Stress-controlled oscillatory flow initiated at time zero: A linear viscoelastic analysis

Hassager, Ole

Published in:
Journal of Rheology

Link to article, DOI:
10.1122/1.5127827

Publication date:
2020

Document Version
Peer reviewed version

Citation (APA):

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.
Stress-controlled oscillatory flow initiated at time zero: 
A linear viscoelastic analysis

Revision December 5, 2019.

Ole Hassager
Danish Polymer Center
Department of Chemical and Biochemical Engineering
Technical University of Denmark
DK 2800 Kongens Lyngby
Denmark

Abstract

In a recent article [1] Lee et al. consider the start-up of stress-controlled oscillatory flow both theoretically and experimentally. In particular they derive an analytical expression for the non-zero value around which the resulting strain (relative to the configuration before start-up) ultimately oscillates. Their derivation is based on the concept of recovery rheology in which strain is decomposed into a sum of recoverable and unrecoverable components. Here the same problem is treated based directly on the general theory of linear viscoelasticity. In this analysis a transiently decaying contribution emerges that is not present in the Lee expression. That contribution is important since it gives an assessment of the timescale on which steady time-periodic oscillatory flow is established.

Introduction

The classical method for analysing small amplitude oscillatory flow is to wait until steady time-periodic oscillations have been established and then use Fourier transformation to obtain the complex modulus \( G^* = G' + iG'' \) or the complex compliance \( J^* = J' - iJ'' \). The advantage of restricting consideration to the periodic flow alone is that Fourier transformation is straightforward to implement, and that it is easy to go from the complex modulus \( G^* \) to \( J^* = 1/G^* \) [2]. The disadvantage is that any information on the strain measured from some initial configuration is lost. Lee et al. [1] define zero strain as the state before any flow has occurred and consider the resulting flow problem to extract information on the zero shear-rate viscosity from the resulting strain shift. In this connection they call attention to the following intriguing statement by Pipkin [3]: “Show that if a fluid is
subjected to a stress history \( \sigma(t) = H(t) \sin(\omega t) \), then after a long time the shear oscillates about a non-zero value”. Pipkin left it as an exercise for the reader to solve. Before proceeding to a quantitative analysis it is worthwhile to note, that liquids, as opposed to solids, have no unique stress-free shape to which they will ultimately recover if left unstressed. Liquids respond with rates of strain rather than with strain to applied stress. Thus while the strain in a viscoelastic solid would indeed at long time oscillate around zero (as observed experimentally by Lee et al.) one would not \textit{a priori} expect the same for a liquid. The purpose of this note is provide a quantitative analysis of the Pipkin problem on the basis of linear viscoelasticity. In this process, the Lee expression for the long-time behavior is re-derived (albeit in a different way) and the timescale on which it is approached is analyzed. In the spirit of Pipkin, the preferred method is that of integral transformations but numerical methods are employed where no other path seems navigable. In closing a remark will be made on complex materials that are slowly changing over time.

**Analysis**

Consider a liquid described by the general equation of linear viscoelasticity [4, 5]

\[
\sigma(t) = \int_{t'=\infty}^{t} G(t-t') \dot{\gamma}(t') dt'
\]

(1)

where \( \sigma \) is the shear component of the stress, \( G(t) \) the relaxation modulus and \( \dot{\gamma} \) the strain rate. For simplicity subscripts are omitted on the tensors involved. The object of the following is to find the strain rate \( \dot{\gamma}(t) \) and corresponding strain \( \gamma(t) \) for \( t \in [0; \infty[ \) subject to the the forcing function

\[
\sigma(t) = \sigma_0 H(t) \sin(\omega t + \psi)
\]

(2)

