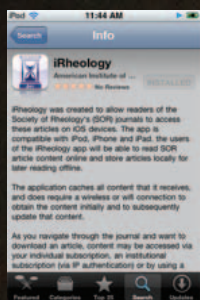


# Rheology Bulletin



**New *iRheology* App  
makes debut**



**Inside:**

Cleveland 2011  
ICR 2012 Lisbon  
Interfacial Rheology  
Notable Passing: Tschoegl

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### On the Cover:

The mascot of the Cleveland Indians baseball team is *Slider*, a big, pink, furry, . . . well, let's just say, animal-like mascot. And, he (she?) was the star of the Bingham Award Reception at Progressive Field in Cleveland in October 2011. The occasion was joyous, as captured in our cover photograph of Local Arrangements Chair Pat Mather with *Slider*.

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Bingham medalists in attendance in Cleveland included (back row) Chris Macosko, Greg McKenna, Gerry Fuller, John Brady, Henning Winter, Mort Denn, (front row) Bill Schowalter, Eric Shaqfeh, and Andy Acrivos.



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# Cleveland: SOR 2011

The 83<sup>rd</sup> Annual Meeting of The Society of Rheology was held 9-13 October 2011 at the Intercontinental Hotel Cleveland, Ohio USA. The meeting kicked off Sunday with an Industry/Faculty/Student Forum and Mixer on the topic *Rational Design with Soft Materials*. This event, the second of its type, was sponsored by the Society and the American Institute of Physics. Organized by Philip 'Bo' Hammer of AIP, Will Hartt of Procter & Gamble Company, and Suraj Deshmukh of the Dow Chemical Company, the forum featured a panel of scientists and engineers demonstrating successful applications of rheology in the commercial sector. The panelists were Marco Caggioni, of Procter & Gamble Co., Randy Ewoldt, of the University of Illinois, Randy Schunk of Sandia National Laboratories, Gareth McKinley of MIT, and Adam Burbidge of Nestlé Research Center. There was time for questions during and after the event as well as for social networking. The event was very popular, with the room completely full. The success of the Forum bodes well for the health of industrial rheology; members interested in becoming involved with future events focused on industrial rheology should contact the organizers.

The Industrial Forum led immediately to the Opening Reception of the meeting, sponsored by TA Instruments and held in the Founders Ballroom of the Intercontinental. As always this was a fabulous kick-off to the meeting, with delicious food and plenty of opportunities to catch up with colleagues, friends, and guests.

The technical sessions began promptly on Monday and continued through noon Thursdays. Plenary talks were offered by Juan de Pablo (University of Wisconsin, Madison), Bingham medalist Eric Shaqfeh (Stanford University), and David Pine (New York University). On Thursday morning, in a possibly new tradition, the winner of the Metzner Early Career Award, Richard Graham, was scheduled for a keynote talk. Coffee breaks were scheduled in and around the displays of the equipment exhibitors, allowing ample time for practical shopping.

Unusual for SOR meetings, the Society Business Meeting was held on Monday at noon with a box lunch provided. The atypical schedule was due to issues related to the Tuesday off-site banquet, but the

arrangement worked to produce a record turnout for the Society Business Meeting. President Faith Morrison and various ExCom members brought the members up-to-date on Society activities and accounts. At the end of the Business meeting Morrison handed



over the Society's gavel to incoming president Jeff Giacomini. In a surprise presentation, Gerry Fuller made note of Giacomini's enthusiasm for biking with rheology colleagues and to commemorate this activity presented Giacomini with an SOR-themed biking jersey.

The Monday evening Society Reception, sponsored by Malvern Instruments, was



2011 Bingham medalist Eric Shaqfeh with his wife, Terhilda Garrido. Below, Susan Muller makes her Banquet presentation honoring Shaqfeh.

held at the Cleveland Museum of Natural History, which gave participants a chance to see all that the museum had to offer. Planetarium shows were included, including a comically narrated star show.

On Tuesday, the Bingham Awards Reception was held at the Terrace Club Pub at Progressive Field, an event sponsored by Xpansion Instruments. The Terrace Club Pub has excellent views of the playing field, and during the reception a slide show of rheologists scrolled by on numerous video displays and, most prominently, on the 26 by 37 feet (7.9 by 11.2m) *Jumbotron*. Shortly after the guests arrived, another local host

(continues, page 7)

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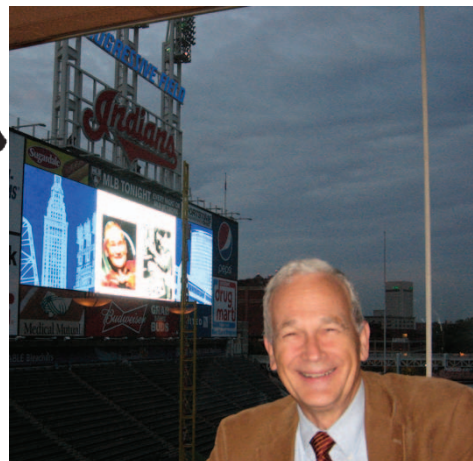
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showed up, *Slider*, the mascot of the home baseball team, the Cleveland Indians. *Slider* brought out the kid in Society members, sharing “high fives” and hugs with us and posing for pictures.



2004 Bingham medalist Chris Macosko shows up on the *Jumbotron* at Progressive field. Meeting host Pat Mather arranged for this once-in-a-lifetime experience. The slide show included photos of Bingham medalists and other prominent rheologists.



After the Awards Reception, the banquet attendees moved downstairs to the luxury box seats where the Bingham Banquet was held in perhaps the most unusual venue ever chosen. Dinner was served at tables for (mostly) four persons that were stepped downward so that all diners could have a view of the playing field. This meant that the awards ceremonies were hosted from a position near the top of the slanted facility, but attendees were able to see the presentations on numerous small monitors scattered throughout the facility.

The Banquet agenda included the awarding of the Publication Award and the Metzner Early Career Award (see accompanying photographs), and, of course, the highlight of the evening was the roasting of the 2011 Bingham Medalist, Eric Shaqfeh. The presenters for Shaqfeh’s event were Bamin Khomami and Susan Muller, who took turns getting laughs in Shaqfeh’s name. The newest Bingham medalist was good natured about the ribbing and was particularly magnanimous when reclaiming a missing pen Muller had “kidnapped” as part of the comedy.

The last social event of the meeting was the Poster Session Reception, sponsored by Anton Paar USA. Again the Society was treated to delicious food and beverages to accompany the technical discussions surrounding the poster papers. The Student/Postdoc Best Poster Competition was judged during this session, and Morrison presented prizes to the winners (see article and photos in the Society News section of this *Bulletin*).

The meetings of The Society of Rheology are an enjoyable opportunity to discuss science and to meet colleagues and old friends. An important component of the success of the meetings is the generous sponsorship of the rheological instrument manufacturers. The Society would like to once again thank all the sponsors and organizers of the 83<sup>rd</sup> Annual Meeting in Cleveland.



The 2011 *JOR* Publication Award went to Evelyne van Ruymbeke (FORTH; shown at right), E. B. Muliawan (University of British Columbia, Canada), Savvas G. Hatzikiriakos (University of British Columbia, Canada; shown at left), T. Watanabe (Tokyo Institute of Technology, Japan), A. Hirao (Tokyo Institute of Technology, Japan), and Dimitris Vlassopoulos (University of Crete, Greece; second from left) for their paper “Viscoelasticity and extensional rheology of model Cayley-tree polymers of different generations” *J. Rheol.* 54(3), 643-662 (2010). Second from right is John Brady, *JOR* Editor, 2005-2011, who presented the award.

## Cleveland Rocks!

### Sponsors:

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### Local Arrangements:

Pat Mather  
Andy Kraynik

### Technical Program:

Victor Breedveld  
Jonathan Rothstein



Richard Graham receives the Metzner Early Career Award from President Faith Morrison.



# Come to Lisbon!

Dear Fellow Rheologist,

The XVI<sup>th</sup> International Congress on Rheology will take place in Lisbon, Portugal from August 5 to August 10, 2012 ([www.rheology-esr.net/ICR2012](http://www.rheology-esr.net/ICR2012)). The ICR series of conferences is the premier event in the rheological community, convening only once every four years and brings together the world's leading rheologists to present the latest advances and developments in this field. The last ICR, held in Monterey, CA, USA, was the most successful ever, having attracted more than 1,000 participants. Although the deadline for submissions for oral presentations at the ICR 2012 is already passed (we had more than 500 submissions), there is still time to submit your poster presentations, since the deadline there is February 15.

The Congress will have eighteen symposia covering all the aspects of rheology and will take place in the Belém Cultural Center, which was inaugurated in 1992 and is a outstanding example of modern European architecture. It has a modern and well equipped Conference Center, one of Europe's last private modern art collections (in the Berardo Museum) and is primly located by the Tagus River, on the Lisbon riverfront next to several historical buildings and landmarks.

The list of plenary speakers is an illustrious one and includes top academic and industrial rheologists that, together with the more than 50 keynote presentations (each symposium will have between one and five keynote talks, depending on their size), are sure to bring to the participants a glimpse of the wide breadth and state-of-the-art of our science and will no doubt confirm its vitality.

Two short courses will also be offered on the weekend before the Congress, 3-4 August 2012, one on *Colloidal Suspension Rheology*, taught by Norman Wagner and Jan Mewis and based on their recent and acclaimed book, and one on *IRIS: Synergy of Rheological Data Analysis and Modeling*, with Henning Winter and Manfred Wagner, two of the top international rheologists, as instructors.

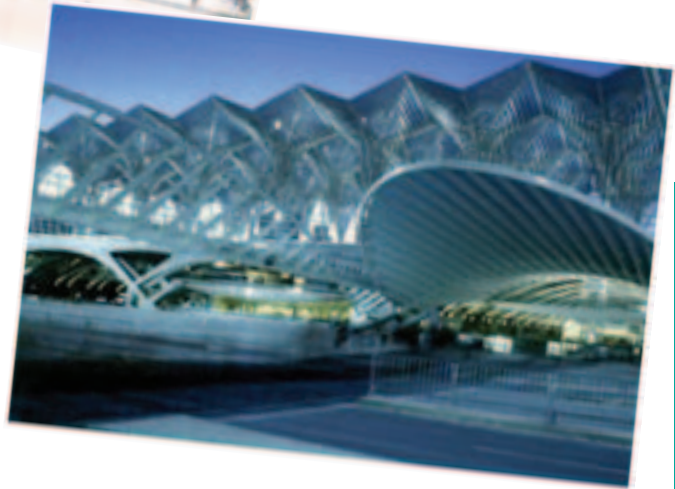


Portugal in general and Lisbon in particular, are very attractive tourist destinations, whilst being amongst the most affordable and easily reachable in Europe. In fact, Lisbon, which ranks seventh in the list of Europe's most popular weekend destinations in Europe, is a city with more than two millennia of History, starting with the Phoenicians, continuing with the Romans and the Moors and reaching its Golden Age during the

## General Symposia of ICR Lisbon:

- *Non-Newtonian Fluid Mechanics*
- *Constitutive and Computational Modeling*
- *Advanced Experimental Methods*
- *Materials Processing*
- *Interfacial Rheology, Micro-rheology & Microfluidics*
- *Colloids and Suspensions*
- *Emulsions and Foams*
- *Biopolymers, Biofluids and Foods*
- *Polymer Solutions, Melts and Blends*
- *Associative Polymers, Surfactants and Liquid Crystals*
- *Solids and Granular Materials*
- *Industrial Rheology*
- *Complex Flows*
- *General Rheology*
- *Professor Ken Walters Commemorative Symposium*
- *Non-Conventional Rate Effects in Materials*
- *Rheology of Bio-Pharmaceutical Systems*
- *Rheology of Nano- and Natural Composites*





Enjoy the delights of Lisbon, Portugal, from left to right: A typical electric tram; the *Estoril*, a seaside resort 20 minutes away from Lisbon; the beaches; Imperial Square (Praça do Império); and the Oriente train station (Estação do Oriente), a masterpiece of modern architecture built by master architect Santiago Calatrava with a roof of glass and steel.

discoveries period from the XV<sup>th</sup> to the XVII<sup>th</sup> centuries. This allows it to have a unique blend of flair, south European quality of life, cultural and historical offer and cost of living that are unmatched by any other major European cities.

