An Analysis of the Corrections to the Normal Force Response for the Cone and Plate Geometry in Single-Step Stress Relaxation Experiments

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Synopsis

An analysis and experimental results are presented for the transient response in single-step stress relaxation experiments in a cone and plate geometry. Results from experiments on a polyisobutylene solution show deviations from unity of the ratio of the first normal stress difference to the product of the shear strain times the shear stress. These are accounted for by including three important corrections in the analysis. First, it is shown that the finite time required to apply the step introduces errors in the normal stresses which are greater than those for the shear stress. Second, the machine compliance introduces errors in the normal force by causing an increased gap separation which subsequently relaxes as the normal force relaxes. Third, the constrained geometry of the cone and plate results in the compliance errors being "magnified" by some 1600 times, leading to the need for large corrections and apparent violations of the universal relation at long times. Experimental results for extension and compression in a parallel plate geometry are presented for different gap settings and used to demonstrate that the constrained cylinder problem in viscoelastic fluids is similar to that observed in elastic bodies.

INTRODUCTION

For incompressible, simple fluids subjected to single-step stress relaxation histories in simple shear there is a universal relationship, *viz.*, the first normal stress difference divided by the product of the shear strain times the shear stress is equal to unity. The roots of this relationship can be traced to early work by Rivlin¹ in which he described an "elastic stress relaxing" material for which isochronal data in single-step deformation histories

could be treated as though they were data for an elastic material. The result of such a treatment is that the so-called "universal relation" between the shear stress and the first normal stress difference which is valid for elastic bodies² should also hold for the "elastic stress relaxing" material, which is viscoelastic.

There has been sporadic interest over the years in this universal relation for viscoelastic materials. In 1967 Mills³ recognized that it results from the Lodge⁴ elastic liquid theory. Subsequently, Lodge and Meissner⁵ also obtained the universal relation from this elastic liquid theory and Lodge⁶ showed it to be valid for incompressible, simple fluids. We note in passing that the universal relation also results from the BKZ⁷ elastic fluid theory. At the time of Mills'³ derivation he carried out experiments using a Weissenberg rheogoniometer in a cone and plate geometry, the results of which contradicted the universal relation. Although Mills'³ experiments did not agree with the theory, it was subsequently argued by several authors^{5,6,8-11} that errors introduced into the transient normal force response due to finite rigidity or non-zero compliance of the testing machine could significantly affect the observed response. In addition, Kearsley and Zapas¹² noted that predictions of steady-state normal force response from transient shear stress measurements were quite accurate while the prediction of steady-state shear stress response from transient normal force measurements was not. This raised a general question about the validity of normal stress measurements in transient experiments such as start of steady shearing flows and stress relaxation. However, a difficulty existed in explaining the response in stress relaxation experiments which cannot be answered without a quantitative analysis of the errors involved in the cone and plate geometry; *viz.*, there have been prior reports¹¹ and we have observed in our laboratory¹³ the following type of response: at short times the ratio of the first normal stress difference to the product of the shear stress times the shear strain is significantly less than unity, while at long times the ratio becomes significantly greater than one. Although a finite machine rigidity explains (qualitatively) a low normal force at short times due to an increased platen separation in the cone and plate apparatus, it does not readily explain increased normal stresses, and thus a ratio greater than unity, at longer times as the gap is still wider than that of an infinitely rigid machine.

A crude analysis of the problem as an extension superimposed on the shearing deformation simply does not sufficiently correct the observed normal force response to give agreement with the universal relation. However, in parallel plate experiments, we had found^{14,15} for a different PIB solution that the transient normal forced response was independent of plate separation for gaps greater than approximately 2 mm, but at smaller separations the normal force measurements begin to deviate significantly from those obtained at greater gap settings. Again, a simple analysis does not explain the variation at small gaps. As a result, we were led to consider another problem — that of the magnification of the uniaxial modulus in a “constrained” cylinder geometry.^{16–19} An important result of the experiments and analyses presented in the following sections is that the response in the constrained deformation due to the adhesion of the viscoelastic fluid to the surfaces of the cone and plate introduces a large correction to the superimposed extension itself. Even though the extensional deformation superimposed due to the machine compliance is small, the magnification due to the constrained geometry is sufficient (>1600) that, upon appropriate analysis, one can account for the differences between the experimental observations and the universal relation.