The inclusion of the phase shift \( \psi \) is a generalization of the Pipkin problem due to Lee et al. [1]. The phase shift \( \psi \) is in principle arbitrary, but the attention here will be on \( \psi \in [0; \pi/2] \) with \( \psi = 0 \) corresponding to a pure sine function and \( \psi = \pi/2 \) a cosine function. The Heaviside step function \( H(t) \) is omitted in [1], but is included here to distinguish the resulting start-up problem from the steady time-periodic oscillations that would result from the familiar and much simpler forcing function \( \sigma_0 \sin(\omega t) ; t \in ]-\infty; \infty[ \). Equations 1 and 2 form a linear Volterra integral equation for \( \dot{\gamma}(t) \). In the following, that flow problem will be referred to as the Pipkin problem irrespective of the value of \( \psi \).
The Pipkin problem is readily solved by Laplace transformation. Let

\[ x(s) = \int_{t=0}^{\infty} \exp(-st)\sigma(t)dt, \quad g(s) = \int_{t=0}^{\infty} \exp(-st)G(t)dt \] (3)

and

\[ \dot{y}(s) = \int_{t=0}^{\infty} \exp(-st)\gamma(t)dt, \quad y(s) = \int_{t=0}^{\infty} \exp(-st)\gamma(t)dt \] (4)

where \( \gamma(t) = \int_{t'=0}^{t} \dot{\gamma}(t')dt' \). It follows that \( y(s) = (1/s)\dot{y}(s) \). For later use note that the zero shear-rate viscosity \( \eta_0 \) is simply related to the Laplace transform of the relaxation modulus

\[ \eta_0 = \int_{t=0}^{\infty} G(t)dt = g(0) \] (5)

where it has been assumed that the integral in Eq.5 exists, i.e. that the material is a liquid.

Note also [7] for later use, that the complex modulus

\[ G^*(\omega) = i\omega \int_{t=0}^{\infty} G(t) \exp(-i\omega t)dt = i\omega g(i\omega) \] (6)

From the convolution theorem it follows that the Laplace transformation of Eq.1 reads

\[ x(s) = g(s)\dot{y}(s) \] (7)

Moreover by simple integration

\[ x(s) = \frac{\sigma_0}{s^2 + \omega^2} (\omega \cos \psi + s \sin \psi) \] (8)

It follows that

\[ y(s) = \frac{\sigma_0}{s(s^2 + \omega^2)} (\omega \cos \psi + s \sin \psi) \frac{1}{g(s)} \] (9)

To proceed from here it is convenient to establish some properties of the function \( g(s) \). Assume for example that the relaxation modulus may be

\(^1\)The reference state \( (t = 0) \) is omitted in the notation for strain.
represented by a multi-mode Maxwell model with discrete relaxation times \( \tau_i, i = 1, \ldots, n \) and associated viscosities \( \eta_i \) as follows

\[
G(t) = \sum_{i=1}^{n} \frac{\eta_i}{\tau_i} \exp(-t/\tau_i); \quad g(s) = \sum_{i=1}^{n} \frac{\eta_i}{1 + s\tau_i} \tag{10}\]

The function \( y(t) \) may now be obtained as the inverse Laplace transformation of \( y(s) \). For this purpose consider the poles of \( y(s) \) given by

1. \( s = 0 \)
2. \( s = \pm i\omega \)
3. The zeroes of \( g(s) \)

The contribution from \( s = 0 \) is obtained is obtained as \( \lim_{s \to 0} sy(s) \):

\[
\gamma_{\infty} = \frac{\sigma_0 \cos \psi}{\omega g(0)} = \frac{\sigma_0 \cos \psi}{\omega \eta_0} \tag{11}\]

as stated correctly in [1] (where it is denoted \( \gamma_S \)).