In addition, Lisbon is set on the largest estuary in Europe and is 15 minutes away from one of its longest continuous stretches of white sandy beaches (more than 20 km), with the Algarve only a further two hours drive away. Alternatively, the north of Portugal, with the Port



João Maia,  
Local Organizer

Wine Route and its magnificent historical locations is a very interesting alternative for those looking for more culture-oriented vacations. With those facts in mind, we also have a number of pre- and post- conference packages organized that will allow participants to take full advantage of the experience of coming to Portugal, and we have prepared an active social program during the conference, so that this trip may also be an unforgettable family and social one.

As to the social program during the Congress, these will include Port Wine tasting sessions, eight different excursion possibilities, a Beach Party and a Banquet in one of Lisbon's trendiest restaurants.

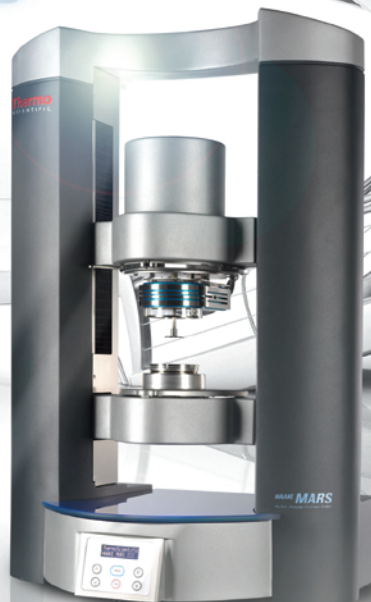
Lisbon, founded by the Phoenicians, styled by the Romans and the Moors, and enriched by the spice trade in the Golden Age of the discoveries invites you! Join us at the ICR Lisbon.

The Co-Chairs of ICR2012

João Maia  
Igor Emri  
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# Interfacial Rheology

Carlton F. Brooks  
Sandia National Laboratories  
Albuquerque, New Mexico, USA

Interfaces that arise from two immiscible fluids are commonplace in material processing applications. These interfaces can exhibit resistance to deformation, or interfacial rheology, and because of the high surface area in many applications, the observed bulk behavior can be a strong function of the interfacial rheology. Multiphase applications involving fluid-fluid interfaces are broad and include distillation, enhanced oil recovery, ore flotation, spraying and atomization, microemulsions, coating processes [1], polymeric foam processing [2], food and personal care products [3], as well as biomedical applications such as medical diagnostics [4] and lung surfactant therapy [5,6]. Interfacial rheology plays a role in numerous fundamental surface flow problems such as the stability of liquid threads [7], the drainage time of thin liquid films [8], the stability of liquid films on solid surfaces [9], as well as the rheology [10] and stability [11] of foams. Not only is interfacial rheology important in systems that have high surface area, but it becomes more significant at smaller and smaller length scales. To demonstrate the importance of length scales we can examine how the effective viscosity  $\langle\mu\rangle$  of a dilute emulsion is influenced by surface rheology when the flow is sufficiently weak to not distort the droplets from spherical shape (i.e. small Capillary number,  $Ca \ll 1$ ) [12, 13]

$$\frac{\langle\mu\rangle}{\mu_c} = 1 + \frac{1 + \frac{5}{2} \left[ \lambda + \frac{2}{5} \left( \frac{2\mu^s + 3\kappa^s}{\mu_c a} \right) \right]}{1 + \left[ \lambda + \frac{2}{5} \left( \frac{2\mu^s + 3\kappa^s}{\mu_c a} \right) \right]} \phi \quad (1)$$

where  $\phi$  is the volume fraction of the dispersed phase ( $\phi \ll 1$ ),  $a$  is the drop radius,  $\lambda \equiv \mu_d / \mu_c$  is the ratio of the viscosities of the dispersed ( $\mu_d$ ) and continuous ( $\mu_c$ ) phases,  $\kappa^s$  is the surface dilatational viscosity, and  $\mu^s$  is the surface shear viscosity. In the limit of drops with no interfacial rheology, this approaches the classic result  $\langle\mu\rangle/\mu_c = 1 + (1 + 2.5\lambda)/(1 + \lambda)\phi$ , as derived by G.I. Taylor [14]. Upon inspection of eqn. 1 we can see that the presence of surface rheology has the qualitative effect of making the droplets appear as being more rigid and the surface rheology becomes more important as the drop size is reduced.

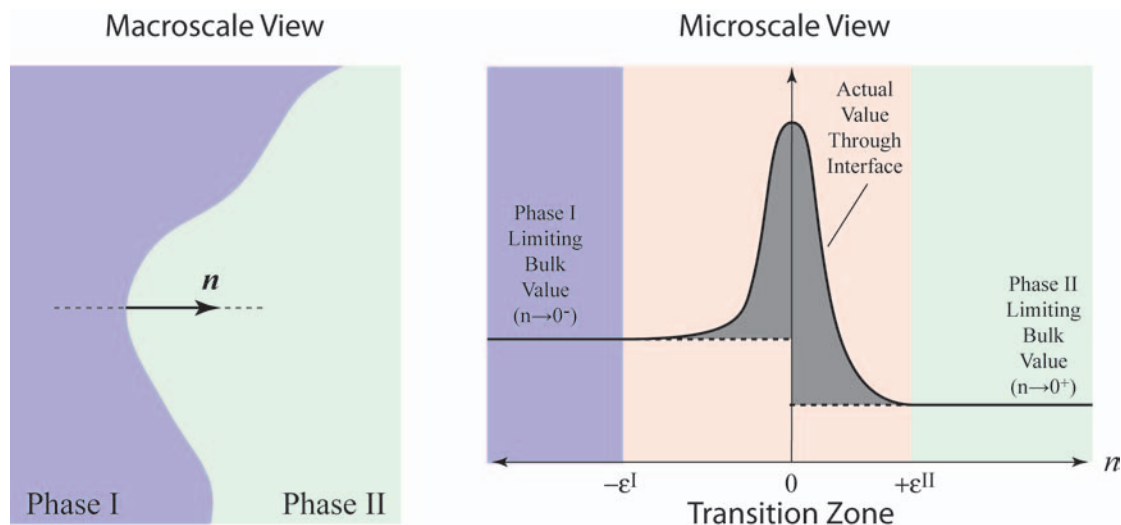
The numerous applications mentioned above along with the recent maturation and commercialization of different measurement techniques have created the conditions for growing interest in interfacial rheology. In this article several aspects of interfacial rheology are highlighted to give a conventional rheologist a better understanding of the concepts and challenges of working in the field. Starting from the basic concept of what an interface is, the article reviews different types of interfaces, presents the equations for momentum transport along with simple constitutive relations, and discusses some of the techniques used to measure interfacial rheology. In closing, some areas for future efforts are suggested to help advance the field.

## Fluid-Fluid Interfaces

To a macroscale observer, an interface appears as a 2D surface between two bulk phases. In reality, as one travels from one phase into the other, there is a rapid change in the material properties which occurs within a few molecular dimensions that a macroscale observer cannot resolve (see Figure 1). To avoid the large disparity of length scales and the need to resolve molecular level details, it is convenient to model the interface as a separate entity. In general, the true values of a property in the transition zone are different than its limiting value as the interface is approached from the adjacent bulk phases. The interface is assigned properties that quantify the difference from the adjacent bulk phases, which we call *surface excess* quantities [1,15,16,17]. If, for example, we are interested in the concentration of species  $i$  ( $c_i$ ), the surface excess concentration ( $\Gamma_i$ ) is the integral over the transition zone thickness of the difference between the true concentration profile and the limiting concentration profile [1].

$$\Gamma_i = \int_{-\varepsilon^I}^0 c_i^I(n) - c_i^I(0-) dn + \int_0^{\varepsilon^{II}} c_i^{II}(n) - c_i^{II}(0+) dn \quad (2)$$

where the superscripts indicate the phase,  $n$  is the coordinate in the direction normal to the interface with the dividing surface located at  $n=0$ ,  $\varepsilon^I$  and  $\varepsilon^{II}$  are the thickness of the transition zone in phases I and II, respectively, and  $c_i^I(0-)$  and  $c_i^{II}(0+)$  are the limiting values of the bulk concentration as the interface is approached. For this example we are using molar concentrations, so the surface excess concentration,  $\Gamma_i$ , has units of moles/area. In general we assign this excess property value to the interface, which has units of the property times length. It is important to note that the surface excess concentration is not the actual surface concentration, but merely represents the additional material located at the interface due the existence of the interface. Real concentration values can only be



**Figure 1:** Views of the interface region at different scales. On the left is an image of an interface between two phases at a macroscale level, where, for example, the concentration of surfactant jumps discontinuously on passing through the interface. On the right is how the concentration,  $c_p$ , actually changes on the microscale, showing the preferential segregation of surfactant to the interface as it changes continuously through the transition zone. The integral of the difference of the actual and bulk phase limiting values (area of the shaded region) is called the *surface excess concentration*,  $\Gamma_p$ , and is attributed to the interface. Note that the surface excess is not to be interpreted as the amount at the interface, but the extra amount in the interfacial region that cannot be accounted for by the bulk properties. Negative values of surface excess species are possible, for example, if the presence of the interface repels the species. Other intensive variables will have surface excess quantities as well. Surface tension is the extra energy introduced to the system due to interfaces that cannot be accounted for by the bulk volume, or the surface excess energy density. Intensive rheological parameters such as stress, viscosity, and elasticity also have surface excess values which we can assign to the interface.

non-negative. *Negative* values of the surface excess concentration (i.e. a surface deficit) are possible since material can be depleted from the interfacial region. The location of the dividing surface affects the surface excess values, and it is conventional to judiciously locate it where the surface excess concentration of one of the solvents (e.g. water, air, oil, etc.) is zero.

Another example of a scalar intensive quantity that changes going from one phase to the other is the energy per unit volume. The energy per unit volume can change rapidly passing through the interfacial zone due to the disliking of the molecules for the molecules in the opposing phase. The integral of the difference between the actual energy per unit volume and the limiting energy per unit volume gives the surface excess energy density, which we commonly refer to as surface tension,  $\sigma$ . In a more general sense, other intensive quantities can have surface excess values, and of interest to rheologists in particular, the stress tensor can rapidly change in the interfacial zone. The integral of the difference between the true stress tensor and limiting stress tensor is the surface excess stress tensor,  $\mathbf{P}^s$ .

### Types of Interfaces

One challenge working with interfaces is the diversity

of interfaces, each of which involves a rich variety of physical behavior depending on how the interface is created. Fig. 2 is an attempt (by no means exhaustive or rigid) to classify interfaces into surfactant and non-surfactant groups, along with some subcategories and examples. Generally, surfactants are a class of chemicals that are amphiphilic, containing regions that are hydrophilic (polar) and hydrophobic (nonpolar), and will readily adsorb to an air-water or water-oil interface. We characterize their ability to lower interfacial tension by measuring a quantity called the surface pressure,  $\Pi$ , which is defined as

$$\Pi \equiv \sigma_0 - \sigma \quad (3)$$

where  $\sigma_0$  is the interfacial tension of the pure fluid-fluid interface and  $\sigma$  is the interfacial tension in the presence of the surfactant.

