

## Determination of Parameters in Convected Maxwell Model from Linear Viscoelastic Parameters

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### Synopsis

Owing to its simplicity and general ability to correctly portray a number of important flow phenomena, the two-parameter Maxwell model has been employed in a number of important engineering studies. The relation of this equation to linear viscoelasticity and to some molecular theories is considered. A new rule is developed which shows how the shear-dependent relaxation time and viscosity of the Maxwell model can be determined from linear viscoelastic parameters. It is thus shown that the two-parameter Maxwell model may be more general than earlier anticipated.

### INTRODUCTION

The convected Maxwell model,

$$\mathbf{P} + \theta \frac{\delta \mathbf{P}}{\delta t} = 2\mu \mathbf{d}, \quad (1)$$

was introduced some time ago by White and Metzner<sup>1</sup> utilizing ideas of rubber rheology as well as the formalizations of Oldroyd.<sup>2</sup> This equation, which has recently been shown to be quantitatively correct at the large deformation rates of interest in practical problems,<sup>3,4</sup> has proved useful in a number of other studies including turbulent drag reduction and flow through porous media.<sup>5-7</sup> A number of equations similar to eq. (1) have appeared (see, for example, refs. 8, 9, and 10) which are based on molecular arguments and which may be thought of as superposing the effects of a large number of linear Maxwell elements. The possibilities are of course unlimited. Although generalizations based on molecular arguments are capable of defining the shear dependence of the functions  $\theta$  and  $\mu$  the inherent simplicity of eq. (1) is lost, and, as will be shown later, there are severe difficulties in a unique determination of a large number of physical property parameters.

In eq. (1), the material parameters in general need to be functions of the invariants of the deformation rate tensor  $\mathbf{d}$  and are not restricted in form. From a molecular point of view, these functions may be viewed as representing integral properties of a large number of molecules in solution. There has been no precise determination of the relation of these functions in the White-Metzner model to the behavior of individual molecules.

We consider first the possibility of reduction of a large number of linear viscoelasticity parameters to a smaller number of parameters. Surprisingly, to the authors' knowledge, this has never been considered in detail before (usually the problem is considered from the opposite point of view wherein an experimental function is used to generate a large number of parameters). The results of the parameter reduction will then be applied to show how the White-Metzner parameters  $\theta(\text{II,III})$  and  $\mu(\text{II,III})$  are related to simple constant Maxwell elements in both shear and elongational flows.

### PARAMETER REDUCTION

For small gradients or deformations, we have  $\delta/\delta t$  equal to the ordinary partial time derivative and require that

$$\lim_{\text{II,III} \rightarrow 0} \theta(\text{II,III}) = \text{const} \quad (2a)$$

$$\lim_{\text{II,III} \rightarrow 0} \mu(\text{II,III}) = \text{const} \quad (2b)$$

or that only two constants are necessary for defining the fluid. In simple shear flow, the function  $\theta$  and  $\mu$  in eq. (1) are defined through the physical components of the stress tensor as

$$\mu = \frac{P_{12}}{\dot{\gamma}} \quad (3)$$

$$\theta = \frac{P_{11} - P_{22}}{2P_{12}\dot{\gamma}}.$$

For a linear viscoelastic area, which is characterized for most polymers through many constant relaxation times (for example, the number of characteristic relaxation times  $p$  in the Rouse theory<sup>9</sup> is usually greater than 50) or through continuous spectra, it seems superficially that eqs. (1) and (2a, 2b) are entirely unsatisfactory. In fact, we will show that excellent predictions of the linear viscoelastic functions can be obtained over at least two decades of independent variables. This property of parameter reduction is a fundamental property of the basic viscoelastic functions and is not restricted in applicability to the nonlinear Maxwell model. An equivalent problem is determination of a continuous box spectrum and its relation to  $\theta$ .