In the following sections we describe and analyze the phenomena which contribute to the apparent violation of the “universal relation.” First we describe the errors introduced due to the application of the deformation including the finite rate of the step and overshoot in the step relative to the final value of the deformation. The normal stresses are affected differently than are the shear stresses. The result is that the short time behavior, even for an infinite stiffness machine, can differ from the universal relation. We will ultimately set down the solution to the problem of the machine compliance by recalling the analysis of Zapas and Wineman²⁰ of combined extensional and shearing deformations in viscoelastic materials. This analysis combined with the correction on the uniaxial modulus due to the constrained cylinder geometry and that due to the history of the step introduction results in corrections which are of sufficient magnitude that we will conclude that the data which we have obtained obey the universal relation over the range of experimental parameters investigated here.

Prior to describing the analysis required to correct the normal force data in the cone and plate instrument, we present the experimental results for single-step stress relaxation responses in the cone and plate geometry obtained in our laboratory which show the apparent discrepancy with the universal relation. In addition, experiments in simple extension and compression in the parallel plate geometry using a polymer solution which demonstrate the modulus magnification effect due to the constrained geometry will be described.

EXPERIMENTAL

Materials

The fluid used in this study is a 16% polyisobutylene (PIB) in a white mineral oil (Primol* 355, Exxon Chemicals). We have previously reported results from this fluid for the shear stress response in single-step stress relaxation histories²¹ and note that the results presented here differ slightly (5–10%) from those—a result for which we have no current explanation since the solution was prepared over 20 years ago and we expect that it should be homogeneous.

Rheological Measurements

The experimental apparatus used for our measurements is a Rheometrics* RMS-7200 rheometer for which the electronics used for load cell excitation and signal conditioning have been upgraded using an Analog Devices* 3B subsystem and which has been interfaced with a personal computer for the purpose of data acquisition and control. We carried out experiments using both a cone and plate geometry and a parallel plate geometry. The cone angle was 0.04 radians. In both geometries the plate diameters were 7.2 cm. The parallel plate experiments were carried out with gap settings of 0.24, 0.22, 0.16, 0.12, 0.080, and 0.040 cm.

*Certain commercial materials and equipment are identified in this article to specify the experimental procedure. In no instance does such identification imply recommendation or endorsement by the National Institute of Standards and Technology or that the materials and equipment identified are necessarily the best available for the purpose.

The single-step stress relaxation experiments were performed by introducing a step in two ways. In the shear experiments, a voltage was applied to the RMS-7200 by the computer through the external command connection on the face of the instrument. Instrument overshoot was brought to less than 6% of the total angular displacement by programming a series of steps (3 or 4) in voltage. The exact sequence chosen depended upon the magnitude of the angular displacement. The angular displacement was applied by the original RMS-7200 servomotor controlled by the original servocontrol system. Extension and compression tests were performed by implementing the deformation manually using the knurled knob on the Rheometrics* and measuring the applied deformation using the micrometer on the instrument. The application of the force was initiated on a tone from the computer at which time data acquisition was also started.

The RMS-7200 is an extremely stiff apparatus. We used the 10,000 g-cm/2000 g capacity load cell. Our measurements of the instrument compliance are not accurate, because the displacement of the top of the instrument under a 2 kg weight was less than 1 μm . Similarly, the placement of a 2 kg weight on the load cell results in less than 1 μm of displacement. We will subsequently show calculations of the machine compliance derived from our measurements and analyses which are consistent with these numbers and with measurements reported in the literature for similar instruments.^{11,22}

RESULTS AND DISCUSSION

Presentation of the Data

Uncorrected Shear Stress and Normal Stress Responses in the Cone and Plate Geometry

Figures 1–3 depict double logarithmic plots of the shear stresses $\sigma_{12}(t)$ and normal stress differences, $\sigma_{11}(t) - \sigma_{22}(t)$, for the PIB solution in stress relaxation experiments at strain levels of $\gamma = 1.3, 5.3$, and 10.6 . Note that these figures depict not only the relaxation response, but also the response during the loading portion of the step (dashed lines). Notice from these figures that the step is applied in 0.1 s or less for all deformations. [As an aside, we remark that we also carried out tests at $\gamma = 21.5$.