Surfactants can be categorized into insoluble and soluble surfactants. As the name implies, insoluble surfactants (also referred to as Langmuir films), partition to the interface and have negligible solubility in the surrounding bulk phase. They are usually deposited to a liquid-air interface from a solution in a volatile solvent. Typically, these are amphiphiles with



| Souble<br>(Gibbs Monolayer) | Soluble<br>with Irreversible<br>Adsorption | Insoluble<br>(Langmuir Monolayer) | Self-Quenching<br>Interface Reactions |
|-----------------------------|--|-----------------------------------|---------------------------------------|
| <i>Surfactants</i>          | Proteins/Biofilms                          | Fatty Acids                       | Interfacial Polymerization            |
| -Nonionic                   | Asphaltenes                                | Fatty Alcohols                    | Oxide Skins on Metals                 |
| -Cationic                   |  |                                   |                                       |
| -Anionic                    | Particles                                  | Phospholipids                     |                                       |
| -Zwitterionic               |  |                                   |                                       |
| Polymers/Oligomers          | Polymers                                   | Polymers                          |                                       |

**Figure 2:** Different types of interfaces that are encountered in fluid-fluid systems that can have a measurable surface rheology.

small polar headgroups and long hydrocarbon chains. Common examples include fatty acids, fatty alcohols, and phospholipids [18]. Polymeric materials can also have this type of behavior, such as poly(octadecyl methacrylate), poly(tert butyl methacrylate), and poly(vinyl acetate) [19,20]. Insoluble surfactants are typically studied in a Langmuir trough, where the surfactant is spread on a fluid surface and the confining area can be readily changed using movable barriers. Changes in surface pressure with area ( $\Pi$ - $A$  isotherms) can be measured, analogous to pressure-volume isotherms for gases. While these insoluble systems are ideal models, the majority of surfactants used in applications are soluble in one or both phases. These soluble amphiphiles are classified by their charged state as being nonionic, cationic, anionic, or zwitterionic [17,21]. Short chained polymers can also be soluble and surface active. In these systems, attention must be given to both equilibrium and dynamic adsorption (discussed further below). There are also interfaces that are encountered in which the surfactant is soluble in the bulk phase, but upon attaching to the interface it undergoes structural changes and becomes irreversibly adsorbed and can potentially build up into a multilayer film. This is common with proteins, where in water they adopt a conformation that minimizes the exposure of hydrophobic groups, but at the interface they unfold and denature to present hydrophilic groups to the water phase and hydrophobic groups to the air/nonpolar phase [22]. Asphaltenes in crude oil exhibit similar irreversibility at oil-brine interfaces [23]. In addition to molecules, there are also particles that will adhere strongly to the interface due to a finite contact angle that the interface makes with the surface of the particle. The binding energy can be as large as  $1000kT$ , and while they are not strictly amphiphiles, they can effectively irreversibly adsorb at the interface while still being dispersible/soluble in one phase [24,25]. Another type of interface that is encountered that can have an appreciable interfacial rheology is when two

phases react at their boundary and form products that are insoluble in both phases. An example would be nylon skins formed at the interface between an aqueous phase containing diethylene triamine and a silicone oil containing sebacyl chloride [26]. Additional examples are the rigid skins that form at the interface when monolayers are exposed to an external stimulus, such as UV crosslinking [27] or when liquid metals react with an oxygen containing atmosphere to form oxide skins [28].

Since soluble surfactants can escape from the interface, we must understand adsorption/desorption phenomena at the interface. In an ideal dilute solution, the concentration ( $c$ ), surface excess concentration ( $\Gamma$ ), and interfacial tension ( $\sigma$ ), are related by the Gibbs equation [1,15,17, 29]:<sup>1</sup>

$$\Gamma = -\frac{1}{RT} \left( \frac{\partial \sigma}{\partial \ln c} \right)_T \quad (4)$$

where  $R$  and  $T$  are the ideal gas constant and temperature, respectively. There are numerous equilibrium adsorption isotherms that describe how the bulk concentration of surfactant affects the surface excess concentration (see Table 1). Using these adsorption isotherms to describe the functional form of  $\Gamma(c)$ , the Gibbs equation can be integrated to determine the surface pressure as a function of surface excess concentration, which is called a surface equation of state. Henry's isotherm, valid at low surface concentrations, results in a two-dimensional analog of the ideal gas law. The Langmuir isotherm introduces the feature of a maximum amount of surface adsorption, and the Frumkin isotherm introduces nonideal interactions between surface species through the parameter  $B$ . The

<sup>1</sup>Strictly speaking, the Gibbs equation is derived using activity coefficients. We use the ideal, dilute assumption to allow the use of concentration in lieu of activity coefficients. For surfactants that dissociate into multiple surface active species,  $m$ , the  $RT$  term should be replaced by  $mRT$ . For simplicity the  $m$  is omitted in this discussion.

resulting surface equations of state for these isotherms are also presented in Table 1, adhering to the naming convention used by Chang and Franses [29]. Although not mentioned here, there are additional surface equations of state analogous to non-ideal gas equations of state in 3D, such as the van der Waals and Volmer equation that could also be employed [15].

Because rheology generally examines dynamic processes, the effects of mass transport to the surface as well as kinetic effects within the layer must also be considered with soluble surfactants. Once molecules reach the interfacial zone, there are timescales associated with adsorption and desorption, molecular rearrangements, denaturing, multi-layer buildup, monolayer collapse, etc., all of which can affect rheological behavior.

Working with interfaces poses additional challenges since it requires a high level of attention to chemical cleanliness to obtain repeatable results. Minute amounts of foreign material can behave like surfactants and influence results. I have experienced contamination from a duct located in the ceiling for the building's climate control system exhausting over my Langmuir trough, causing  $\Pi$ -A isotherms to be inconsistent. The purity of the liquids used also matter, since the impurities can result in a source of variation in addition to affecting surface behavior. The quality of normal house-supplied deionized (DI) water varies depending on your facility's purification system. To ensure control

of the concentration of solutions it is best to work with ultra pure water (18.2 M $\Omega$ -cm resistivity) which requires additional purification processes beyond house DI water (e.g. by using a Milli-Q water purification system). Polar phases also need to be well prepared, and these too sometimes require additional purification such as removal of polar contaminants by adsorption onto alumina powder [30].

### Deformation and Momentum Transport at Interfaces

Fluid-fluid interfaces, by their nature, are in intimate coupling with their surrounding phases, and consequently when they are deformed, there is concomitant deformation inside the adjacent bulk due to viscous coupling between the interface and the bulk. One of the primary challenges for interfacial rheology is in understanding this coupling and developing ways to minimize it so the effect of the interface can be isolated. To begin to model the momentum transport at interfaces, a force balance on a surface area element with a unit normal,  $\mathbf{n}$ , is needed [1]:

$$\rho^s \frac{D_s \mathbf{v}^0}{Dt} = \nabla_s \cdot \mathbf{P}^s + \mathbf{f}^s + \mathbf{n} \cdot [\mathbf{P}(0+) - \mathbf{P}(0-)] \quad (5)$$

where  $\rho^s$  is the surface excess mass density,  $\mathbf{v}^0$  is the velocity of the interface,  $\mathbf{P}^s$  is the surface excess stress tensor,  $\mathbf{f}^s$  is the surface-excess force density vector,  $\mathbf{P}(0+)$  is the limiting value of the bulk phase stress tensor

**Table 1: Some Equilibrium Adsorption Isotherms and their Corresponding Surface Equations of State\* [29]**

| Equilibrium Adsorption Isotherm  |  | Surface Equation of State  |  |
|--|--|--|--|
| Henry Isotherm<br>• low $\Gamma$ only<br>• no $\Gamma_{\max}$          | $\Gamma = K_H c$   | $\Pi = RT\Gamma$   | 2D Ideal Gas Law                           |
| Langmuir Isotherm<br>• $\Gamma_{\max}$                                 | $\Gamma = \Gamma_{\max} \frac{K_L c}{1 + K_L c}$   | $\Pi = RT\Gamma_{\max} \ln(1 + K_L c)$   | Szyszkowski Equation                       |
|  | $K_L c = \frac{\Gamma/\Gamma_{\max}}{1 - \Gamma/\Gamma_{\max}}$  | $\Pi = -RT\Gamma_{\max} \ln\left(1 - \frac{\Gamma}{\Gamma_{\max}}\right)$  | Frumkin Equation                           |
| Frumkin† Isotherm<br>• $\Gamma_{\max}$<br>• Includes non-ideal effects | $K_F c = \frac{\Gamma/\Gamma_{\max}}{1 - \Gamma/\Gamma_{\max}} \exp\left[-B \frac{\Gamma}{\Gamma_{\max}}\right]$ | $\Pi = -RT\Gamma_{\max} \left[ \ln\left(1 - \frac{\Gamma}{\Gamma_{\max}}\right) + \frac{B}{2} \left(\frac{\Gamma}{\Gamma_{\max}}\right)^2 \right]$ | Equation of State for the Frumkin Isotherm |

\* The parameters  $K_H$ ,  $K_L$ , and  $K_F$  are the equilibrium adsorption coefficients for Henry, Langmuir, and Frumkin isotherms.

† In Frumkin's isotherm, the parameter  $B$  is a measure of the non-ideality of mixing at the interface layer. In the limit of  $B \rightarrow 0$  the Frumkin isotherm becomes the Langmuir isotherm.



of the phase in the direction of the surface normal (Phase II in Fig. 1), and  $\mathbf{P}(0^-)$  is the limiting value of the bulk phase stress tensor of the inner phase (Phase I in Fig. 1). The surface coordinate system introduces some additional terms. One is a second-order surface identity tensor ( $\mathbf{I}_s$ ) based on the conventional identity tensor ( $\mathbf{I}$ ), and the surface normal dyadic ( $\mathbf{n} \mathbf{n}$ )

$$\mathbf{I}_s = \mathbf{I} - \mathbf{n} \mathbf{n} \quad (6)$$

Another is the surface gradient operator

$$\nabla_s = \mathbf{I}_s \cdot \nabla \quad (7)$$

There also appears a surface convective derivative term

$$\rho_s \frac{D_s \mathbf{v}^0}{Dt} = \rho_s \left( \frac{\partial \mathbf{v}^0}{\partial t} + \mathbf{v}^0 \cdot \nabla_s \mathbf{v}^0 \right) \quad (8)$$

In comparison to the more familiar 3D Cauchy momentum balance, a 2D interface introduces a term that is the difference between the bulk stress components, or the “jump” boundary condition in stress across the interface (eqn. 5). It is the mathematical representation of the momentum exchange between the interface and the bulk.

We can neglect inertia effects<sup>2</sup> since  $\rho^s$  is  $10^{-8}$  to  $10^{-6}$  g/cm<sup>2</sup> for surface densities of 100 Å<sup>2</sup>/molecule and molecular weight of 100-1000g/mol. Rearranging we can solve for the difference between the two limiting stress tensors.

$$\mathbf{n} \cdot [\mathbf{P}(0^-) - \mathbf{P}(0^+)] = \nabla_s \cdot \mathbf{P}^s + \mathbf{f}^s \quad (9)$$

A common constitutive relation for the surface excess pressure tensor includes interfacial tension and assumes an ideal frictionless interface (i.e. no interfacial rheology):

$$\mathbf{P}^s = \sigma \mathbf{I}_s \quad (10)$$

Taking the divergence of the surface excess stress tensor yields

$$\nabla_s \cdot \mathbf{P}^s = \nabla_s \cdot (\sigma \mathbf{I}_s) = -\sigma (\nabla_s \cdot \mathbf{n}) \mathbf{n} + \nabla_s \sigma \quad (11)$$

The first term on the right hand side results in a force that is normal to the surface and arises from surface curvature. When we substitute in the principal radii of curvature ( $R_1$  and  $R_2$ ) using the relation  $\nabla_s \cdot \mathbf{n} = 1/R_1 + 1/R_2$ , we recognize this first term as the Laplace-

<sup>2</sup>Although not shown here, one could formally construct a surface Reynolds number using surface density and surface viscosity to demonstrate that inertia at the surface is negligible.

Young equation for pressure drop across an interface. The second term arises from variations in interfacial tension along the interface, and is called a Marangoni stress. The Marangoni stress results in a force that is in the plane of the surface (orthogonal to  $\mathbf{n}$ ). Gradients in interfacial tension can be caused by variations in temperature due to the temperature dependence of interfacial tension or convection of surfactant along the surface due to an external flow field. Another example of Marangoni phenomena is the tears of wine effect. Ethanol, being more volatile, evaporates from the aqueous ethanol mixture and becomes depleted in the region near the sides of the glass. As the ethanol concentration drops, the interfacial tension increases, creating an interfacial tension gradient that draws the liquid up the side of the glass.