To obtain the contribution from \( s = \pm i\omega \) the first step is to evaluate the function \( f(s) = (\omega^2 + s^2)y(s) \) at the point \( s = i\omega \):

\[
f(i\omega) = \sigma_0 (\sin \psi - i \cos \psi) \frac{1}{g(i\omega)} \tag{12}\]

Now use the relation in Eq. 6 and reformulate the expression for \( f \) in terms of the complex compliance \( J' - iJ'' = J^* = 1/G^* \) as follows

\[
f_i = \sigma_0 \omega (J' \sin \psi - J'' \cos \psi) \tag{13}
\]
\[
f_r = \sigma_0 \omega (J' \cos \psi + J'' \sin \psi) \tag{14}\]

where \( f_i \) and \( f_r \) are, respectively, the imaginary and real parts of \( f \). The combined contribution from the two poles is then given [6] as

\[
\gamma_p(t) = \frac{1}{\omega} (f_i \cos \omega t + f_r \sin \omega t)
= \sigma_0 (J' \sin(\psi + \omega t) - J'' \cos(\psi + \omega t)) \tag{15}\]

The subscript \( p \) on \( \gamma \) signifies the periodic part of the signal.
Finally the contributions from the poles (if any) corresponding to the zeros of 
\( g(s) \) need to be considered. Note first of all, that the function \( g(s) \) itself has 
a series of singularities at each of the points \( s = -1/\tau_i, \ i = 1 \cdots n \). Outside 
of the singularities
\[
\frac{dg}{ds} = -\sum_i \frac{\eta_i \tau_i}{(1 + s \tau_i)^2} < 0 
\] (16)
Therefore, if all \( \tau_i \) are different and arranged in the order of ascending mag-
nitude it follows that a root, \( s_i \) is found in each of the intervals
\[
-1/\tau_i < s_i < -1/\tau_{i+1} 
\] (17)
This amounts to \( n - 1 \) poles all on the negative real axis. Hence we may 
define the positive retardation times \( \lambda_i = -1/s_i, \ i = 1, 2 \cdots n - 1 \) arranged 
as follows:
\[
\tau_i < \lambda_i < \tau_{i+1} 
\] (18)
The retardation times describe the creep compliance spectrum in the same 
way that the relaxation times describe the relaxation spectrum \([7, 5]\). Or in 
other words, while the retardation times scale the strain response to stress, 
the relaxation times scale the stress response to strain. There is one fewer 
retardation time than relaxation time. Thus if \( n = 1 \) (the single mode 
Maxwell model) there are no poles on the negative real axis and therefore no 
retardation times.
At any rate, for \( n \geq 2 \) we have contributions from a series of first order 
poles \( s = -1/\lambda_j \) on the negative real axis. The total contribution may 
be obtained as the sum of the residues of \( g(s) \exp(st) \) at each of the poles. 
Close to a given pole \( s_j = -1/\lambda_j \), the function \( g(s) \) may be expanded as
\[
g(s) = (s + 1/\lambda_j)g'(-1/\lambda_j) + \cdots 
\] Hence we have the contributions
\[
\gamma_t(t) = \sigma_0 \sum_{j=1}^{n-1} \frac{(\omega_\lambda_j \cos \psi - \sin \psi) \exp(-t/\lambda_j)}{(1 + (\lambda_j \omega)^2)} \sum_{i=1}^{n} \frac{\eta_i}{(\lambda_j - \tau_i)^2} 
\] (19)
The subscript \( t \) on \( \gamma \) indicates that this contribution is a transient term that 
ultimately decays to zero. The final result for the Pipkin problem is then
\[
\gamma(t) = \gamma_\infty + \gamma_p(t) + \gamma_t(t) 
\] (20)
where the ultimate strain shift, the periodic response and the transient re-
response are given by Eqs. 11, 15 and 19 respectively. While this general
formula may be used to evaluate the strain for all \( \psi \in [0; \pi/2] \) and all \( t \in [0; \infty[ \), the strain immediately after imposition of the stress signal is most conveniently evaluated from the Laplace transform:

\[
\gamma(0+) = \lim_{t \to 0^+} \gamma(t) = \lim_{s \to \infty} s y(s) = \frac{\sigma_0 \sin \psi}{\sum_{i=1}^{n} \eta_i/\tau_i} = \frac{\sigma_0 \sin \psi}{G(0)}
\]  

(21)

Thus for \( \psi = 0 \) the strain is continuous at \( t = 0 \). This is reasonable, since the stress is continuous at \( t = 0 \) for the sine function. The maximum strain jump for \( t = 0 \) is obtained for imposed cosine stress, for which on the other hand the strain shift is zero.