Fig. 1. Double logarithmic representation of the shear stress and first normal stress difference vs. time in single-step stress relaxation for a 16% PIB solution in the cone and plate geometry. Dashed lines represent the responses during step application. $\gamma = 1.3$. $T = 24.5^\circ\text{C}$.

Surprisingly, the results of these tests did not appear reproducible. Upon closer examination, however, we observed that both the shear stress and the normal stress responses would take on one of two behaviors which differed in magnitude (or time scale) by perhaps a factor of two. Such results are consistent with an instability in the deformation and should be examined in detail in the future.] An interesting feature of the data presented in Figure 3 is the appearance of an abrupt increase in the double logarithmic rate of relaxation in the normal stress response at $\gamma = 10.6$. The analysis presented subsequently accounts for this behavior.

Figure 4 depicts the ratio of $U = (\sigma_{11} - \sigma_{22})/\gamma\sigma_{12}$, that is, the universal relation, for several different values of strain and at times from 0.20 to 35 s. This figure is of great interest in this

Fig. 2. Double logarithmic representation of the shear stress and first normal stress difference vs. time in single-step stress relaxation for a 16% PIB solution in the cone and plate geometry. Dashed lines represent the response during step application. $\gamma = 5.3$. $T = 24.5^\circ\text{C}$.

study. Note that for all of the data, U is less than unity at short times and becomes greater than unity at long times. There is also a possibility that, at the longest times, U decreases towards unity.

*Extension and Compression in the Parallel Plate Geometry:
The Constrained Cylinder Problem*

The constrained cylinder problem can be described as follows: because the sample is not free to move at the boundaries, that is, the end surfaces of the cylinder, the deformation of the material when a uniaxial displacement is applied to the surfaces is not a simple extension or compression. This is most readily seen in rubber samples which are bonded and for which barrelling in compression results. The result is that the forces required to apply

Fig. 3. Double logarithmic representation of the shear stress and first normal stress difference vs. time in single-step stress relaxation for a 16% PIB solution in the cone and plate geometry. Dashed lines represent the response during step application. $\gamma = 10.6$. $T = 24.5^\circ\text{C}$.

even a small apparent deformation are magnified tremendously. The ratio of the apparent modulus E_A to the actual modulus $E = 3G$ (where G is the shear modulus at small strains) in such a geometry has been calculated for elastic solids¹⁶⁻¹⁸ including rubber¹⁹ and has been found to vary approximately with the square of the ratio of the diameter to the height of the cylinder. Experimental results show that the effect can lead to errors in measurement of the elastic modulus in rubber of up to 40% even for values of the diameter to height ratio near unity.²³ (Importantly, the constrained geometry results in a complicated deformation which is not uniaxial compression or extension but rather varies from shear at the adhering surface to the uniaxial deformation at the center of the gap if this latter is large enough. In the following paragraphs it will be seen that the linear analysis,

Fig. 4. Ratio of the first normal stress difference to the product of the shear strain times the shear stress vs. the logarithm of time for a 16% PIB solution at the shear strains indicated. (x) $\gamma = 10.6$; (Δ) $\gamma = 5.3$; ($\bullet$) $\gamma = 1.3$.

which results in a simple magnification of the modulus, is sufficient to describe the constrained cylinder problem as it presents itself in our analysis of the viscoelastic fluid and the normal force errors.)

To our knowledge, there have been no analyses of the constrained cylinder geometry for viscoelastic fluids. To quantify the magnification effect for the PIB solution we carried out extension and compression experiments in the parallel plate geometry using gap settings, h_0 , which ranged from 0.040 to 0.24 cm. In all cases the deformation was calculated as the platen displacement measured using the micrometer on the test machine divided by h_0 . The value of d was always less than 15 μm and the strains were always less than 0.012. The data were analyzed as a function of the diameter to gap ratio, D/h_0 ,

and times from approximately 1 s to 132.5 s. Values of D/h_0 ranged from 30 to 180. Figure 5 depicts the relaxation response as apparent modulus versus t in a double logarithmic representation for these D/h_0 ratios. Also shown is the value of $E(t)$ obtained from small strain shear experiments as $3G(t)$. The responses shown in Figure 5 are corrected for the application of the step by subtracting $t_1/2$ from the total time. This was applied manually, and the step time varied from 0.25 to 3.5 s. In-

