF THE SOCIETY

75<sup>th</sup> Annual Meeting Pittsburgh, Pennsylvania October 12-16, 2003

76<sup>th</sup> Annual Meeting Lubbock, Texas February 13-17, 2005

77<sup>th</sup> Annual Meeting Vancouver, BC, Canada October 16-20, 2005



Andy Kraynik receives the Distinguished Service Award in Bethesda (see write up in the January 2002 Bulletin).

### To the Membership:

The documents below describe the financial state of the Society of Rheology at the end of 2001. Also included is a tentative 2003 budget, which the Membership will be asked to approve at the Annual Meeting in October. Note that the Journal of Rheology, the Society's biggest operation, is likely to operate at a loss--possibly a substantial loss--depending upon the number of pages that are published and the ad income. Although the rate of fall of institutional subscriptions appears to have decreased, we have ever increasing costs. In particular, electronic publishing costs are expected to rise, with little hope of any offsetting income except through increased subscription rates, a risky option.

As for the overall report for 2001, please note that the interest income we have enjoyed in the past is decreasing due to absurdly low interest rates. We are, of course, looking into possibilities for prudently increasing this income. Note that the several expense categories are being changed on this sheet, for example, both the Annual Meeting and Short Course will be reported only as net income. The Bethesda meeting and Short Course netted about \$15,000, which will appear on the 2002 actual.

While the Assets of the Society remain at a high level, we face increasing uncertainties, especially with respect to liabilities for imperative cancellation of meetings. In addition to doubling our meeting reserve to \$70000, we are pursuing a lead on insurance against this type of unfortunate event.

Respectfully submitted,

Montgomery Shaw, Treasurer

	(All amou	nts: USD)				
	2003 Budget	2002 Budget	2001 Actual	2001 Budget	2000 Actual	2000 Budget
RECEIPTS						
Subscriptions	190,850	195,250	211,351	211,750	194,536	186,000
Reprint Sales	6,500	7,000	6,514	7,400	6,709	7,800
Ad Sales	35,000	25,000	32,537	21,000	28,135	18,000
JORO revenue	4,300	4,300	2,922	200	141	0
Miscellaneous	500	1,500	615	2,350	288	1,900
TOTAL RECEIPTS	237,150	233,050	253,938	242,700	232,343	213,700
DISBURSEMENTS						
Ads	9,000	9,000	8,459	10,400	12,146	8,500
Reprints, Single Copy	5,000	9,000	6,656	12,700	11,596	9,000
Paper, Printing	36,000	36,000	37,288	39,000	31,659	42,000
SOR Editorial	45,000	45,000	49,395	45,000	38,297	49,000
Production	78,400	78,400	74,088	78,400	73,251	79,000
Fulfillment	8,300	6,700	7,507	7,950	7,673	7,900
Distribution	20,500	27,000	19,759	21,800	14,847	22,000
Electronic publishing	44,000	42,500	40,943	39,100	47,615	24,500
Miscellaneous	4,000	2,900	4,944	0	0	0
TOTAL DISBURSEMENTS	250,200	256,500	249,039	254,350	237,084	241,900
Net	-13,250	-23,450	4,900	-11,650	-4,741	-28,200

### Journal of Rheology, Year-End Summary

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### The Society of Rheology Statement of Receipts and Disbursements December 2001

	Budget	Budget	Actual	Budget	Actual	Budget
RECEIPTO	2003	2002	2001	2001	2000	2000
RECEIPTS	00.000	~~~~~	50 400	~~ ~~~	05 000	
Dues	60,000	68,000	58,163	68,000	65,089	61,000
Interest	16,000	32,000	34,438	41,000	54,673	38,000
Journal of Rheology	237,150	233,050	270,072	242,700	229,405	213,700
Mailing List Sales	500	500	1,101	300	584	300
Donations	0	0	0			
Bulletin Advertising	2,500	2,500	2,448	2,800	3188	850
Annual Meeting (net)	0	0	460	0	17,165	0
Short Course (net)	0	0	-900	4,000	4,005	4,000
TOTAL RECEIPTS	316,150	336,050	365,782	358,800	374,109	317,850
DISBURSEMENTS						
AIP Dues Bill & Collect.	6,000	8,500	5,660	9,800	8,097	9,000
AIP Adm. Services	9,500	9,500	9,144	9,000	9,000	9,000
AIP Mem. Soc. Dues	7,500	7,500	7,431	8,200	7,272	7,800
AIP Phys. Olympiad	- asis	1,500	1,500	1,500	1,500	1,500
Misc. Contributions & Prizes		1,000	1,512	1,000	0	1,000
Contributions and Prizes	3,000					
Renewal Billing	3,000	4,500		5,200	3,229	5,000
Journal of Rheology	250,400	256,500	256,386	258,000	239,070	241,900
Bulletins and Abstracts	7,000	7,000	18,880	12,000	6,777	13,000
Short Courses	0	0	0	0	0	3,000
Bingham Award	7,500	5,500	2,540	11,000	126	6,000
Executive Cmt. Meetings	7,500	7,500	2,979	7,900	11,830	7,500
Pres. Discretionary Fund	1,500	1,500	0	1,500	1,500	1,500
Treas. Discr. Fund	1,500	1,500	176	1,500	303	1,500
Progr. Chm. Discr. Fund	2,000	2,000	1,000	4,000	0	2,000
Secretarial Services		500		500	0	1,000
Mailing		1,000		4,000	357	4,000
Office Expense, misc		200		1,500	227	2,000
Office Expense	500		560			
Banking Services	100	200	88	250	61	250
Liability Insurance	4,000	3,500	3,656	3,500	3,407	1903
Membership Broch. & Appl.	200	200	0	0	234	1500
Accountant	2,200	1,900	1,900	1,900	1,560	1,800
Student member travel	5,000	4,000	8,404	9,000	0	7,000
Annual meetings, future	3,000	3,000	2,665	3,000	0	3,000
Website	1,000	-,	126	-,		0,000
Miscellaneous	1,500	1,500	700	1,500	2,239	2,500
TOTAL DISBURSEMENTS	323,900	330,000	325,307	355,750	296,789	334,653
Net	-7,750	6,050	40,474	3,050	77,320	-16,803

# The Society of Rheology, Inc. Year-End Balance Sheet

(all amounts: USD)

	2001	2000	1999
Assets			
Cash in checking account	9,374	9,400	10,735
CD's	0	15,000	0
Balance in AIP account	843,151	827,040	766,911
Total Assets	852,525	851,440	777,646
Liabilities and Net Assets			
Liabilities			
Deferred subscription revenue	96,465	138,500	141,827
Deferred member dues	41,003	43,300	41,376
Total Liabilities	137,468	181,800	183,203
Net Assets			
Publication reserve	450,000	450,000	450,000
Student travel grant reserve	10,000	10,000	10,000
Annual Meeting reserve	70,000	35,000	35,000
Operating reserve	70,000	70,000	70,000
Unrestricted	115,057	104,640	29,443
Total Net Assets	715,057	669,640	594,443
Total liabilities and net assets	852,525	851,440	777,646