**Comparison with the Lee expression**

It is now possible to compare the solution to the Pipkin problem with the expression stated by Lee et al. [1]:

\[
\gamma_{\text{Lee}}(t) = \sigma_0 \left( \frac{\cos \psi}{\omega \eta_0} + J' \sin(\omega t + \psi) - J'' \cos(\omega t + \psi) \right)
\]  

(22)

Clearly the Lee expression is the sum of the ultimate strain shift and the periodic solutions in Eq.20, but the transient part is missing. In other words the Lee expression describes the asymptotic behavior of the Pipkin problem after all transient contributions have died out. This is also the regime in which their experimentation and data analysis is performed. In the following Eq. 22 will be referred to as the asymptotic expression. Also the two expressions are identical for the single mode Maxwell model since there is no retardation time for that model.

**Example 1: Two-mode Maxwell model**

The absence of a retardation time for the single mode Maxwell model may be understood without recourse to Laplace transformation. The single mode Maxwell model is special since it may be formulated as an explicit expression for the strain-rate:

\[
\dot{\gamma}(t) = \frac{1}{\eta_1} \left( \sigma(t) + \tau_1 \frac{d}{dt} \sigma(t) \right)
\]  

(23)

In the universe of mechanical analogies[2] this is interpreted as the deformation of a dashpot and a spring connected in series. Thus the single-mode Maxwell model has a clear distribution of the strain rate into a sum of an irrecoverable part from the dashpot (the first term) and a recoverable part from the spring (the second term). If the force is removed, the elastic deformation is immediately recovered in full. To obtain the strain as function of
Figure 1: Strain (full lines) and mean values (dashed lines) for a two-mode Maxwell model subjected to Pipkin’s forcing function, Eq. 2 with $\psi = 0$. Parameters in consistent units: $\sigma_0 = 1$, $\eta_1 = 1$, $\eta_2 = 10$, $\tau_1 = 0.01$, $\tau_2 = 10$, (i.e. $\lambda \approx 0.9$). Blue: Full solution (Eqs. 27, 28, 29 and 30); Red: Asymptotic expression (Eqs. 22, 29 and 30). Left: $\omega = 10$, Right: $\omega = 50$. The black dots that overlap the blue line (left) is the result of a numerical solution of the Volterra equation.

time in the present problem beware that the stress in Eq. 2 is discontinuous for $\psi \neq 0$. Therefore the time derivative must be expressed as

$$\frac{d\sigma}{dt} = \sigma_0 \left( \delta(t) \sin(\omega t + \psi) + H(t) \omega \cos(\omega t + \psi) \right)$$  \hfill (24)

where $\delta(t)$ is the Dirac delta function. Now the strain is obtained simply by insertion of Eqs. 2 and 24 in Eq. 23 and integration to get

$$\gamma(t) = \int_{t'=0}^{t} \dot{\gamma}(t') dt'$$

$$= \frac{\sigma_0}{\omega \eta_0} \left( \cos \psi - \cos(\omega t + \psi) + \omega \tau_1 \sin(\omega t + \psi) \right)$$  \hfill (25)

which is exactly of the form of both Eqs. 20 and 22 since $J' = \tau_1/\eta_1$ and $J'' = 1/(\omega \eta_1)$.

With more spring-dashpot combinations in parallel however, the multi-mode Maxwell model does not allow for instantaneous recovery of the elastic strain. In a recovery experiment some of the elastic energy in the springs will be dissipated in the dashpots during recovery. It is this dissipation process that
gives rise to the retardation times.