As noted above, eq. (1) reduced to a one-parameter Maxwell model for differentially small deformations and gradients. The measured quantities, for example, the relaxation modulus  $G(t)$ , the real part of the dynamic viscosity  $\eta'(\omega)$ , or the dynamic modulus can be written in the form of a series.<sup>11-13</sup>

$$G(t) = \sum_{p=1}^n G_p e^{-t/\tau_p} \tag{4}$$

$$\eta'(\omega) = \sum_{p=1}^n \frac{G_p \cdot \tau_p}{1 + \omega^2 \tau_p^2} \tag{5}$$

$$G'(\omega) = \sum_{p=1}^{\infty} \frac{G_p \omega^2 \tau_p^2}{1 + \omega^2 \tau_p^2} \tag{6}$$

$$P_{11} - P_{22}(\dot{\gamma}) = 2 \sum_{p=1}^{\infty} \frac{\tilde{G}_p \dot{\gamma}^2 \tau_p^2}{1 + \dot{\gamma}^2 \tau_p^2} \tag{7}$$

where  $\omega$  is angular frequency,  $\dot{\gamma}$  is the steady shear gradient, and  $\tau_p$  and  $G_p$  may be viewed as constants for each Maxwell element. In eqs. (6) and (7) if constants  $\tilde{G}_p$  and  $G_p$  are the same, then the functions are the same and

$$\lim_{\dot{\gamma} \rightarrow 0} \frac{P_{11} - P_{22}}{\dot{\gamma}^2} = \lim_{\omega \rightarrow 0} \frac{2G'(\omega)}{\omega^2} \tag{8}$$

In general, it appears that eq. (8) is incorrect and that better agreement is obtained without the 2.<sup>14,15</sup> We account for this possibility by the non-equality of  $G_p$  and  $\tilde{G}_p$ . We rewrite eq. (4) into a discrete form with parameter  $t_i$  (noting that in matrix notation lower-case letters will refer to the function  $G(t)$ ):

$$\begin{bmatrix} g(t_1) \\ g(t_2) \\ \cdot \\ \cdot \\ g(t_n) \end{bmatrix} = \begin{bmatrix} e^{-t_1/\tau_1} \dots e^{-t_1/\tau_n} \\ e^{-t_2/\tau_1} \dots \\ \cdot \\ \cdot \\ \dots \dots \dots e^{-t_n/\tau_n} \end{bmatrix} \cdot \begin{bmatrix} G_1 \\ G_2 \\ \cdot \\ \cdot \\ G_n \end{bmatrix} \tag{9a}$$

or

$$\mathbf{g} = \mathbf{E}_1 \cdot \mathbf{G} \tag{9b}$$

The individual elasticity constants  $G_1, G_2 \dots$  are connected with the relaxation spectra  $H(\log \tau)$  through the relation<sup>16</sup>

$$G_i = H(\log \tau_i) \Delta \log \tau \tag{10}$$

We will now show that the matrix  $\mathbf{E}_1$  in eq. (9b) has such properties that a small change in the measured matrix  $\mathbf{g}$  is reflected in a large change in  $\mathbf{G}$ . Equivalently, through eq. (10), we note that a small numerical change in  $G(t)$  is reflected as a large change in the function  $H(\log \tau)$ . Thus, if a series of functions  $\psi_i(t) \sim G(t)$  are possible whose shape and values are in the short interval as, for example,

$$\psi_i, \psi_2 \dots \psi_j \dots \psi_m \epsilon \mathbf{g} \pm \frac{3\mathbf{g}}{100},$$

we can find a corresponding series of functions  $H_1(\log \tau)$ ,  $H_2(\log \tau) \cdots H_m(\log \tau)$  which differ significantly from one another. From this set, the function which can be characterized through the smallest number of parameters will be chosen. Similar properties are exhibited by the matrices  $\mathbf{E}_2$  and  $\mathbf{E}_3$  derived from eqs. (5) and (6) such that

$$\begin{aligned} \mathbf{n}' &= \mathbf{E}_2 \cdot \mathbf{G} \\ \mathbf{g}' &= \mathbf{E}_3 \cdot \mathbf{G} \end{aligned} \tag{11}$$

$$\mathbf{n}' = \begin{bmatrix} \eta'(\omega_1) \\ \cdot \\ \cdot \\ \eta'(\omega_n) \end{bmatrix} \quad \mathbf{g}' = \begin{bmatrix} g'(\omega_1) \\ \cdot \\ \cdot \\ g'(\omega_n) \end{bmatrix}$$

For norm of a vector  $\mathbf{x}$ ,  $\|\mathbf{x}\|$ , we will assume the usual properties:

- (a)  $\|\mathbf{x}\| > 0$  if  $\mathbf{x} \neq \mathbf{0}$
- (b)  $\|\bar{c}\mathbf{x}\| = \bar{c} \cdot \|\mathbf{x}\|$
- (c)  $\|\mathbf{x} + \mathbf{y}\| \leq \|\mathbf{x}\| + \|\mathbf{y}\|$