One can introduce additional terms to the surfaces excess stress tensor by adding terms that are a function of the rate of surface deformation. The simplest extension is to assume these stresses are proportional to the surface rate of deformation, which is called the Boussinesq-Scriven model [1,31]:

$$\mathbf{P}^s = \sigma \mathbf{I}_s + (\kappa^s - \mu^s)(\mathbf{I}_s : \mathbf{D}_s) \mathbf{I}_s + 2\mu^s \mathbf{D}_s \quad (12)$$

where  $\kappa^s$  is the surface dilatational viscosity,  $\mu^s$  is the surface shear viscosity, and  $\mathbf{D}_s$  is the surface rate of deformation tensor, which is a symmetric construct of the surface velocity gradient tensor

$$\mathbf{D}_s = \frac{1}{2} \left[ (\nabla_s \mathbf{v}^0) \cdot \mathbf{I}_s + \mathbf{I}_s \cdot (\nabla_s \mathbf{v}^0)^T \right] \quad (13)$$

Typically in 3D rheology most liquids are not very compressible, and it is customary to invoke the incompressibility approximation, which is the mathematical statement that the trace of the rate of deformation tensor is zero. As a consequence of this approximation, the dilatational viscosity for 3D materials is not typically considered. Unfortunately this simplification is not a good approximation for interfaces. Interfaces can have a range of different compressibilities depending on the phase the molecules adapt at the interface. For fatty acids and alcohols, which are within the class of insoluble surfactants discussed earlier, the surface can go through different phases depending on the surface density, and can range from a highly compressible 2D gas, to a moderately compressible liquid state, to solid-like states with low compressibility. Additionally, soluble surfactants have the added ability to relieve compressive stresses in the film by escaping into the bulk. As a result, an incompressible interface is something that is not easily guaranteed when working with surfaces, and this term needs to be carried through.

(continues, page 25)



N.W. Tschoegl at his home in Pasadena, August, 2006

## Nicholas W. Tschoegl

1918 – 2011

Professor Tschoegl was born in 1918 in Gross-Seelowitz (Židlochovice) in the South Moravian region of the current Czech Republic. When he was just three months old, his father died on the Italian front during the end of World War I. Raised by his mother, he would spend his formative years in Hungary, Germany, and Czechoslovakia. By the time he was nine years old, he became fascinated with electricity, which sparked his interest in science. Later in his life he often remembered his times in Premonstratensian School in Gödöllő, and his great interest in languages. He spoke more than dozen languages, including Slovenian, which he learned relatively late in his life. His passions were different writing systems, including Egyptian hieroglyphics, Assyrian and Babylonian cuneiform, Chinese, and Japanese. In 1936 he graduated from Gödöllő School and entered compulsory service in the Hungarian Army. In 1938 he entered the Tschögl firm where he worked until the beginning of the Second World War. He served as an officer in the Hungarian army in Ukraine from 1942 through 1943 and fought three major battles. After

that he returned to Hungary, where he was wounded during the siege of Budapest, at which time Sophia Glazmak (Glasman), an acquaintance but later his wife, saved his life. At the end of the war Hungary came under Soviet control. In 1946 Nicholas married Sophia and had his first son, Adrian, who was born in 1947. In October of 1948, he and his family fled from communist rule to Austria, and from there in 1949 to Sydney, Australia, where his second son Christopher was born in 1954.

Nick, as friends used to call him, finished his education in Australia, receiving a bachelor's degree at the New South Wales University of Technology in 1954, and a PhD in physical chemistry with A. E. Alexander in 1958 from the same institution, which was renamed the University of New South Wales. He then started a job at the Bread Research Institute of Australia, doing pioneering work on the rheology of wheat flour dough. In 1961, he accepted a position at the University of Wisconsin working on synthetic polymers with John D. Ferry. In 1963, Nicholas spent two years at the Stanford Research Institute working with T. Smith, before joining Caltech in 1965 as an associate professor of materials science in the Division of Engineering and Applied Science. He worked with Professor Max Williams, who left Caltech in June of 1966 to take up the position of dean of the School of Engineering at the University of Utah. NWT took over his group and continued intensive research on behavior of polymers and synthetic rubbers used in solid propellants for rockets, which was funded by the U.S. Air Force. At that time he formed a strong team of graduate students with members such as Robert (Bob) E. Cohen (PhD '72), currently St. Laurent Professor of Chemical Engineering at MIT and co-director of the DuPont-MIT Alliance. Nick also met Wolfgang G. Knauss, a former graduate student of Professor Williams, who later became one of his best friends.



During the years between 1971 and 1977 Professor Tschoegl visited and lectured at several European universities. In 1971 he became visiting professor at the Technische Hogeschool in Delft. In 1976 he received the *Humboldt Award* and spent a sabbatical year in Europe: six months at Gutenberg University, Mainz, three months at Imperial College, London, and two months in Strasbourg at the Centre de Recherches sur les Macromolécules. In 1977 Professor Tschoegl spent a year as a visiting professor at ETH, Zurich, and accepted an invitation to join the faculty of École

and began a collaboration with Professor Igor Emri for many, many years.

Professor Tschoegl was a consultant to many leading companies, among them Phillips Petroleum, 1968-1983, Firestone Tire & Rubber, 1974-1980, as well as research institutions such as the Naval Weapons Center and the NASA Jet Propulsion Laboratory (JPL).

Professor Tschoegl was also one of the key figures in the formation of the International Committee on



Polytechnique Fédérale de Lausanne. However, he decided to return to Caltech and continue pioneering research work on time-dependent properties of block copolymers and spectral functions. Attempts to apply the WLF [Williams-Landel-Ferry] equation to block copolymers and other multitransition systems lead to the development of the FMT [Fillers-Moonan-Tschoegl] equation, which was a major breakthrough in the understanding of the effect of pressure and temperature on the behavior of polymers and their composites. Some of these results were summarized in his two books, *The Phenomenological Theory of Linear Viscoelastic Behavior*, which remains the authoritative text on the mechanical response of polymeric materials, and *Fundamentals of Equilibrium and Steady-State Thermodynamics*. In addition to his research and teaching work, Nick managed Caltech's Watson lectures and gave one of the most attended Watson lectures on *The Lost City of Atlantis*. He became an emeritus faculty member in 1985.

After retirement Professor Tschoegl took a visiting professorship in 1986 at the University of Ljubljana,

Rheology, and became the US delegate to the ICR from 1974 through 1976. At the International Congress in Göteborg, Sweden he became secretary of the ICR and held that post for twelve years, from 1976 through 1988. Along with Wolfgang Knauss and Igor Emri he helped found the journal *Mechanics of Time-Dependent Materials*.

Nicholas W. Tschoegl passed away on the morning of November 14 at his home in Pasadena. He was 93. Tschoegl is survived by his son Adrian, daughter-in-law Naomi, and two grandchildren, Elizabeth and Matthew. His wife Sophia died in 2008 and his son Christopher died in 1995.

He will be missed and remembered by all.

Igor Emri  
Adrian E. Tschoegl





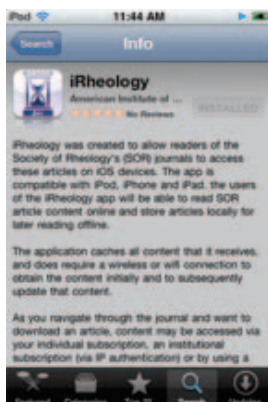
## NEWS

### SOR *iRheology* App Now available on iTunes

The SOR ExCom authorized the programming of the *iRheology* app for the iPhone/Pod/Pod platform, and this app is now available. Apps for other operating systems are also under discussion.

*From the iTunes Store*  
Updated 13 December 2011

*iRheology* was created to allow readers of the Society of Rheology's (SOR) journals to access these articles on iOS devices. The app is compatible with iPod, iPhone and iPad. The users of the *iRheology* app will be able to read SOR article content online and store articles locally for later reading offline.



The application catches all content that it receives and does not require a wireless or wifi connection to obtain the content initially and to subsequently update that content.

As you navigate through the journal and want to download an article, content may be accessed via your individual subscription, an institutional subscription (via IP authentication) or by using a pay per view account. If you would like an article, save it locally to your iPhone, iPad, or iPod touch.

Best use case: Log in to your institution's wifi network and open the *iRheology* app. Navigate through the *Journal* and select the articles you are interested in. If your institution has access to the article, the PDF will be

displayed on the screen. If you wish to save the article for reading or research later, click the "Save Locally" button. The PDF is now saved locally on your device and may be read at any time without needing a wireless or wifi connection.

Publications currently included are:

- *Journal of Rheology*
- *Rheology Bulletin*
- SOR Nomenclature

Note: The app is best viewed in landscape.

### 2011 Mason Award goes to McGill's Rey

*from the Canadian Society of Rheology*

The Canadian Society of Rheology presents the Stanley George Mason Award every three-years to a distinguished Canadian who has contributed in an outstanding fashion in the domain of rheology. The 2011 recipient is Chemical Engineering Professor Alejandro Rey of the McGill Materials Modeling Research Group. This seventh CRS Mason Award acknowledges Professor Rey's international stature in the field and his unique contributions to, and impact upon, the fundamental



John Vlachopoulos presents the 2011 Stanley George Mason Award to Alejandro Rey.



2011 Poster Contest Winners, clockwise from left: first place Joseph Samaniuk, Wisconsin Madison (with advisor Daniel Klingenberg); second place Simon Rogers, Institute of Complex Systems (post doc) (shown with 2009-2011 SOR President Faith Morrison); third place Tom Verwijlen, K. U. Leuven (with advisor Paula Moldenaers; advisor Jan Vermant not present); fourth place Tao Cong, Syracuse University (with advisor Radhakrishna Sureshkumar).

science and technology of complex fluids and soft matter. Stanley George Mason, the man for whom the prize is named, is considered one of the founding fathers of suspension rheology. The award was presented at the Current Topics and Trends in Rheology Workshop sponsored by the Canadian Society of Rheology, held 6-7 June 2011 at the École Polytechnique Montréal. During the award ceremony Professor Rey received the Mason award from 2007 award-winner John Vlachopoulos, Professor Emeritus at McMaster University.

Professor Rey has been a faculty member at McGill University since 1988 and is now James McGill Professor of Chemical Engineering and executive member of the McGill Advanced Materials Institute. Professor Rey's research interests include computational material science of structural and functional materials, thermodynamics and interfacial science of soft matter, biological materials, biological polymer processing, and liquid crystal physics.

## Cleveland Poster Contest Winners Recognized

Since 2001 the Society of Rheology has sponsored a *Best Student Poster Award* in conjunction with the annual meeting. Since 2009 the contributions of postdoctoral fellows have also been eligible in the competition. Posters are submitted electronically and finalists are identified by the prize committee prior to the meeting. During the poster session on Wednesday of the annual meeting, the prize committee meets all the poster authors and

deliberates on their choice. The awards are presented at the end of the Poster Reception, an event sponsored in 2011 by Anton Paar. At the 83<sup>rd</sup> Annual Meeting in Cleveland, four posters were singled out for first through fourth prizes; the award includes being featured on the SOR website ([www.rheology.org/sor/awards/Student\\_Poster/](http://www.rheology.org/sor/awards/Student_Poster/)) and cash prizes of \$500, \$300, \$200, and \$100, for the four awards, respectively. The 2011 poster-contest winners were Joseph Samaniuk, Simon Rogers, Tom Verwijlen, and Tao Cong (see accompanying photographs).