Fig. 5. Logarithm of the apparent modulus vs. logarithm of time for a 16% PIB solution in the parallel plate geometry and subjected to uniaxial deformations. Plate diameter was 7.2 cm. Gap settings, h_0 , are indicated beside curves. Data points are for extension (◆), (×), and compression (*), (●), (□), (▽), (△), (○), (+). Lowest curve is the uniaxial modulus determined as $E(t) = 3G(t)$.

terestingly, as the gap became smaller, the deformations became more and more difficult to apply rapidly. In Figure 6 we present isochrones at 1, 10, and 100 s calculated from the data of Figure 5 in a double logarithmic plot of E_A/E versus D/h_0 .

There are several important points to be made from examination of Figures 5 and 6. First, whereas if there were no magnification due to the constraint on the material, the data for E_A at different gaps in Figure 5 would coincide and in Figure 6 all values of E_A/E would be unity. This is not observed for any of the gap settings and the values of E_A/E increase progressively

Fig. 6. Double logarithmic plot of the reduced apparent modulus vs. diameter to height ratio for a 16% PIB solution in uniaxial stress relaxation deformation histories. The values are for isochrones at (Δ) 1, ($\circ$) 10, and ($\square$) 100 s, as indicated. Heavy solid line is interpolated from values obtained by Messner¹⁸ using a finite-difference analysis. The light solid line is an extrapolation from the same values.

as the value of the gap decreases or D/h_0 increases. In our experiments E_A/E varies from approximately 130 at $D/h_0 = 30$ to approximately 6000 at $D/h_0 = 180$. Second, at the largest gap settings ($h_0 = 0.24$ and 0.16 cm) the shapes of the relaxation curves in Figure 5 are nearly the same, the only differences between these curves being the magnitude of the applied stress. Furthermore, these curves have the same shape as does the curve for $E(t)$. On the other hand, at lower values of the gap setting, we observe an apparent increase in the relaxation times for the solution as the relaxation response at short times becomes very flat. Examination of Figure 6 indicates what is happening. The value of E_a/E at D/h_0 values above approximately 100 and short times is much lower than the value given by the Messner¹⁸ finite-difference analysis (solid line in Fig. 6). As the time increases, we find that the data move toward the theoretical line and by 100 s the experimental points nearly coincide with the line even for the highest D/h_0 ratio studied. We will show in a subsequent section that one can account reasonably well for this behavior by considering the machine compliance. Here, it is sufficient to conclude that, as in the case of the elastic cylinder bonded at the ends, the apparent relaxation modulus for a viscoelastic fluid in the constrained geometry of the parallel plate experiment is magnified by several orders of magnitude. At sufficiently small gaps this can affect the apparent relaxation response dramatically.

The Constrained Cone and Plate

In the context of the work discussed above, we also carried out an experiment in simple compression in the cone and plate geometry. A displacement of $5 \mu\text{m}$ was applied to the top platen and the force response was measured. We found that the material response was similar to that obtained in the parallel plate experiments using a gap of 0.080 cm. From this we concluded that the constraint in the cone and plate is the same as that in the parallel plate, but with the effective gap setting being the distance of the cone from the plate at a distance $R/2$ from the center of the cone. In the case of our cone and plate, this distance is 0.0722 cm. We will use this value in the analyses of machine compliance effects in the following section.

**Analysis of the Problem: Relaxation
Experiments in the Cone and Plate Geometry**

*Corrections to the Shear and Normal Force Responses Due to
the Introduction of the Step: Infinite Stiffness Machine*

The universal relation which we are considering here is strictly valid only for an ideal experiment, that is, one in which the step is applied instantaneously. In addition, the testing apparatus must have infinite stiffness. In this section we develop the equations required to account for the strain history actually applied to the material assuming an infinitely stiff machine. In the next section we will deal with the problem introduced by the machine compliance. The interesting result presented here is that, even for the infinitely stiff testing machine, the actual strain history required to apply the step introduces errors in the normal stress relaxation response which differ from those for the shear stress response. This can lead to apparent deviations from the universal relation at short times.