Thus, for the norm of  $\mathbf{g}$  and  $\mathbf{G}$ , we can use the functions

$$\|\mathbf{g}\| = \sum_{i=1}^n |g(t_i)| \tag{12}$$

and

$$\|\mathbf{G}\| = \sum_{i=1}^n |G_i| \tag{13}$$

in which  $|\quad|$  means absolute value. Similarly, for differences in the functions, we define in discrete form

$$\Delta \mathbf{g} \equiv \mathbf{g} - \psi_j,$$

and therefore

$$\|\mathbf{g} - \psi_j\| \equiv \|\Delta \mathbf{g}\| = \sum_{i=1}^n |\Delta g(t_i)| \tag{14}$$

$$\|\Delta \mathbf{G}\| = \sum_{i=1}^n |\Delta G_i| \tag{15}$$

or for the relative value of the differences,

$$\frac{\|\Delta \mathbf{g}\|}{\|\mathbf{g}\|} = \frac{\sum_{i=1}^n |\Delta g(t_i)|}{\sum_{i=1}^n |g(t_i)|} \tag{16}$$

$$\frac{\|\Delta \mathbf{G}\|}{\|\mathbf{G}\|} = \frac{\sum_{i=1}^n |\Delta G_i|}{\sum_{i=1}^n |G_i|}. \tag{17}$$

Let us suppose that the functions  $G(t)$ ,  $H(\log \tau)$ , and  $\Delta G(t)$  from the interval  $\Delta G(t)\epsilon \pm \frac{3G(t)}{100}$  are given. The largest difference in  $H(\log \tau)$ , as measured by the absolute value of the difference at all points, occurs if the quantity  $\nu$ , defined as

$$\nu(\|\Delta g\|) = \max \frac{\|\Delta \mathbf{G}\|}{\|\mathbf{G}\|} \div \frac{\|\Delta \mathbf{g}\|}{\|\mathbf{g}\|}, \tag{18}$$

is a maximum. Or, rearranging eq. (18),

$$\nu(\|\Delta \mathbf{g}\|) = \frac{\|\mathbf{g}\|}{\|\mathbf{G}\|} \max \frac{\|\Delta \mathbf{G}\|}{\|\Delta \mathbf{g}\|}, \tag{19}$$

and substituting eq. (9b), we obtain

$$\nu(\|\Delta \mathbf{g}\|) = \frac{\|\mathbf{g}\|}{\|\mathbf{G}\|} \max \frac{\|\mathbf{E}_1^{-1} \Delta \mathbf{g}\|}{\|\Delta \mathbf{g}\|}. \tag{20}$$

According to Fadejev and Fadejeva,<sup>17</sup> it is possible for every norm of a vector  $\|\mathbf{x}\|$  to define the corresponding norm of a quadratic matrix  $\mathbf{A}$  in such a way that the following equation is valid:

$$\frac{\|\mathbf{Ax}\|}{\|\mathbf{x}\|} = \|\mathbf{A}\|. \tag{21}$$

Therefore, eq. (20) becomes

$$\nu(\|\Delta \mathbf{g}\|) = \|\mathbf{E}_1\| \cdot \max \|\mathbf{E}_1^{-1}\|. \tag{22}$$

In eq. (22), the right-hand side is independent of the choice of  $\|\Delta \mathbf{g}\|$  and therefore  $\nu$  is a constant given by

$$\nu = \|\mathbf{E}_1\| \cdot \|\mathbf{E}_1^{-1}\|. \tag{23}$$

For every eigenvalue  $\lambda$  of a matrix  $\mathbf{A}$ ,

$$|\mathbf{Ax}| = |\lambda| \cdot |\mathbf{x}| \leq |\mathbf{A}| \cdot |\mathbf{x}|;$$

therefore, in eq. (23),

$$\nu \geq \frac{\max |\lambda_i|}{\min |\lambda_j|} \geq 1 \tag{24}$$

in which  $\max |\lambda_i|$  and  $\min |\lambda_j|$  are the maximum and minimum eigenvalues of  $\mathbf{E}$ . It follows that the error interval  $\Delta G$  is minimum if  $\mathbf{E}_1$  is a unit matrix

and increases as  $\mathbf{E}_1$  differs from a unit matrix. The properties of  $\mathbf{E}_1$  in this connection can be shown as follows:

A. Equation (4), for example, can be rewritten in terms of a continuous spectrum:

$$G(t) = \int_{-\infty}^{\infty} e^{-t/\tau} H(\log \tau) d \log \tau. \quad (25)$$