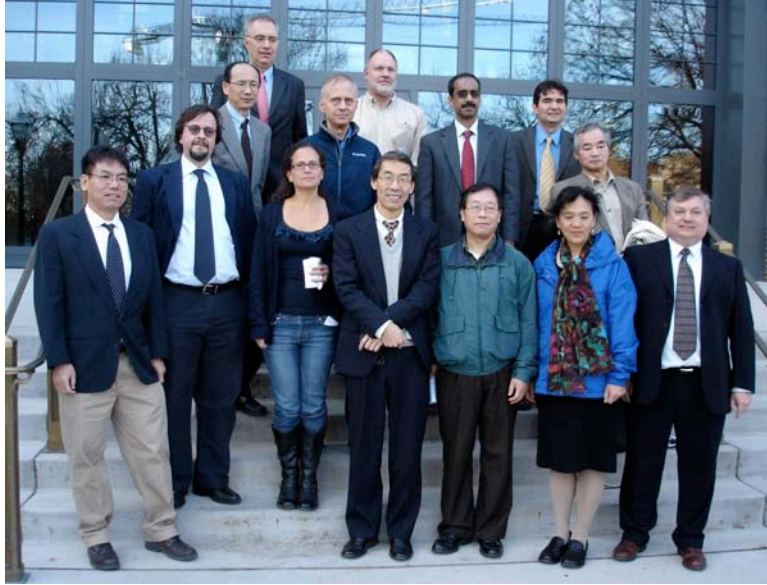
## Franklin D. Dexter, former President of SOR

Franklin D. Dexter, who was president of the Society of Rheology during the period 1956-57, died on 14 October 2011 at age 93. Additional information will be supplied when available.

## Memorial Symposium Held for Dan Joseph

*submitted by Jimmy Feng*

The Daniel D. Joseph Memorial Symposium, organized by the Department of Aerospace Engineering and Mechanics (AEM), University of Minnesota, took place on 4 November 2011 in the



Former students of Dan Joseph attending the memorial symposium included, *front row (from left):* Kang Ping Chen, Geraldo Ribeiro, Clara Mata, Jimmy Feng, Runyuan Bai, Ling Jiang, Mike Arney; *back row:* Howard Hu, Jurgen Sanders, Todd Hesla, Dave Hultman, Pushpendra Singh, Juan Carlos Padrino, Toshio Funada.

[umn.edu/info/JosephMemorial.shtml](http://umn.edu/info/JosephMemorial.shtml). An informal collection of presentations, videos and photos from the symposium has been posted here: [www.math.ubc.ca/~jfeng/DDJ\\_Nov4\\_2011](http://www.math.ubc.ca/~jfeng/DDJ_Nov4_2011). The AEM department is building a more formal webpage collecting materials from the memorial symposium.

same building where the late Professor Joseph had worked since 1963 until shortly before his death on 24 May 2011.

Born on 26 March 1929 in Chicago, Joseph received his engineering education at the Illinois Institute of Technology, earning a Ph.D. in Mechanical Engineering in 1963. He was well-known for his many contributions to non-Newtonian fluid dynamics and rheology. He received the Bingham medal from the Society of Rheology in 1993 and was a member of the National Academy of Sciences and the National Academy of Engineering and a fellow of the American Academy of Arts and Sciences. The July 2011 issue of *Rheology Bulletin* carried an obituary that described his remarkable career in greater detail.

The morning session of the symposium consisted of technical presentations by Kathepalli Sreenivasan (New York University), Roland Glowinski (University of Houston), Pushpendra Singh (New Jersey Institute of Technology) and James J. Feng (University of British Columbia). The afternoon session was devoted to personal recollections by Joseph's former students, postdocs and colleagues. Several fluid dynamicists and rheologists who could not attend wrote about their memories of Joseph, as did his alma mater, and these were shared with the audience. The symposium ended with a banquet in Dinkytown next to the university campus. The symposium was attended by Joseph's former colleagues at the University of Minnesota, former students, postdocs and collaborators from other institutions in the US, Canada, Brazil, Japan, and Europe, and family members and friends. Xi'an Jiaotong University, where Joseph served as an honorary professor, sent in a special poster presentation. More information about the symposium is available from the AEM departmental website [www.aem](http://www.aem).

## Minutes of the ExCom Meeting

Sunday, October 9, 2011  
Cleveland, Ohio

Attending: Faith Morrison, Jeffrey Giacomini, Albert Co, Monty Shaw, Bob Prud'homme, Ole Hassager, Norm Wagner, Andy Kraynik, Philip (Bo) Hammer (AIP), Doreen Hall (AIP), Robert Harrington (AIP), Pat Mather, Marie-Claude Heuzey, Victor Breedveld, Shelley Anna, Anne M. Grillet, Gerry Fuller, Greg McKenna, Matthew Liberatore, Will Hartt, Gareth McKinley, Saad Khan, Joao Maia.

President Faith Morrison called the meeting to order at 8:00 a.m. in Room 201, InterContinental Cleveland in Cleveland, Ohio.

The minutes of April 10, 2011 were read by Secretary Albert Co. A motion to approve the minutes was passed.

Monty Shaw reported on the financial status of the Society and the *Journal of Rheology (JOR)*. Subscription and usage of *JOR* were discussed. Shaw pointed out that *JOR* royalties jumped from the expected \$4,000 to \$38,185. A motion to include \$30,000 for student travel to the International Congress on Rheology in the 2012 budget was passed. A motion to approve the treasurer's report was passed.

Albert Co reported that 476 members (34% of total members) voted in the 2011 election. The trend line of voting turnout showed a step rise when e-mail reminders were sent to non-voters. Co presented plots that showed the trends of total number of registrations and number of papers submitted since the spring 2005 Lubbock Meeting. The data also indicated a linear relationship between the number of papers submitted and the total number of registrations. Co demonstrated the poster



competition website, which allows poster competition entries to be uploaded and judges to view the uploaded files. Co reiterated that SOR now owns the domain name *rheology.com*, which was donated to the Society in 2011 by Dow Chemical.

John Brady gave the *JOR* Editor report. There were 124 papers submitted in 2010, with a sharp drop in submissions in April followed by a peak in May. In 2010 the average time to first decision of regular articles was 100.5 days; the average time to final decision was 149 days. The current impact factor of *JOR* is 3.117. Brady is stepping down as *JOR* Editor; the Executive Committee thanked him for his service. Ralph Colby was appointed by the Executive Committee (email vote) to fill the remaining time of Brady's term (October 2013 elections). The *JOR* Editor's honorarium is reviewed in years with an International Congress (2012).

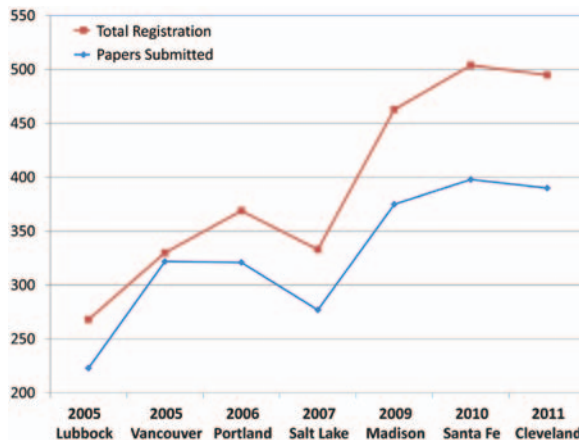
Anne Grillet reported for the Education Committee. For the Pasadena (February 2013) meeting, the Committee recommends the two-day short course "Microfluidics and Its Application" (Instructors: Anubhav Tripathi, Annie Colin, and Charles Schroeder). Possible short courses for the Montreal (October 2013) meeting were discussed. Assigning continuing education units for the short course was discussed. The consensus of the Executive Committee was for the Education Committee to proceed with this. Shaw suggested getting a lawyer to check any trademark issue regarding using the term "continuing education units." Grillet reported she was still collecting links to interesting rheology web pages.



Robert Harrington (American Institute of Physics, AIP) gave updates on AIP's focus on member societies. AIP will prepare a strategy plan to start the discussion. Doreen Hall reported that the *iRheology* app will be available for download in a week. Hall also discussed *iPeerReview*, an app for authors to check status of submitted papers. Hall demonstrated the website *RightsLink* for copyright clearance. For consideration by the Executive Committee, AIP will provide the pricing structure of *RightsLink* and any service charge for customization. Hall also indicated that they are able to supply the option of adding a cover page with advertisement for papers downloaded from the *JOR* site.

Bo Hammer reported on the program for the AIP Industrial/Faculty/Student Forum on Soft Materials, which he co-organized with William Hartt and Suraj Deshmukh. The two one-hour sessions were scheduled to start at 4 p.m. this afternoon.

Shelley Anna reported for the Membership Committee.



Meetings data for SOR Annual Meetings since 2005.

As of August 2011, there were 1429 members. The first batch of student gifts have been sent to graduating Ph.D. students.

Gerry Fuller reported on international outreach. The ICR 2012 meeting in Lisbon is on course. The Brazilian society was formed last year. Next month Fuller and Giacomini will travel to South Africa to teach a short course; they will encourage South African rheologists to hold an event outside of Cape Town to broaden the impact of the society. The Indian Society of Rheology will restart in January 2012. The ExCom thanked Fuller for his efforts at promoting rheology internationally.

At noon, the meeting entered into executive session. The regular meeting resumed after lunch.

Norm Wagner reported on the Student Travel Grant program. There were 34 travel grants awarded for the Cleveland meeting.

Victor Breedveld reported on the technical program for the Cleveland meeting. Policy on cancelled talks was discussed. Breedveld suggested that sessions with large number of submitted papers (such as "Rheology of Polymer Melts and Blends" and "Suspensions, Colloids, and Emulsions") be split in future meetings. At the Cleveland meeting both of these sessions were scheduled for the whole three and a half days. A number of papers originally submitted to these sessions had to be moved to other related sessions.

Pat Mather reported on the local arrangement of the Cleveland meeting. The venues of the social events were reviewed. As of Sunday morning there were 454 meeting registrants and 16 exhibitors; 240 banquet tickets were sold. The number of registrants for the short course was 31.

John Brady reported on the 2013 (February) Pasadena meeting. Brady described the meeting room layout for

five parallel sessions, with contingency plans for one extra parallel session. Social program and places to visit were discussed. The Pasadena technical program (chaired by Shelley Anna and Carlos Rinaldi) will be presented at the Spring 2012 Executive Committee meeting in Chicago.

Joao Maia reported on ICR 2012 (August 5-10, 2012, Lisbon, Portugal). The venues, technical program, and social program were discussed. The abstract submission is now opened. Important deadlines can be found at [www.rheology-esr.net/ICR2012](http://www.rheology-esr.net/ICR2012). For each talk there must be one meeting registration. Maia indicated that he was planning for 9 parallel sessions; he will set the parallel session structure after the April 2012 deadline.

Morrison reported for Watanabe that the international representatives (delegates) in the Asia/Pacific area had a meeting in Daejeon, Korea on September 26 and decided on a plan for Japan to organize the ICR2016 in the period of 1-6 August 2016 (Monday – Saturday) in Kyoto, Japan. The final approval of this plan is to be made by the International Committee on Rheology at ICR2012 in Lisbon, and the Kyoto plan will be more detailed by that time.

Marie-Claude Heuzey reported on the 2013 (October) Montreal meeting. Meeting room layout was presented. Possible venues for Monday night reception were discussed. Heuzey will work with Shaw to set up registration fees.

Matthew Liberatore presented a proposal for the October 2017 annual meeting in Denver, Colorado. Saad Khan presented a proposal for the October 2018 annual meeting in Raleigh, North Carolina. Faith Morrison presented for Amy Shen a proposal for the 2017 or 2018 annual meeting in Seattle, Washington.

After discussion, the Executive Committee agreed to pursue the Denver proposal for 2017 and the Raleigh proposal for 2018.

Greg McKenna will contact Don Baird (for Pensacola, Florida) and potential hosts in Gainesville, Florida; Houston, Texas; and Austin, Texas to solicit February 2017 annual meeting proposals for discussion at the Spring 2012 Executive Committee meeting.