We consider a ramp from zero strain to the deformation at which the relaxation measurements are to be carried out. That is, the material being at rest up to time $\tau = 0$ is subjected to a constant rate of shear, κ , then for times $0 < \tau < t_1$, $\gamma(t) = \kappa\tau$. At t_1 the strain rate becomes zero, then for all $\tau > t_1$, $\gamma(t) = \kappa t_1 = \gamma$. For such a history, the BKZ elastic fluid theory⁷ gives:

$$\sigma_{12}(t) = H(\gamma, t) - \int_0^{t_1} H_*[(1 - \tau/t_1)\gamma, t - \tau] d\tau \quad (1)$$

for the shear stress response and

$$\frac{\sigma_{11}(t) - \sigma_{22}(t)}{\gamma} = \frac{N(t)}{\gamma} = H(\gamma, t) - \int_0^{t_1} (1 - \tau/t_1) H_* \cdot [1 - \tau/t_1)\gamma, t - \tau] d\tau \quad (2)$$

for the normal stress response.

$H(\gamma, t)$ is the response of the shear stress in a single-step stress relaxation experiment, H_* is the time derivative of H and we introduce here the notation $N(t)$ for $\sigma_{11}(t) - \sigma_{22}(t)$. It turns out that in absolute value, the integral in (1) is greater than that in (2). An example calculation can be made assuming that the mean value theorem is a reasonable approximation, in spite of

the nonlinear material behavior. Then (1) and (2) become, after changing variables:

$$\sigma_{12}(t) = H(\gamma, t) + \frac{2t_1 H(\gamma/2, t - t_1/2)}{2t - t_1} \left[\frac{\partial \ln H(\gamma/2, t - t_1/2)}{\partial \ln(t - t_1/2)} \right] \quad (3)$$

$$\frac{N(t)}{\gamma} = H(\gamma, t) + \frac{t_1 H(\gamma/2, t - t_1/2)}{2t - t_1} \left[\frac{\partial \ln H(\gamma/2, t - t_1/2)}{\partial \ln(t - t_1/2)} \right] \quad (4)$$

Thus, one can see that the "correction" term in (4) is half that in (3). At long times both of these terms approach zero. Therefore the ratio of $(\sigma_{11}(t) - \sigma_{22}(t))/\gamma\sigma_{12}(t)$ can be less than unity at short times, even for an infinitely rigid machine.

In our experiments, we found that the actual application of the step included a region which was close to a constant rate of deformation. However, the servocontrol system of the RMS-7200 could not be adjusted to eliminate overshoot, even by applying the command voltage in several steps, as described in the Experimental section. Although the overshoot in the deformation was kept to below 6%, we decided to analyze the material response to the actual applied deformation. Again using the BKZ theory, we calculated the shear stress and the normal stress responses to the actual deformation history. The relevant equations were solved numerically for the overshoots observed experimentally. Interestingly, the overshoot compensates somewhat for the errors introduced in the ratio of $(\sigma_{11} - \sigma_{22})/\gamma\sigma_{12}$ due to the finite step rate. The results of the analysis described here will be used subsequently.

In concluding this section, we note that apparent violations of the universal relation at short times can result from errors introduced due to the specific strain history required to apply the step. Not only does the rate at which the deformation is applied affect the apparent material response, but the amount and duration of any overshoot also has a significant effect on the measured behavior. We remark here that the problem of the finite step rate was solved previously by Zapas and Phillips²⁴ for the shear stress response in a BKZ material. Laun²⁵ solved the problem for the Wagner^{26,27} model. He gave the solution for both the shear and normal stress responses, but did not make the observation made here that the errors introduced affect the apparent

values of the ratio for the universal relation. The next section examines the effects of machine compliance on the observed normal force response.

Corrections to the Normal Force Due to Machine Compliance

The effects of the torsional compliance are negligible for our machine over the time ranges studied, while the effects of the axial compliance on the observed normal force response are quite dramatic. In this case, we find that we must consider the entire history of the gap separation from application of the step, overshoot included, to the long time elastic "recovery" of the test machine as the normal force itself relaxes. What we find is that the axial compliance of the test machine influences the measured normal force over the entire period of measurement.

We first analyze the response in uniaxial extension and compression for the parallel plate apparatus, we then consider the problem in shear deformations in the cone and plate geometry. We signal the reader that in both of these geometries, the amplification effect of the "constrained" cylinder described previously is important.

