Linear Viscoelastic Systems in Free Oscillation

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ABSTRACT: Fourier transform methods were used to analyze the behavior of linear viscoelastic systems in free oscillation. After impulse loading, the asymptotic behavior is as a damped harmonic oscillator. Although the complex dynamic modulus $G^*(\omega)$ can be easily calculated from this asymptotic response, it is determined at a complex value of ω with a real part equal to the frequency of oscillation and an imaginary part equal to the damping constant. For many systems of interest, however, a simple analytic continuation can be used to obtain values of G^* at real values of ω.

Instruments based on linear viscoelastic systems in free oscillation offer useful (and often relatively inexpensive) methods for measuring viscoelastic properties of polymers and other materials.[1] Struik[2] pointed out, however, that all previous analyses of such devices were in error, and gave a detailed analysis of the problem. In his approach, he assumed the existence of a discrete distribution of relaxation times and then developed an equation for the response of such linear systems in terms of the set of Maxwell model spring constants and relaxation times. He then showed that the asymptotic behavior was a damped harmonic oscillation and suggested a method of successive approximations for determining the real and imaginary parts of the complex dynamic modulus.

In this paper we present an alternative analysis of freely oscillating linear viscoelastic systems that requires no assumptions about a distribution of relaxation times. Indeed, the only assumption required is that of linear behavior. The analysis is cast in terms of a torsional pendulum driving a viscometer containing a viscoelastic fluid since this is the experimental arrangement used in our laboratory in a study of concentrated polystyrene solutions.[3]

Analysis

We will consider a torsional pendulum driving a viscometer probe in a viscoelastic fluid. Writing a torque balance on the inertial element of the pendulum gives

$$I\left(\frac{\mathrm{d}^2\theta}{\mathrm{d}t^2}\right) + T(t) = T_\mathrm{E}(t) \qquad (1)$$

where θ is the angle of deflection, I is the moment of inertia, $T(t)$ is the sum of the torques due to the viscoelastic responses of the fluid in the viscometer and of the pendulum itself, and $T_\mathrm{E}(t)$ is any externally applied torque. If we take the Fourier transform of eq 1 we find

$$-I\nu^2\bar{\theta} + \bar{T} = \bar{T}_\mathrm{E} \qquad (2)$$

where ν is the transform variable and a bar over a function of time implies its Fourier transform. We know that if an element of any linear viscoelastic fluid is subjected to an arbitrary shear strain as a function of time, $\gamma(t)$, and responds with an associated shear stress, $\tau(t)$, we can write[4]

$$\tau(\nu) = G^*\bar{\gamma}(\nu) \qquad (3)$$

where G^* is the dynamic modulus considered as a function of ν. Consequently, the transform of the viscoelastic torques can be written

$$\bar{T} = (KG^* + k^*)\bar{\theta} \qquad (4)$$

where K is a constant which is a function of the geometry of the viscometer and k^* is the contribution from the pendulum (preferably an experiment should be designed so that k^* is small compared to KG^*).

If the pendulum is set into oscillation with an impulse torque at $t = 0$

$$T_\mathrm{E} = T_0\delta(t) \qquad (5)$$

where $\delta(t)$ is a Dirac delta function. We can write

$$\bar{\theta} = T_0/[(KG^* + k^*) - I\nu^2] \qquad (6)$$

and

$$\theta = \frac{T_0}{2\pi}\int_{-\infty}^{+\infty} \frac{\exp(i\nu t)\mathrm{d}\nu}{(KG^* + k^*) - I\nu^2} \qquad (7)$$

where i is $\sqrt{-1}$. Since we are not interested in the transients, we look for the asymptotic solution to the above contour integration. This is most easily done by the saddle-point technique[5] (sometimes called the method of steepest descent). To apply that technique we write the above integral as

$$\int_{-\infty}^{+\infty} \exp[g(\nu, t)]\mathrm{d}\nu \qquad (8)$$

where

$$g = i\nu t - \ln\,[(KG^* + k^*) - I\nu^2] \qquad (9)$$

We need that value of ν that maximizes g. Thus

$$\frac{\mathrm{d}g}{\mathrm{d}\nu} = it - \left.\frac{[\mathrm{d}(KG^* + k^*)/\mathrm{d}\nu] - 2I\nu}{(KG^* + k^*) - I\nu^2}\right|_{\nu=\nu_0} = 0 \qquad (10)$$

or

$$KG^* + k^* - I\nu_0^2 = \left.\frac{[\mathrm{d}(KG^* + k^*)/\mathrm{d}\nu] - 2I\nu}{it}\right|_{\nu=\nu_0} \qquad (11)$$

After a sufficiently long time, the right-hand side of eq 11 effectively vanishes and the appropriate value of ν_0 is defined by the equation

$$\nu_0^2 = (KG^* + k^*)/I \qquad (12)$$

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(1) J. D. Ferry, "Viscoelastic Properties of Polymers," 2nd ed, Wiley, New York, N. Y., 1970.

(2) L. C. E. Struik, *Rheol. Acta*, **6**, 119 (1967).

(3) R. I. Wolkowicz and W. C. Forsman, *Macromolecules*, **4**, 184 (1971).

(4) B. Gross, "Mathematical Structure of the Theories of Viscoelasticity," Hermann et Cie., Paris, 1953.

(5) P. M. Morse and H. Feshback, "Methods of Theoretical Physics," McGraw-Hill, New York, N. Y., 1953, p 434.