The meeting was adjourned at 4:19 p.m.  
Submitted by Albert Co, Secretary

## Minutes of the Business Meeting

Monday, October 10, 2011  
Cleveland, Ohio

President Faith Morrison called the meeting to order at

12:23 p.m. in Founders Ballroom C, InterContinental Cleveland, in Cleveland, Ohio (101 in attendance). The minutes of the previous Business Meeting in Santa Fe, New Mexico were read by Albert Co and approved without addition or correction.

Monty Shaw presented the Treasurer Report. A motion to accept the report was seconded and passed.

John Brady presented the *JOR* Editor Report. The impact factor of *JOR* is currently at 3.117. Brady also reported that he had been working with the new *JOR* Editor Ralph Colby to ensure a smooth transition. Faith Morrison, as well as the members in attendance, thanked Brady for his exemplary service as *JOR* editor and member of the Executive Committee.

Pat Mather, Chair of the Local Arrangement Committee for the Cleveland meeting, reported that the meeting had 465 registrants (as of Monday noon). There were 244 banquet tickets sold. He also announced details for the Monday Reception and the Bingham Banquet.

Secretary Albert Co presented a plot that showed the rising trend in meeting attendance since the 2005 Lubbock meeting. The Santa Fe meeting has the highest attendance, with the Cleveland meeting close behind.

Shelley Anna reported for the Membership Committee. The first batch of gifts to graduating Ph.D. students has been sent.

Faith Morrison reported that the *iRheology* app developed by AIP would be available at the iTunes store in a week and that the industrial/faculty/student forum organized by Bo Hammer of AIP, Will Hartt, and Suraj Deshmukh was held on Sunday afternoon. Morrison also thanked Gerry Fuller for his works on international outreach, recently in Russia and South Africa. The Executive Committee is considering using *RightsLink* for *JOR*. AIP has refocused on member societies and will prepare a strategy plan to discuss with the Executive Committee.

Morrison thanked retiring Executive Committee members Bob Prud'homme, John Brady, Ole Hassager and Hiroshi Watanabe for their services and welcomed new Executive Committee members Greg McKenna, Ralph Colby, Gareth McKinley, and Shelley Anna.

Gerry Fuller thanked Jeffrey Giacomini for his service on international outreach and presented him with a biking shirt with the SOR logo.

The SOR gavel was passed from Faith Morrison to Jeffrey Giacomini. Giacomini thanked Morrison for her

outstanding service as President.

The meeting was adjourned at 1:06 p.m.  
Submitted by Albert Co, Secretary

## Treasurer's Report

To the Membership:

The tables below depict the financial state of The Society of Rheology as reported to the Membership at the 2011 Annual Meeting in Cleveland. A major change from the 2012 Budget appearing in the July 2011 *Bulletin* is the addition of \$30,000 to the Student Member Travel line item to support student travel to the 2012

International Congress on Rheology in Lisbon, Portugal. The result is a deficit budget, which will be covered from reserves.

On the income side, the trends discussed in past reports continue: slowly declining dues receipts, variable *Journal* income and negligible interest income. The costs from the Cleveland meeting are not yet cleared up, but it looks like both meeting and short course will show a surplus after accounting for student travel and executive committee expenses.



Respectfully submitted,  
Montgomery T. Shaw, Treasurer

| <b>The Society of Rheology</b> |                      |                          |                      |                      |                        |
|--------------------------------|----------------------|--------------------------|----------------------|----------------------|------------------------|
| Receipts and Disbursements     |                      |                          |                      |                      |                        |
| (all amounts, USD)             |                      |                          |                      |                      |                        |
|                                | <b>2012</b>          | <b>2011</b>              | <b>2011</b>          | <b>2011</b>          | <b>2010</b>            |
|                                | <b><u>Budget</u></b> | <b><u>Projection</u></b> | <b><u>August</u></b> | <b><u>Budget</u></b> | <b><u>Year End</u></b> |
| <b>RECEIPTS</b>                |                      |                          |                      |                      |                        |
| Dues                           | 46,000               | 46,520                   | 45,724               | 49,000               | 47,969                 |
| Interest                       | 3,000                | 3,020                    | 1,724                | 5,000                | 2,744                  |
| Journal of Rheology            | 267,600              | 331,791                  | 307,283              | 275,000              | 287,488                |
| Mailing List Sales             | 100                  | 80                       | -15                  | 300                  | 80                     |
| Bulletin Advertising           | 10,000               | 9,600                    | 7,200                | 10,000               | 10,800                 |
| Annual Meeting (net)           | 0                    | 9,377                    | 29,907               | 0                    | 13,106                 |
| Short Course (net)             | 0                    | 11,624                   | 37,075               | 0                    | 16,247                 |
| <b>TOTAL RECEIPTS</b>          | <b>326,700</b>       | <b>412,012</b>           | <b>428,899</b>       | <b>339,300</b>       | <b>378,433</b>         |
| <b>DISBURSEMENTS</b>           |                      |                          |                      |                      |                        |
| AIP Dues Bill & Collect.       | 11,500               | 10,642                   | 6,817                | 11,000               | 11,386                 |
| AIP Adm. Services              | 8,000                | 7,568                    | 5,000                | 8,000                | 7,568                  |
| AIP Mem. Soc. Dues             | 7,500                | 13,069                   | 8,713                | 7,500                | 7,500                  |
| Contributions and Prizes       | 12,000               | 12,585                   | 1,585                | 11,000               | 11,825                 |
| Journal of Rheology            | 199,375              | 216,762                  | 142,795              | 192,125              | 214,638                |
| Bulletin                       | 22,000               | 15,707                   | 13,406               | 19,000               | 22,127                 |
| Bingham Award                  | 0                    | 10,000                   | 0                    | 500                  | 12,972                 |
| Executive Cmt. Meetings        | 13,000               | 20,766                   | 14,766               | 13,000               | 16,695                 |
| Pres. Discretionary Fund       | 1,500                | 0                        | 0                    | 1,500                | 814                    |
| Treas. Discr. Fund             | 1,500                | 0                        | 0                    | 1,500                | 0                      |
| Bulletin Editor Discr. Fund    | 1,500                | 0                        | 0                    | 1,500                | 0                      |
| Progr. Chm. Discr. Fund        | 3,000                | 2,000                    | 0                    | 3,000                | 0                      |
| Webmaster Discr. Fund          | 3,000                | 200                      | 0                    | 3,000                | 1,030                  |
| International Activities Fund  | 5,000                | 2,000                    | 0                    | 5,000                | 2,000                  |
| Office Expenses                | 4,000                | 1,595                    | 1,129                | 4,000                | 2,224                  |
| Banking Services               | 100                  | 229                      | 152                  | 100                  | 60                     |
| Liability Insurance            | 5,200                | 5,079                    | 1,249                | 3,900                | 3,830                  |
| Membership Broch. & Appl.      | 2,000                | 1,500                    | 0                    | 1,500                | 2,193                  |
| Accountant                     | 2,200                | 2,200                    | 2,200                | 2,000                | 2,200                  |
| Student member travel          | 30,000               | 16,100                   | 0                    | 21,000               | 14,541                 |
| Annual meetings, future        | 6,000                | 3,000                    | 0                    | 8,000                | 2,299                  |
| Website                        | 3,000                | 200                      | 50                   | 3,000                | 215                    |
| Miscellaneous                  | 100                  | 0                        | 0                    | 500                  | 0                      |
| <b>TOTAL DISBURSEMENTS</b>     | <b>341,475</b>       | <b>341,202</b>           | <b>197,862</b>       | <b>321,625</b>       | <b>336,117</b>         |
| <b>Net</b>                     | <b>-14,775</b>       | <b>70,810</b>            | <b>231,037</b>       | <b>17,675</b>        | <b>42,316</b>          |



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

| (all amounts, USD)                      | 2011<br>August   | 2010<br>Year End | 2010<br>August   | 2009<br>Year End | 2009<br>August   |
|---|------------------|------------------|------------------|------------------|------------------|
| <b>Assets</b>                           |                  |                  |                  |                  |                  |
| Cash in checking account(s)             | 77,396           | 13,257           | 87,882           | 18,330           | 61,234           |
| Securities                              | 0                | 0                | 0                | 0                | 0                |
| Balance in AIP account                  | 1,513,618        | 1,435,019        | 1,427,891        | 1,425,005        | 1,390,221        |
| <b>Total Assets</b>                     | <b>1,591,014</b> | <b>1,448,276</b> | <b>1,515,773</b> | <b>1,443,335</b> | <b>1,451,455</b> |
| <b>Liabilities and Net Assets</b>       |                  |                  |                  |                  |                  |
| <b>Liabilities</b>                      |                  |                  |                  |                  |                  |
| Deferred revenue                        | 0                | 89,283           | 0                | 125,501          | 1,130            |
| <b>Total Liabilities</b>                | <b>0</b>         | <b>89,283</b>    | <b>0</b>         | <b>125,501</b>   | <b>1,130</b>     |
| <b>Net Assets</b>                       |                  |                  |                  |                  |                  |
| Publication reserve                     | 450,000          | 450,000          | 450,000          | 450,000          | 450,000          |
| Student travel grant reserve            | 30,000           | 30,000           | 30,000           | 30,000           | 30,000           |
| Annual Meeting reserve                  | 300,000          | 300,000          | 300,000          | 300,000          | 300,000          |
| Operating reserve                       | 150,000          | 150,000          | 150,000          | 150,000          | 150,000          |
| Unrestricted                            | 661,014          | 428,994          | 585,773          | 387,834          | 520,325          |
| <b>Total Net Assets</b>                 | <b>1,591,014</b> | <b>1,358,994</b> | <b>1,515,773</b> | <b>1,317,834</b> | <b>1,450,325</b> |
| <b>Total liabilities and net assets</b> | <b>1,591,014</b> | <b>1,448,276</b> | <b>1,515,773</b> | <b>1,443,335</b> | <b>1,451,455</b> |

**Journal of Rheology**

**Receipts and Disbursements**

| (all amounts, USD)         | 2012<br><u>Budget</u> | 2011<br><u>Projection</u> | 2011<br><u>August</u> | 2011<br><u>Budget</u> | 2010<br><u>Year End</u> |
|----------------------------|-----------------------|---------------------------|-----------------------|-----------------------|-------------------------|
| <b>RECEIPTS</b>            |                       |                           |                       |                       |                         |
| Subscriptions              | 150,000               | 150,166                   | 149,880               | 165,000               | 159,285                 |
| Royalties & Reprint Sales  | 5,500                 | 38,185                    | 38,185                | 4,000                 | 5,337                   |
| Ad Sales                   | 45,000                | 48,547                    | 35,788                | 43,000                | 49,814                  |
| JORO revenue               | 65,000                | 92,893                    | 83,431                | 61,000                | 70,946                  |
| Miscellaneous              | 2,100                 | 2,000                     | 0                     | 2,000                 | 2,105                   |
| <b>TOTAL RECEIPTS</b>      | <b>267,600</b>        | <b>331,791</b>            | <b>307,283</b>        | <b>275,000</b>        | <b>287,488</b>          |
| <b>DISBURSEMENTS</b>       |                       |                           |                       |                       |                         |
| Ads                        | 12,000                | 12,533                    | 8,859                 | 10,000                | 13,180                  |
| Reprints, Single Copy      | 1,800                 | 559                       | 454                   | 2,200                 | 1,382                   |
| Paper, Printing            | 29,000                | 33,042                    | 22,117                | 27,000                | 28,605                  |
| SOR Editorial              | 45,000                | 42,474                    | 28,316                | 36,000                | 46,217                  |
| Production                 | 35,000                | 40,770                    | 27,180                | 39,000                | 36,322                  |
| Fulfillment                | 5,925                 | 5,328                     | 3,438                 | 5,725                 | 5,882                   |
| Distribution               | 22,650                | 21,385                    | 14,256                | 22,700                | 20,855                  |
| Electronic publishing      | 41,000                | 53,139                    | 32,681                | 41,000                | 55,765                  |
| Miscellaneous              | 7,000                 | 7,531                     | 5,495                 | 8,500                 | 6,431                   |
| <b>TOTAL DISBURSEMENTS</b> | <b>199,375</b>        | <b>216,762</b>            | <b>142,795</b>        | <b>192,125</b>        | <b>214,638</b>          |
| <b>Net</b>                 | <b>68,225</b>         | <b>115,030</b>            | <b>164,488</b>        | <b>82,875</b>         | <b>72,850</b>           |

end

Taking the divergence of the surface excess stress tensor and noting that  $\mathbf{I}_s : \mathbf{D}_s = \nabla_s \cdot \mathbf{v}^0$  we obtain

$$\nabla_s \cdot \mathbf{P}^s = \begin{cases} -\left[\sigma + (\kappa^s - \mu^s)(\nabla_s \cdot \mathbf{v}^0)\right](\nabla_s \cdot \mathbf{n})\mathbf{n} + \nabla_s \left[\sigma + (\kappa^s - \mu^s)(\nabla_s \cdot \mathbf{v}^0)\right] \\ + 2\mu^s \nabla_s \cdot \mathbf{D}_s \end{cases} \quad (14)$$

Terms have been grouped such that the first term is a Laplace-Young term directed normal to the interface and is proportional to the surface curvature  $\nabla_s \cdot \mathbf{n}$ , the second term is a Marangoni term that is in the plane of the interface and is related to both gradients in surface tension and the product of the surface viscosities and dilatation rate. Upon further manipulation, the in-plane and normal components of  $\nabla_s \cdot \mathbf{P}^s$  can be determined (Table 2). Examining the result in component form helps to highlight the additional terms that come into play as a consequence of surface curvature. When surfaces are flat, the in-plane shear-curvature term and all normal component terms drop out.