The Constrained Cylinder Problem in Tension and Compression

For purposes of analysis, we represent the test machine as depicted in Figures 7(A) and (B). Essentially the machine consists of two platens; one on top and one on the bottom. The bottom is attached to the laboratory bench through a load cell whose stiffness is represented by a spring element of rigidity K_1 . The upper platen is attached to a cantilever which is represented by a spring element of rigidity K_2 . In addition, we note that the measurements of platen displacement during the extension and compression experiments were performed using a micrometer attached to the cantilever in a way that the measured displacement captures neither the deflection of the cantilever itself nor that of the load cell. (The reader is referred to the RMS-7200 manual for explicit description of the configuration.) The result is that in our measurements of platen displacement we do not measure the changes in gap separation due to the compliances

Fig. 7. Schematic of test apparatus for cone and plate and parallel plate experiments. (A) Apparatus with no load applied. (B) Apparatus after a displacement, d , has been applied. See text for discussion.

represented by either $1/K_1$ or $1/K_2$. Thus, in the extension and compression experiments, we measure a displacement d which is time independent, while the actual displacement of the platens is $d - \delta(t)$, where $\delta(t)$ is the displacement due to the force times the total compliance of the machine. Then, examining Figure 7(B), the total gap, $h(t)$, in a uniaxially deformed sample is given by:

$$h(t) = h_0 + d - \delta(t) \quad (5)$$

where h_0 is the initial gap separation, d is the applied displacement, and $\delta(t) = F(t)(1/K_1 + 1/K_2) = F(t)C$. $F(t)$ is the force measured by the load cell and $C = 1/K_1 + 1/K_2$ is the machine compliance. As $F(t)$ decays with time, $\delta(t)$ will diminish and the gap will approach a value of $h_0 + d$.

If d is small with respect to h_0 (the case in our experiments), we can use linear viscoelasticity to describe the total thrust response. Assuming that the step, d , is applied instantaneously then $\lambda(\tau) = 1 + (d - \delta(\tau))/h_0$ at all times $\tau > 0$ and $\epsilon(\tau) = (d - \delta(\tau))/h_0$. λ is the stretch and $\epsilon(\tau)$ is the strain. Keeping in mind that the apparent modulus is not the actual modulus but the one which is magnified due to the constrained geometry of deformation, we can write an equation for the stress as a function of the deformation history:

$$\frac{F(t)}{\pi R^2} = \sigma(t) = \varepsilon(t)E_A(t) - \int_0^t [\varepsilon(t) - \varepsilon(\tau)]E_{A*}(t - \tau) d\tau \quad (6)$$

Where $E_A(t)$ is the apparent modulus and the subscript * represents the time derivative. Since $\varepsilon(t) = d/h_0 - F(t)C/h_0$ we can substitute into Eq. (6):

$$\sigma(t) = \frac{d}{h_0}E_A(t) - \frac{\delta}{h_0} \int_0^t [\delta(t) - \delta(\tau)]E_{A*}(t - \tau) d\tau \quad (7)$$

Changing variables in the integral, we get:

$$\begin{aligned} \sigma(t) = & \frac{d}{h_0}ME(t) \\ & - \frac{M}{h_0} \left\{ F(t)E(t)C - \int_0^t [F(t - \xi) - F(t)]E_*(\xi) d\xi \right\} \end{aligned} \quad (8)$$

where $M = E_A/E$ is the magnification factor due to the constrained geometry. When the gap setting, h_0 , is relatively large and at long times, the term in brackets in Eq. (8) is small. In this case the solution looks like the elastic solution and the correction factor, M , can be calculated from the experimental results obtained in the tension, compression and shear measurements reported above. Recalling the long time data of Figure 6 and the data obtained at low values of D/h_0 (large values of h_0), we see that the values of M are indeed close to those reported by Messner¹⁸ from his finite-difference solution to the constrained cylinder problem.

For small values of h_0 and at short times, the term in brackets in Eq. (8) can contribute significantly to the response. Using the mean value theorem to estimate the value of this term we can rewrite Eq. (8) as:

$$\begin{aligned} \sigma(t) = & \frac{d}{h_0}ME(t) - \frac{M}{h_0} \left\{ F(t)E(t)C \right. \\ & \left. - \frac{2[F(t/2) - F(t)]E(t/2)}{t/2} \left[\frac{\partial \ln F(t/2)}{\partial \ln(t/2)} \right] \right\} \end{aligned} \quad (9)$$

For the subsequent analysis of the transient normal stress response in shearing experiments, we need to find both the machine compliance, and the modulus magnification factor, M (we have no way, *a priori*, to know whether or not this value must

equal that of Messner's¹⁸ analysis). We know the relevant stress history, $\sigma(t)$, in Eq. (9) from our measurements. Equation (9) can then be solved iteratively for both C and M .