Returning to eq 8, we now write $g(\nu, t)$ as a Taylor series about ν_0, and get

$$\theta = \frac{T_0}{2\pi}\int_{-\infty}^{+\infty} \exp\left\{g(\nu_0, t) + \frac{g''(\nu_0)}{2!}(\nu - \nu_0)^2 + \ldots\right\}\mathrm{d}\nu \quad (13)$$

The term $g''(\nu_0)$ is the second derivative of $g(\nu_0, t)$ with respect to ν evaluated at ν_0, and it is not a function of t. Neither, of course, are any of the higher derivatives. It has been shown[5] that for sufficiently large values of t only the first two terms in the series are required, and we obtain

$$\theta = \frac{T_0}{2\pi(KG^* + k^*)} \exp(i\nu_0 t)\int_{-\infty}^{+\infty} \exp\left\{\frac{1}{2}g''(\nu_0)(\nu - \nu_0)^2\right\}\mathrm{d}\nu \quad (14)$$

Since it can be shown that the real part of $g''(\nu_0)$ is negative, the above integral exists. The product of the integral and the factor in any system is a constant, so we can write

$$\theta = \theta_0 \exp(i\nu_0 t) \quad (15)$$

Or by identifying ν_0 with the decay frequency of the pendulum after steady damped sinusoidal motion has been established, we can write

$$\theta = \theta_0 \exp(i\omega t) \quad (16)$$

Now if we express ω in its complex form

$$\omega \equiv \nu_0 \quad (17)$$

where

$$\omega = \omega' + i\omega'' \quad (18)$$

the final result is

$$\theta = \theta_0 \exp(i\omega' t - \omega'' t) \quad (19)$$

We thus find that the limiting behavior of a torsion pendulum (in this case coupled to a dynamic viscometer) after being given an impulsive loading is as a damped harmonic oscillator, and we can use the frequency (ω') and damping constant (ω'') to determine G^* without assuming any rheological model.

From eq 12, 17, and 19 we find that if $G^* = G' + iG''$ and $k^* = k' + ik''$

$$G' = [I(\omega'^2 - \omega''^2) - k']/K \quad (20)$$

$$G'' = (I2\omega'\omega'' - k'')/K \quad (21)$$

The complex constant k^* can be determined from the dynamic behavior of the system without polymer solution in the viscometer. The geometric constant K can be determined for any cup-and-bob or cone-and-plate combination by calibration with a nonviscoelastic Newtonian fluid.

By changing the interpretation of the various constants, one could apply the above analysis to any freely damped linear viscoelastic system.

One subtle aspect of the results is that G^* is determined at a complex value of the angular frequency. But, as was pointed out by Struik,[2] the loss modulus can be determined at real frequencies by analytic continuation using a Taylor series. We wish to point out, however, that in many cases (and indeed maybe most cases) of interest to polymer rheologists, the correction to real frequencies is a small one. Measurements with freely damped systems are most easily made when $\omega' \gg \omega''$. If this inequality holds, the Cauchy–Riemann equations[6] give

$$G'(\omega') = G'(\omega' + i\omega'') + \frac{\partial G''}{\partial \omega'}\,\omega'' \quad (22)$$

$$G''(\omega') = G''(\omega' + i\omega'') - \frac{\partial G'}{\partial \omega'}\,\omega'' \quad (23)$$

to the first order in ω'', where the derivatives are evaluated at the real frequency ω' ($\omega'' = 0$). If we write the above equations in terms of the errors in G' and G'' we find

$$\frac{G'(\omega') - G'(\omega' + i\omega'')}{G'(\omega')} = \tan\delta\,\frac{\partial \ln G''}{\partial \ln \omega'}\left(\frac{\omega''}{\omega'}\right) \quad (24)$$

and

$$\frac{G''(\omega') - G''(\omega' + i\omega'')}{G''(\omega'')} = -\frac{1}{G''}\,\frac{\partial G'}{\partial \ln \omega'}\left(\frac{\omega''}{\omega'}\right) \quad (25)$$

where $\tan\delta = (G''/G')$. For all polymer systems the absolute value of $(\partial \ln G''/\partial \ln \omega)$ is less than or equal to 1.0; in addition, $\tan\delta$ rarely exceeds 1.0. Furthermore, approximate relationships between viscoelastic functions[1] can be used to show that $G'' \sim (\partial G'/\partial \ln \omega)$. It follows, therefore, that the correction to G' and G'' can be made as small as desired by making (ω''/ω') sufficiently small, for example as in the previously mentioned work with concentrated polystyrene solutions.[3]

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(6) R. V. Churchill, "Introduction to Complex Variables and Applications," McGraw-Hill, New York, N. Y., 1948, Chapter 2.

Notes

Production of Organometallic Polymers by the Interfacial Technique. XVI. Importance of Hydrolysis in the Synthesis of Poly[oxyadipoyloxy(diphenylsilylene)][1]

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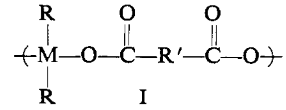
Recently we have been interested in the synthesis of group IV polyesters of the below form using the interfacial technique.[2,3]



$$\left(\begin{array}{c} R \\ | \\ M \\ | \\ R \end{array}-O-\overset{\overset{\displaystyle O}{\|}}{C}-R'-\overset{\overset{\displaystyle O}{\|}}{C}-O\right)$$

I

Hydrolysis is important in the aqueous interfacial reaction between organodichlorosilanes or organodichlorostannanes

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(2) (a) C. Carraher and R. Dammeier, *Makromol. Chem.*, **135**, 107 (1970); (b) C. Carraher and R. Dammeier, *J. Polym. Sci., Part A-1*, **8**, 3367 (1970).

(3) C. Carraher and R. Dammeier, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **11**, 606 (1970).