It is rare for interfaces to be purely dissipative, with many surfaces containing elasticity and nonlinearity. While these are not captured in the Boussinesq-Scriven constitutive relation, it nonetheless is a significant first step in modeling interfacial rheological behavior. Although not widely employed, other constitutive relations exist, such as nonlinear models that depend on the invariants of the surface rate of deformation tensor [1], a generalized viscoelastic interface [12], Maxwell-Voigt models [1,32], and Bingham plastic models [1,32].

### Aspects to Consider for Measurement Techniques

Interfaces can undergo different types of deformation, with the three most basic modes being uniform

increases in area (dilatation), simple shear, and planar extension (Fig. 3).

When measuring the mechanical properties of interfaces, the interfacial rheologist usually examines one of these types of rheometric flows, where the surface rate-of-deformation tensor reduces to a simpler form. A comprehensive review of different rheometer designs will not be provided here since this has been done quite extensively [1,33,34,35,36]. Instead we will briefly identify the main types of rheometers for each type of deformation and briefly illustrate the design principles that are guiding their development.

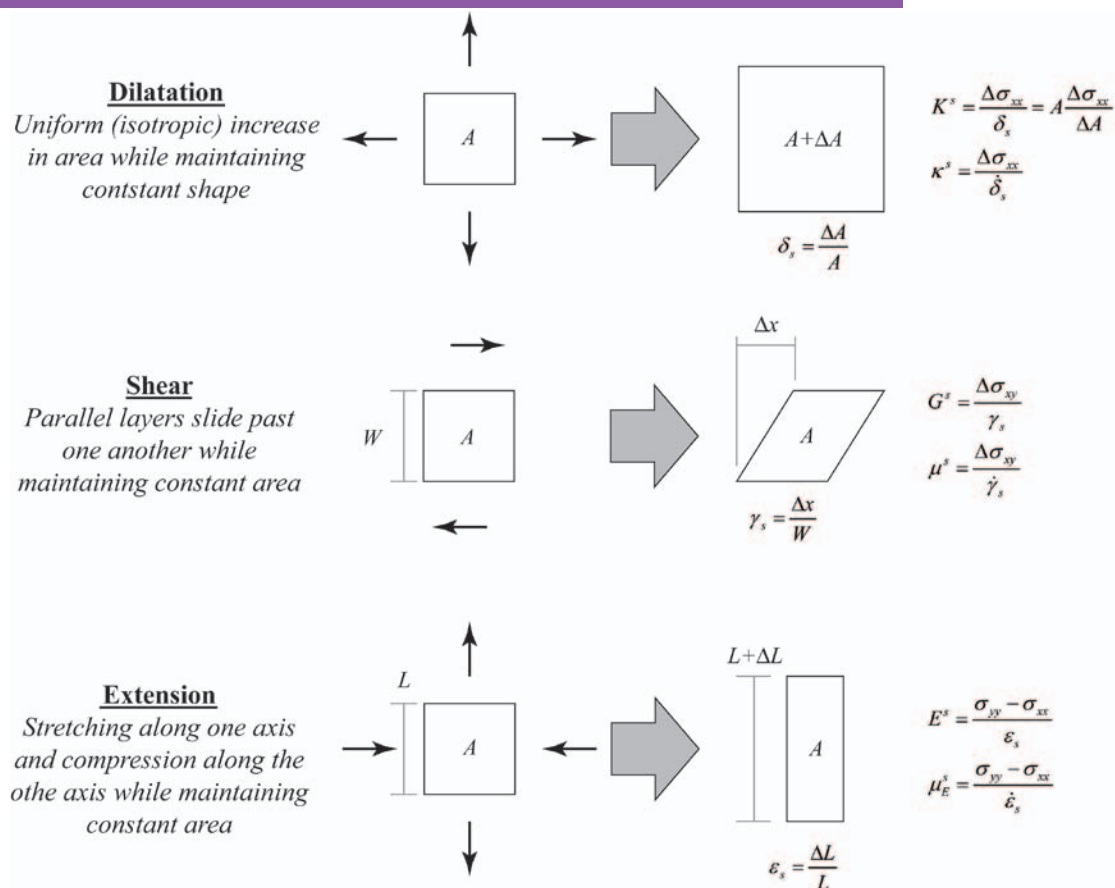
The primary objective in dilatational rheology is to measure the change in interfacial tension with surface area. The surface dilatational modulus,  $K^s$ , is defined as<sup>3</sup>

$$K^s = \frac{d\sigma}{d \ln A} \quad (15)$$

In the case of *insoluble* monolayers, where the surfactant is restricted to the interface, the number of molecules at the interface is constant ( $A\Gamma = \text{const.}$ ). Noting that  $d\sigma = -d\Pi$  (see eqn. 3) the surface dilatational modulus can be rewritten in terms of surface pressure and surface excess concentration as  $K^s = d\Pi/d \ln \Gamma$ . A step change in area will cause a rapid rise in  $K^s$ , followed by a relaxation towards the equilibrium value, which can be determined from the slope of the  $\Pi$ -A isotherm. The rate of approach to equilibrium is determined by the relaxation processes in the film.

**Table 2: Components of  $\nabla_s \cdot \mathbf{P}^s$**

|                                 | In-Plane Components   | Normal Components  |
|---------------------------------|---|--|
| $\nabla_s \cdot \mathbf{P}^s =$ | <i>Marangoni &amp; Gradients in Dilatation</i><br>$\nabla_s \left[ \sigma + \kappa^s (\nabla_s \cdot \mathbf{v}^0) \right]$   | <i>Laplace-Young &amp; Dilatation</i><br>$-(\nabla_s \cdot \mathbf{n}) \left[ \sigma + (\kappa^s - \mu^s) (\nabla_s \cdot \mathbf{v}^0) \right] \mathbf{n}$      |
|                                 | <i>Shear-Diffusive</i><br>$\mu^s (\nabla_s \cdot \nabla_s \mathbf{v}^0) \cdot \mathbf{I}_s$   | <i>Shear-Curvature</i><br>$-\mu^s \left[ (\nabla_s \mathbf{v}^0)^T : (\nabla_s \mathbf{n}) + (\nabla_s \mathbf{n}) : (\nabla_s \mathbf{v}^0) \right] \mathbf{n}$ |
|                                 | <i>Shear-Curvature</i><br>$\mu^s \left[ (\nabla_s \mathbf{n}) \cdot (\nabla_s \mathbf{v}^0) - (\nabla_s \cdot \mathbf{n}) (\nabla_s \mathbf{v}^0) \right] \cdot \mathbf{n}$ |  |



**Figure 3:** Different types of in-plane deformation modes for an interface: dilatation, shear, and extension. Each deformation can be described by a dimensionless surface strain ( $\delta_s, \gamma_s, \epsilon_s$ ). The ratio of the change in interfacial tension/surface stresses that accompanies the strain determines the surface elastic moduli: surface dilatational modulus  $K^s$ , surface shear modulus  $G^s$ , and surface extensional (or Young's) modulus,  $E^s$ . If the strain is varying in time, the ratio of the stress with strain rate with corresponding surface viscosities can be calculated.

For *soluble* monolayers the situation is more complex, as the surfactant can adsorb/desorb from the interface to relieve stress. If the bulk concentration is unaffected by the adsorption/desorption, then for long times any dilatational stress will relax to zero.<sup>4</sup> When the only relevant relaxation process is diffusion between the interface and the bulk, then the complex surface dilatation modulus is [38]

$$K^s = \left( \frac{d\Pi}{d \ln \Gamma} \right)_{eq} \frac{1 + \zeta + i\zeta}{1 + 2\zeta + 2\zeta^2} \quad (16)$$

where  $\zeta^2$  is proportional to a ratio of the experimental

<sup>4</sup>For thin films, where the amount of surfactant in the bulk is limiting, changes in area can give rise to changes in surface tension that do not relax. This is called Gibbs elasticity and the term is used properly in the context of thin films. Note that the Gibbs elasticity depends on the thickness of the film and is generally different than the dilatational modulus. Under some circumstances, however, they can have similar values [37].

time scale ( $1/\omega$ ) and the diffusion timescale based on the depletion depth ( $d\Gamma/dc$ ) and diffusion coefficient,  $D$ :

$$\zeta = \sqrt{\frac{D}{2 \left( \frac{d\Gamma}{dc} \right)^2 \omega}} \quad (17)$$

Under slow deformation  $\zeta$  is large and the dilatational modulus approaches zero. For fast deformations  $\zeta$  goes to zero, and the interface appears insoluble. Under these conditions, the dilatational surface modulus can be determined from the surface equations of state in Table 1,  $K^s = (d\Pi/d \ln \Gamma)_{eq}$ . It is important to note that for higher bulk concentrations as the surface concentration saturates, the slope of the adsorption isotherm,  $d\Gamma/dc$ , asymptotically approaches zero, which has the effect of making  $\zeta$  large. This leads to the somewhat counterintuitive result that the dilatational modulus of soluble surfactants decrease as the bulk concentration



is increased. Additional relaxation modes, such as reorientation, aggregation, monolayer collapse, etc., can be added when there are additional relaxation modes to diffusional exchange [39]. Geometrical effects, such as surface curvature, can affect the diffusive timescales [40], influencing the value of  $\zeta$ , and introducing shape dependence to  $K^s$ . The complexity that arises from diffusion raises a concern as to whether the measured dilatational modulus is truly from the rheology due of the interface or merely the influence of the bulk on the relaxation of surface tension/stress (i.e. an apparent dilatational modulus). This remains an open challenge.

Typical dilatational surface rheometers fall into two major classes: trough or droplet. Trough style dilatational rheometers commonly use a rectangular Langmuir trough and induce area changes by moving the trough barriers. Surface pressure is measured using a Wilhelmy probe (typically a plate or rod). Changing the area of the rectangular trough results in very anisotropic deformations, and the only region that results in uniform dilatational strain is at the center of the symmetrically compressed zone. To overcome this, circular troughs with uniform radial (isotropic) area changes have been designed [41,42]. Drop style dilatational rheometers expand and contract a drop/bubble to induce changes in the surface area and measure the changes in the interfacial tension. If the drop is large enough such that gravity distorts it, the drop profile can be fit to a solution of the Laplace-Young equation to determine the interfacial tension. Since it is not a perfectly spherical shape, changes in volume induce both dilatation and shear in the surface, resulting in a mixed flow that may quantitatively affect results [43]. If the drop is unaffected by gravity and maintains a spherical shape, the pressure inside the drop can be measured directly. When combined with the measurement of the surface radius of curvature, the interfacial tension can be calculated from the Laplace-Young relationship for spherical geometries ( $\sigma = R\Delta P/2$ ).