Because, we found that for large h_0 and long times for all values of h_0 that the value of M which we had measured was close to that reported by Messner,¹⁸ we used this value as an initial guess in our solution of Eq. (9). We also knew from crude measurements that the machine compliance was in the vicinity of ($1 \mu\text{m}/2000 \text{ g}$), and this value was used as an initial guess for C . By iterating Eq. (9) for the tension and compression data at various gap settings we found that a machine compliance value of $0.889 \mu\text{m}/1000 \text{ g}$ corrected the M values for the small gaps and short times to those reported by Messner.¹⁸ The good agreement between the "corrected" experimental values of M and the analytical ones can be seen by examination of Figure 8. We note that in the correction and iteration process we allowed an adjustment to the strain of $\pm 10\%$ due to experimental uncertainty. Also, we could not correct the value of M at 100 s for the smallest gap to the Messner¹⁸ value and simultaneously correct the data for the other times and gaps as well. We do not know whether this is due to experimental uncertainty or to the possibility that the Messner solution, as extrapolated (light line in Fig. 8) to the largest values of D/h_0 , is not valid for this fluid.

The values of M and C determined from the analysis just described are those used for the subsequent analysis of the transient normal force response in the cone and plate geometry. We add that the value of $M = 1600$ which we use below is that corresponding to the value in a parallel plate geometry with the height (gap) being equal to the distance of the cone from the plate at the midpoint between the center and edge of the plate, that is, where $r = R/2$. In our cone and plate geometry this corresponds to an effective gap of 0.0722 cm ($D/h_0 = 99.7$).

The Normal Force Relaxation Response for Simple Shear in the Cone and Plate Geometry

For the analysis of the transient response in the cone and plate geometry for a machine of finite stiffness, we took the solution of Zapas and Wineman²⁰ for a cylinder subjected to simultaneous torsion and extension. This solution assumes a BKZ-type consti-

Fig. 8. Double logarithmic plot of the reduced apparent modulus vs. diameter to height ratio for a 16% PIB solution in uniaxial stress relaxation histories. Lines are as described in Figure 6. Points are for data depicted in Figure 6 but corrected for machine compliance effects as described in text. $\circ$, 1 s, 10 s; $\square$, 100 s.

tutive equation for the material, which we assume to be a reasonable approximation for this type of deformation. We further assume that the displacement resulting from the axial motion due to the machine compliance is small relative to the effective gap (0.0722 cm).

In our analysis we used the measured deformation history in shear including the finite rate step and the overshoot. The axial deformation was calculated from the measured normal force response and the machine compliance determined as described in the previous section. The strain history can then be described

as follows:

$$\left. \begin{aligned} \gamma(\tau) &= 0 \\ \varepsilon(\tau) &= 0 \end{aligned} \right\} \tau \leq 0$$

$$\left. \begin{aligned} \gamma(\tau) &= \kappa\tau \\ \varepsilon(\tau) &= N(\tau) \cdot C \end{aligned} \right\} 0 \leq \tau \leq t_1$$

$$\left. \begin{aligned} \gamma(\tau) &= \kappa t_1 = \gamma \\ \varepsilon(\tau) &= N(\tau) \cdot C \end{aligned} \right\} t_1 \leq \tau$$