The first illustration of the full solution of the Pipkin problem in Eq. 20 therefore, concerns the simplest model with a retardation time namely the two-mode Maxwell model. Given that the idea of Lee et al. is to extract the zero-shear-rate viscosity from the strain shift, it seems natural to use the Pipkin forcing function with $\psi = 0$ to obtain the maximum value of the shift, but an arbitrary $\psi$ is retained here for completeness. The single retardation time for the two-mode Maxwell model is given as

$$\lambda = \frac{\eta_2 \tau_2 + \eta_1 \tau_1}{\eta_1 + \eta_2}$$ (26)

By inserting that value in the formalism above one arrives after some manipulations at

$$\gamma(t) = \sigma_0 \frac{\cos \psi}{\omega(\eta_1 + \eta_2)} + \sigma_0 (J'(\omega) \sin(\psi + \omega t) - J''(\omega) \cos(\psi + \omega t)) + \gamma_t$$ (27)

where

$$\gamma_t(t) = \sigma_0 \frac{(\omega \lambda \cos \psi - \sin \psi) \eta_1 \eta_2 (\tau_1 - \tau_2)^2}{(1 + (\lambda \omega)^2)(\eta_1 + \eta_2)^2(\tau_1 \eta_2 + \tau_2 \eta_1)} \exp(-t/\lambda)$$ (28)

and for the 2-mode Maxwell model:

$$J'(\omega) = \frac{(\eta_1 \tau_1 + \eta_2 \tau_2) + (\eta_1 \tau_2 + \eta_2 \tau_1) \tau_1 \tau_2 \omega^2}{(\eta_1 + \eta_2)^2 + (\eta_1 \tau_2 + \eta_2 \tau_1)^2 \omega^2}$$ (29)

$$J''(\omega) = \frac{1}{\omega} \frac{(\eta_1 + \eta_2) + (\eta_1 \tau_2^2 + \eta_2 \tau_1^2) \omega^2}{(\eta_1 + \eta_2)^2 + (\eta_1 \tau_2 + \eta_2 \tau_1)^2 \omega^2}$$ (30)

The following features may be seen from Eqs. 27, 28, 29 and 30. First of all the steady time-periodic motion is established only after some time (unless either $\eta_1 = 0$, $\eta_2 = 0$ or $\tau_1 = \tau_2$ in which situation the 2-mode model is really just a disguised single mode model). Secondly it may be shown that $\gamma(0) = 0$ for $\psi = 0$, in agreement with Eq. 21. That is to be expected on physical grounds as well, since the stress has been zero for all negative time and is still zero at time zero. Neither of these two features, however, are present in the asymptotic expression in Eq. 22. The difference is illustrated for a specific choice of parameters in Figure 1. The full lines are the predictions by the two models. The dashed lines represent the respective predictions for the mean values obtained by omitting the oscillatory terms. For $\omega = 10$ (left) the
steady strain shift becomes $\gamma_{\infty} \approx 9.0 \times 10^{-3}$. After three oscillations, the average mean is still about 100% above $\gamma_{\infty}$. For $\omega = 50$ (right) $\gamma_{\infty} \approx 1.8 \times 10^{-3}$. At this higher frequency the approach to steady oscillation takes about the same time, but now more oscillations are needed.

For multi-mode Maxwell models the steady oscillation is approached exponentially as $\exp(-t/\lambda_{n-1})$ with $\lambda_{n-1}$ being the longest retardation time. Given that the longest retardation time is smaller than the longest relaxation time, it may be argued that steady time-periodic oscillations are established faster with imposed stress than with imposed strain. But the question may be asked if this advantage is specific to imposed oscillatory stress or if it may occur also for other stress controlled protocols. To answer this question it is illustrative to consider the pure cosine stress recommended by Ewoldt [10] and specialize to the zero frequency case.