Similar to drag flow rheometers for bulk materials [44], surface drag flow rheometers place a probe at the interface and measure the force/torque required to move a probe (plate, cone, rod, cylinder, sphere, etc.). A variety of surface shear rheometer designs have been pursued, and there continues to be active research with rotational geometries, such as a bicone, ring, or microdisk, and geometries with linear motion, such as magnetic rods. One of the primary challenges when measuring the shear rheology of interfaces is understanding the effects of the surrounding subphase on the measurement. The total drag force on the probe will experience contributions from both the bulk phases

and the interface. A dimensionless ratio of the surface drag to the bulk phase drag on the probe is called the Boussinesq number[45,46]

$$Bq_{probe} = \frac{F_{surface}}{F_{bulk}} = \frac{\mu^s \frac{V}{W} P_{probe}}{(\mu^I + \mu^{II}) \frac{V}{H} A_{probe}} = \frac{\mu^s}{(\mu^I + \mu^{II})} \frac{HP_{probe}}{WA_{probe}} \quad (18)$$

where  $\mu^I$  and  $\mu^{II}$  are the viscosities of the bulk phases, respectively,  $H$  is a characteristic length scale of the velocity gradient in the bulk (e.g. fluid depth),  $W$  is the characteristic length scale of the velocity gradient in the interface (e.g. gap width),  $P_{probe}$  is the perimeter that makes contact with the surface, and  $A_{probe}$  is the contact area between the probe and surrounding phases. Sensitivity to surface stresses is improved by either using probes with large ratios of the perimeter to contact area ( $P_{probe}/A_{probe}$ ) or increasing the depth to gap width ratio ( $H/W$ ) to increase  $Bq_{probe} \gg 1$ . Recent trends in surface rheometer techniques have sought to increase sensitivity by maximizing  $P_{probe}/A_{probe}$  through the use of slender rods[45,46], rings[47], and microparticles[48,49].

In addition to the probe, it is also important to understand the effect of the subphase on the deformation of the interface. For the simple case of a planar interface (unit normal in the  $z$ -direction) with unidirectional flow in the  $x$ -direction and no surface tension gradients or external body forces, the surface force balance (eqn. 9 with eqn. 12) reduces to

$$\mu^I \left. \frac{\partial v_x^0}{\partial z} \right|_{0^-} - \mu^{II} \left. \frac{\partial v_x^0}{\partial z} \right|_{0^+} = \mu^s \frac{\partial^2 v_x^0}{\partial y^2} \quad (19)$$

Scaling the normal coordinate by  $H$ , the  $y$ -coordinate by  $W$ , and both sides by the sum of the bulk viscosities results in

$$\psi \left. \frac{\partial \bar{v}_x^0}{\partial \bar{z}} \right|_{0^-} - (1-\psi) \left. \frac{\partial \bar{v}_x^0}{\partial \bar{z}} \right|_{0^+} = Bq_{surface} \frac{\partial^2 \bar{v}_x^0}{\partial \bar{y}^2} \quad (20)$$

where  $\psi$  is a dimensionless viscosity ratio between 0 and 1,

$$\psi = \frac{\mu^I}{\mu^I + \mu^{II}} \quad (21)$$

and  $Bq_{surface}$  is the Boussinesq number for the surface

$$Bq_{surface} = \frac{\mu^s}{(\mu^I + \mu^{II})} \frac{H}{W^2} \quad (22)$$

When  $Bq_{surface} \gg 1$  a majority of the momentum is transmitted in the surface layer to the stationary wall, and the velocity gradient will be constant. When  $Bq_{surface} \ll 1$  most of the momentum is transferred to the bulk phases before it reaches the wall, resulting in curved velocity profiles. Ideally the chosen measurement geometry will have both  $Bq_{probe} \gg 1$  and  $Bq_{surface} \gg 1$  so no corrections are required for subphase drag and nonuniform surface deformation rates. To extend the lower limits of sensitivity, correction schemes have been developed that account for the effects of subphase coupling to the probe and the surface [46,50,51]. It is important to review the relevant calculations on subphase coupling to make sure it is being accounted for correctly in your measurements.

A two-dimensional extensional rheometer has also been investigated for tensile measurements on protein surfaces [52,53]. In this device T-shaped optical fiber bars are placed at the interface and the force required to pull them apart is measured as the gap (extensional strain) is increased. What makes extensional deformations difficult is creating a pure flow that does not include dilatation. While a detailed flow analysis that includes subphase coupling and quantifies the degree of mixed flow in this geometry is still needed, this work will hopefully inspire additional efforts in this area of surface rheology. It is well known that when an elastic material is isotropic, then knowledge of any pair of the bulk modulus, shear modulus, Young's modulus, or Poisson's ratio permits the calculation of the other two. A parallel set of relationships holds for 2D materials (Table 2). The ability to measure the surface elastic moduli in three different deformation modes should allow testing to see under what conditions these relationships hold.

### Summary and Outlook

In summary, aspects of interfacial rheology have been reviewed to give an appreciation of some of the unique challenges it presents. Despite appearing simpler than bulk rheology at first glance, working in a lower dimensional space introduces additional complexities, such as viscous coupling with surrounding bulk phases, adsorption/desorption of surfactant from the interface, surface compressibility, effects of surface curvature, and contamination issues. There are several areas that could help advance the field that I highlight below where any progress would be welcomed.

1. To advance the field of interfacial rheology, a standard interface would be very beneficial when comparing results between different measurement

techniques and to assess whether the bulk drag on the probe and surface have been accounted for. The ideal material would be stable with time and have a linear rheology. The best candidates from a stability standpoint would be an insoluble Langmuir monolayer, which would require a trough with adjustable barriers and a means to measure surface tension with compression. Thin films of silicone oil with uniform thickness on water [46] are another contender. The surface viscosity of the calibrating film will be its thickness times the bulk viscosity. Insoluble monolayers and silicone fluids, however, are not amenable for use with drop dilatational techniques since it requires spreading a known amount material from a volatile solvent. Soluble surfactants would be easy to use on all types of surface rheometers, but most surfactants that have a measurable rheology (e.g. proteins) have slow adsorption kinetics (~ hours). There may be more options to consider, such as short peptide chains. As the field of interfacial rheology matures it must eventually coalesce around a standard interfacial material.

2. A subject of debate is whether dilatational viscous effects for soluble surfactants that arise from diffusion alone (eqn. 16) should be considered surface rheology or merely an expression of the bulk coupling to the interface via diffusion. As discussed for shear rheology, the diffusion of momentum into the bulk must be accounted for to measure a surface excess viscosity. In dilatation, interfacial stresses can escape the interface by both momentum and mass transport coupling. A coupled analysis with both momentum and species transport is needed for a surface with a specified interface to identify the conditions where the measured surface dilatational modulus is an effective value or the true intrinsic value of the surface. In addition, the oscillating pendant drop, which is a common platform for dilatational rheology, undergoes mixed dilatation and shear [43]. Quantifying the influence of this mixed deformation would identify the conditions where accurate dilatation measurements can be made.
3. Most commercial finite element codes for use with multiphase flows account for only surface tension effects. Simulation tools that incorporate interfacial rheology at both stable and deforming/moving interfaces would be valuable. Newtonian surfaces that follow the Boussinesq-Scriven constitutive law appear to be the exception rather than the rule. A survey of surface rheological data shows that most interfaces exhibit non-Newtonian behavior. Codes will need to have the ability to handle a

**Table 3:** Relationships between the elastic constants for isotropic solids in 2D[32]and 3D[54]

| 3D Isotropic Solids                                       |                               |                            | 2D Isotropic Solids   |                                       |                                |
|---|-------------------------------|----------------------------|---|---------------------------------------|--------------------------------|
|   | If $K$ and $G$ are known      | If $E$ and $\nu$ are known |   | If $K^s$ and $G^s$ are known          | If $E^s$ and $\nu^s$ are known |
| <b>Bulk Modulus</b><br>$K$                                | -                             | $K = \frac{E}{3(1-2\nu)}$  | <b>Surface Dilatational Modulus</b><br>$K^s$                        | -                                     | $K^s = \frac{E^s}{2(1-\nu^s)}$ |
| <b>Shear Modulus</b><br>$G$                               | -                             | $G = \frac{E}{2(1+\nu)}$   | <b>Surface Shear Modulus</b><br>$G^s$                               | -                                     | $G^s = \frac{E^s}{2(1+\nu^s)}$ |
| <b>Young's Modulus</b><br>$E$                             | $E = \frac{9KG}{3K+G}$        | -                          | <b>Surface Young's Modulus</b><br>$E^s$                             | $E^s = \frac{4K^s G^s}{K^s + G^s}$    | -                              |
| <b>Poisson's Ratio</b><br>$\nu$<br>$-1 \leq \nu \leq 1/2$ | $\nu = \frac{3K-2G}{2(3K+G)}$ | -                          | <b>Surface Poisson's Ratio</b><br>$\nu^s$<br>$-1 \leq \nu^s \leq 1$ | $\nu^s = \frac{K^s - G^s}{K^s + G^s}$ | -                              |

general nonNewtonian interface in addition to the Boussinesq-Scriven constitutive equation.

- Qualitative observation of normal stress differences have been made[19], but what is needed is a technique to quantitate the normal stress differences in the interface. Perhaps the combination of shear with a normal stress transducer, like used in the extensional rheometer [52,53], is a promising path forward.

Interfacial rheology is an active area of research and the reader interested in learning more will find valuable the recent themed issue of *Soft Matter* on the dynamics and rheology of fluid-fluid interfaces[55].

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(Calendar, continued from page 32)

## 2015

*October 2015*

SOR Short Course on Rheology (topic TBA), Baltimore, Maryland USA

*October 2015*

87<sup>th</sup> Annual Meeting of The Society of Rheology, Baltimore, Maryland USA, Kalman Migler and Jai Pathak.

## 2016

*1-5 August 2016*

XVII<sup>th</sup> International Congress on Rheology, Kyoto, Japan, Hiroshi Watanabe (every four years).

## 2017

*February 2017*

88<sup>th</sup> Annual Meeting of The Society of Rheology, location TBA

*October 2017*

89<sup>th</sup> Annual Mtg of The Society of Rheology, Denver, Matt Liberatore

*October 2018*

89<sup>th</sup> Annual Meeting of The Society of Rheology, Raleigh, NC, Saad Khan

*For other meeting notices, see also*

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

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# CALENDAR OF RHEOLOGY CONFERENCES AND COURSES

## 2012

*5-10 February 2012*

Gordon Research Conference on Colloidal, Macromolecular & Polyelectrolyte Solutions, Ventura, California USA, Norman J. Wagner and Andrey Dobrynin ([www.grc.org](http://www.grc.org))

*26-30 March 2012*

Basic Composition of Coatings, short course,

Missouri S&T Coatings Institute, [coatings.mst.edu/](http://coatings.mst.edu/)

*10-13 April 2012*

6<sup>th</sup> International Symposium on Food Rheology and Structure (ISFRS 2012); Zurich, Switzerland, Peter Fischer ([www.isfrs.ethz.ch](http://www.isfrs.ethz.ch))

*10-15 June 2012*

Rheological Measurements Short Course, University of Minnesota, Chris Macosko ([www.cems.umn.edu/rheology](http://www.cems.umn.edu/rheology))

*24-29 June 2012*

MACRO 2012: World Polymer Congress, Blacksburg, Virginia USA - Timothy Long ([www.cpe.vt.edu/macro2012/](http://www.cpe.vt.edu/macro2012/))

*5-10 August 2012*

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

*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, California, USA

*10-14 February 2013*

84<sup>th</sup> Annual Meeting of The Society of Rheology, Pasadena, California, USA, John Brady

*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, Pennsylvania USA

*5-9 October 2014*

86<sup>th</sup> Annual Meeting of The Society of Rheology, Philadelphia, PA USA, Michael Mackay

*(Continues, page 31)*