The shear stress response can be obtained by numerical solution of the BKZ equations for the measured deformation history. The corrections for the normal force response can be obtained in a similar fashion. Here we write down the relevant normal stress equations to emphasize the important parameters which determine the errors in the response. If we define the single-step normal stress response as $N_1(\gamma, t)$ then the difference between the measured response $N(t) = [\sigma_{11}(t) - \sigma_{22}(t)]$ and $N_1(\gamma, t)$ is:

$$N(t) - N_1(\gamma, t) = \frac{-2CM\pi R^2}{h_0} \left\{ \frac{3H(\gamma, t)}{\gamma} N(t) - \int_0^t [N(t) - N_1(\gamma, t - \xi)] E_*(\xi) d\xi \right\} \quad (11)$$

where $H(\gamma, t)/\gamma$ is the nonlinear shear modulus. Numerical solution of Eq. (11) to the actual applied force history gives the correction to the apparent normal forces. The shear stress corrections for the finite rate step and overshoot were obtained as described previously. We have applied these corrections to the previously described data for the ratio $(\sigma_{11} - \sigma_{22})/\gamma\sigma_{12}$. The results are presented in Table I. We can see that the corrected ratio is close to unity at all times and strain levels investigated here. Therefore, we conclude that the universal relation is valid for the range of experimental conditions investigated in this study.

SUMMARY

We have presented data on the ratio of the first normal stress difference to the product of the shear strain times the shear stress in a cone and plate geometry for a PIB solution. The un-

TABLE I
Comparison of Experimentally Observed and Corrected Values
of $[\sigma_{11}(t) - \sigma_{22}(t)]/\gamma\sigma_{12}(t)$ for Stress Relaxation Experiments on
a 16% Polyisobutylene Solution at Different Strain Levels

Strain, γ	Time/s	$[\sigma_{11}(t) - \sigma_{22}(t)]/\gamma\sigma_{12}(t)$	
		Observed	Corrected
1.3	0.2	0.61	1.00
	0.4	0.70	.99
	1	0.79	.99
	2	0.86	1.00
	4	0.91	1.00
	10	1.01	1.00
	20	1.06	1.00
	35	1.10	1.01
5.3	0.2	0.70	1.00
	0.4	0.79	1.00
	1	0.89	0.99
	2	0.93	1.02
	4	1.02	0.97
	10	1.09	0.99
	20	1.11	0.98
	35	1.08	1.01
10.6	0.2	0.47	0.86
	0.4	0.68	1.00
	1	1.01	1.01
	2	1.10	1.01
	4	1.18	1.02
	10	1.22	0.98
	20	1.19	1.01
	35	1.12	1.00

corrected results are in apparent disagreement with the universal relation for which this ratio should be unity. Specifically, the ratio is found to be less than unity at short times, increasing to values greater than unity at longer times.

In developing an analysis to the problem of the transient response in relaxation experiments for the cone and plate geometry, we were led to carry out experiments in a parallel plate geometry that demonstrate that the apparent magnification of the modulus which occurs in solids when the diameter to height ratio is large and the ends of the specimen are constrained, also occurs in viscoelastic fluids. This magnification effect was found to be in excess of 10^3 at gap settings of less than 0.08 cm. It is

suggested that this sort of amplification may have important consequences for interpretation of surface force measurements on viscoelastic fluids.²⁸

Importantly, results from our analysis indicate that the constrained cylinder magnification effect appears to be a major contributor to errors in the transient normal force response in shear stress relaxation histories for the cone and plate geometry. This effect serves to reduce the early time normal force response even for very stiff machines. It also contributes to the long time deviations from unity of the ratio of the normal stress to strain times the shear stress.

Another important result from the analysis is that, even if the testing apparatus was infinitely rigid, measurements of the ratio given by the universal relation can be less than unity. This is because the correction due to the finite time required to introduce the step is larger for the normal stresses than for the shear stress. We also included the effect of a small but finite overshoot in the application of the deformation in our analysis. Although the analysis is based upon the BKZ theory of an elastic fluid, we do not anticipate that our results are significantly modified by this choice of constitutive models. This is primarily because the BKZ theory, though not reliable in certain unloading histories, works very well in constant rate and in histories for which the deformation is always increasing.

In conclusion, we are able to correct our measured values of the ratio of the first normal stress difference to the product of the shear strain times the shear stress over the entire range of measurement times (0.2 to 35 s). We find no reason to believe that the universal relation is not valid. Furthermore, literature reports of deviations from the universal relation need to be analyzed more carefully, taking into account the factors described and analyzed here to determine whether or not real deviations from the universal relation do exist. Finally, we note that, to our knowledge this is the first analysis of this problem which quantitatively corrects the transient normal stress response using all of the factors described here. Because the procedure is relatively simple and can be carried out using a personal computer, it should extend the range of measurements possible in the cone and plate geometry.

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