**Creep after imposition of constant step stress.**

The general formula in Eqs 20, 11, 15 and 19 includes the ordinary creep after imposition of constant stress $\sigma(t) = \sigma_0 H(t)$. To see this, specialize to $\psi = \pi/2$ and take the limit as $\omega \to 0$. In this process, note that for small frequencies $J' = J_0' + \cdots$ where $J_0' = \int_0^\infty G(s)sds/\eta_0^2$ is the steady state compliance and $J'' = 1/(\eta_0\omega) + \cdots$. The general formula then yields

$$
\gamma(t) = \sigma_0 \left( J_0' + \frac{t}{\eta_0} - \sum_{j=1}^{n-1} \frac{\exp(-t/\lambda_j)}{\sum_{i=1}^{n} \frac{\eta_i\tau_i}{(\lambda_j-\tau_i)^2}} \right) \tag{31}
$$

An alternative formulation may be obtained with the aid of Eq 21

$$
\gamma(t) = \sigma_0 \left( J_0 + \frac{t}{\eta_0} + \sum_{j=1}^{n-1} \frac{1 - \exp(-t/\lambda_j)}{\sum_{i=1}^{n} \frac{\eta_i\tau_i}{(\lambda_j-\tau_i)^2}} \right) \tag{32}
$$

where $J_0 = 1/G(0)$. This second form is immediately recognizable as the expression obtained for creep by other techniques [9, 8]. From the expressions above, it is seen that the approach to the permanent strain shift in imposed oscillatory stress and the approach to steady flow after imposed constant stress are both delayed by exactly the same spectrum of retardation times. The fact that the approach to steady flow is faster for imposed stress is certainly an argument for imposed stress protocols. In fact it carries over to non-linear extensional flows as well [11, 8].
Example 2: Power law relaxation.
The second illustration of the full solution to the Pipkin problem concerns a complex material with a power law relaxation function. For this purpose consider the Segalman relaxation function ([4] p. 285)

\[ G(t) = \frac{\eta_0/\tau}{\Gamma(1-n)} \left( \frac{\tau}{t} \right)^n \exp(-t/\tau) \]
\[ g(s) = \eta_0 (1 + \tau s)^{n-1} \]  \hspace{1cm} (33)

where \( \eta_0 \) is the zero-shear-rate viscosity, \( \tau \) is a time constant and \( n \in [0; 1] \) is a parameter. For \( n = 0 \) it reduces to the single mode Maxwell spectrum, while for \( n = 1/2 \) and \( n = 2/3 \) is similar to the Rouse and Zimm spectra respectively as illustrated in Figure 2. For simplicity the following is restricted to the original Pipkin problem (\( \psi = 0 \)) that has the maximum strain shift. The strain shift may be obtained by inserting the expression for \( g(s) \) above into Eq.9 whereby \( \gamma_{\infty} = \lim_{s \to 0} s \gamma(s) = \sigma_0/(\eta_0 \omega) \) as expected [1]. While the Laplace transform leads directly to the strain shift, it is not convenient for the complete solution. As an alternative, the expression for \( G(t) \) is inserted directly into Eq.1 together with Eq.2 and the Volterra integral equation is solved numerically. Time is discretized into \( N \) equal-sized intervals of length \( \Delta t \). The strain rate is assigned at the midpoints of each interval, while the strain is assigned at the end-points. Most of the integral is evaluated by the mid-point rule, while the treatment of the integral from \( t - \Delta t \) to \( t \) depends on the behavior of \( G(s) \) at the origin. For \( G(0) \) bounded the mid-point rule

![Figure 2: Complex moduli \( G' \) (full red line) and \( G'' \) (dashed blue line) both normalized by \( \eta_0/\tau \) as function of \( \tau \omega \) for the relaxation function in Eq.33. Left: \( n = 1/2 \). Right \( n = 2/3 \).](image-url)
is retained, while for $G(0)$ unbounded, an analytical approximation is employed. The method is verified by comparison with the exact solution for the Maxwell model in Figure 1 left where the black dots represent the numerical solution with $N = 10^4$. The strain for the as function of time is illustrated in Figure 3 (in blue) and compared with the asymptotic expression (in red). The strain for the as function of time is computed as

$$\gamma(t) - \sigma_0 \left( \frac{1}{\eta_0 \omega} + J'(\omega) \sin(\omega t) - J''(\omega) \cos(\omega t) \right)$$

where $\gamma(t)$ is the numerical solution and $J'$ and $J''$ are evaluated from Eq. 33. The difference between the dashed blue line and the dashed red line corresponds to the missing transient term in the asymptotic expression. It is re-plotted on logarithmic scale in Fig. 3 right. It appears that the transient term has an initial very rapid decrease followed by a decay as $\sim \exp(-2.4 t/\tau)$. When $t = \tau$ (the longest relaxation time) the off-set in the mean is reduced to about 4% of the ultimate value.

Figure 3: Oscillatory creep responses for the Segalman relaxation function Eq. 33 subjected to Pipkin’s forcing function, Eq. 2 with $\psi = 0$. Parameters in consistent units: $\sigma_0 = 1$, $\eta_0 = 1$, $\omega = 50$ (i.e. $\gamma_\infty = 0.02$) and $n = 0.67$. Left: Numerical solution of Eqs.1 and 33 with strain (full blue line) and mean value (dashed blue) compared with asymptotic expression in red. Right: Transient response (red) normalized by ultimate strain shift (i.e. difference between blue and red dashed lines right) on semi-log scale. The black line is $\sim \exp(-2.4 t/\tau)$. 
The Segalman function in Eq.33 may alternatively be used to describe a solution that slowly undergoes a gelation process by letting $\tau$ be a (slow) increasing function of time. Moreover keep $G_1 = \eta_0 \tau^{n-1}/\Gamma(1-n)$ constant (with dimension $\text{Pa} \ s^n$). Then the high-frequency behavior of the complex moduli is independent of time, but the terminal relaxation is delayed to lower and lower frequencies as $\tau(t)$ increases. In the limit as $\tau \to \infty$ (and therefore also $\eta_0 \to \infty$) the material\(^2\) becomes a critical gel [12] with relaxation modulus

$$G(t) = G_1 t^{-n} ; \quad g(s) = \Gamma(1-n)G_1 s^{n-1} \quad (34)$$

Such a material will in itself have zero strain shift, but if the gel point occurs at some time during the oscillatory stressing, the material would most likely from then on oscillate around whatever strain it has at that particular time. In other words the strain in the pre-gelled liquid state will have lost any significance, but a well-defined configuration has emerged because the material is now a solid. Indeed Lee et al. make no claim that their protocol should be applicable to materials that are changing with time, and the above example merely serves to emphasize that point. A promising technique for time-resolved rheometry of such materials has been presented recently by Geri et al. [13].

**Closing remark** Lee et al. [1] have suggested a novel and interesting protocol for determining the zero-shear-rate viscosity from the strain shift after imposition of a small amplitude sinusoidal stress. They provide the first explicit expression for the ultimate strain shift in a generalized Pipkin problem. Furthermore they provide a large number of carefully performed experiments both with rheology and scattering to illustrate the technique. The purpose of the present work is in no way to detract from their experiments but to provide the theoretical framework needed to estimate the time-scale on which the strain shift is established. For two specific examples investigated here that time-scale corresponds (perhaps not surprisingly) to the longest relaxation time in the material.

**Acknowledgements**

The author would like to thank M.L. Michelsen for inspiration on localization of poles, S. Wedel, G.H. McKinley, D. Vlassopoulos and R.I. Tanner for useful suggestions, Lee and coworkers for drawing his attention to the strain shift problem and the anonymous reviewer for suggesting a continuous relaxation

\(^2\)One of Pipkin’s favorite materials, R. I. Tanner, personal communication
spectrum. A special thanks goes of course to A. C. (Jack) Pipkin for his wonderful exercise left for the reader.

References


This is the author’s peer reviewed, accepted manuscript. However, the online version of record will be different from this version once it has been copyedited and typeset.

PLEASE CITE THIS ARTICLE AS DOI: 10.1122/1.5127827
\[
\frac{\gamma - \gamma_p - \gamma_\infty}{\gamma_\infty}
\]

This is the author's peer reviewed, accepted manuscript. However, the online version of record will be different from this version once it has been copyedited and typeset.

PLEASE CITE THIS ARTICLE AS DOI: 10.1122/1.5127827