In the continuous form of eq. (25), the unit matrix  $I$  corresponds to a Dirac delta function,

$$I \sim \tau \delta(t - \tau),$$

and we see that the nonequality which is equivalent to eq. (24) is simply that

$$e^{-t/\tau} \neq \tau \delta(t - \tau)$$

(operators  $\int_{-\infty}^{\infty} e^{-t/\tau}(\dots) d \log \tau$  and  $\int_{-\infty}^{\infty} \tau \delta(t - \tau)(\dots) d \log \tau$  are

enormously different) and, consequently, that  $\mathbf{E}_1$  does not have the properties of a unit matrix.

B. The numerical inversion of eq. (9a) has been considered in some detail by Clauser and Knaus<sup>18</sup> (compare also to the numerical solution of general integral equations of the first kind<sup>19,20</sup>). They have shown how  $\mathbf{G}$  is subject to large oscillations which are directly related to the properties of the  $\mathbf{E}$  matrices. According to Appendix I, we have

$$\frac{\|\Delta \mathbf{G}\|}{\|\mathbf{G}\|} = \frac{\|\mathbf{g}\|}{\|\mathbf{G}\|} \cdot \|\mathbf{E}_1^{-1}\| \cdot \left\{ \frac{q}{1-q} + \frac{1}{1-q} \frac{\|\Delta \mathbf{g}\|}{\|\mathbf{g}\|} \right\} \quad (26a)$$

in which

$$\mathbf{E}_1 = \mathbf{E}_1^* + \mathbf{C} \mathbf{E}_1 \quad (26b)$$

and where  $\|\mathbf{C}\| \equiv q \ll 1$  is the norm of the "error" matrix which expresses the (small) numerical nonprecision in the matrix  $\mathbf{E}$ . In eq. (26), the  $\|\Delta \mathbf{G}\|$  is in the order of the average value of the oscillations and may be several orders of magnitude larger than  $\|\mathbf{G}\|$ .<sup>18-21</sup>

Furthermore, since  $q$  and  $\Delta \mathbf{g}$  approach zero, we must have

$$\frac{\|\mathbf{g}\|}{\|\mathbf{G}\|} \|\mathbf{E}_1^{-1}\| \gg \gg 1,$$

and therefore  $\mathbf{E}_1$  is a nonunit matrix. Similar comments apply to all of the functions  $\mathbf{E}_1, \mathbf{E}_2,$  and  $\dots \mathbf{E}_n$ , which are essentially exponential in behavior.<sup>21</sup> A more detailed discussion from a mathematical point of view is available elsewhere.<sup>22,23</sup>

## NUMERICAL EXAMPLE

We illustrate the preceding discussion with a simple numerical example by choosing several different functions  $H(\log \tau)$  and determining the cor-

responding response function  $G'(\omega)$  given by eq. (6). The  $G_i$  in eq. (9a) are determined from eq. (10) with  $\Delta \log \tau = 0.1$ . Table I gives the assumed relaxation spectra  $H(\log \tau)$  numerically.  $H_1$ , and  $H_2, H_3$  are characterized by two- and one-time constants, respectively, while  $H_4$  and  $H_5$  represent continuous functions characterized by 10- and 20-time constants.

TABLE I  
Assumed Relaxation Spectra

$\log \tau$	$H_1$	$H_2$	$H_3$	$H_4$	$H_5$
1.2	0.0	0.0	0.0	0.0	0.0
1.1	0.0	0.0	0.0	0.0	0.101
1.0	0.0	0.0	0.0	0.0	-0.004
0.9	0.0	0.0	0.0	0.0	-0.207
0.8	0.0	0.0	0.0	0.0	-0.216
0.7	0.0	0.0	0.0	0.0	0.184
0.6	0.0	0.0	0.0	0.483	0.954
0.5	0.0	0.0	0.0	2.66	1.84
0.4	10.0	0.0	0.0	3.48	2.59
0.3	0.0	0.0	0.0	2.48	3.06
0.2	0.0	20.0	0.0	1.67	3.22
0.1	0.0	0.0	20.0	2.50	3.08
0.0	10.0	0.0	0.0	3.49	2.62
-0.1	0.0	0.0	0.0	2.66	1.85
-0.2	0.0	0.0	0.0	0.52	0.93
-0.3	0.0	0.0	0.0	0.0	0.15
-0.4	0.0	0.0	0.0	0.0	-0.21
-0.5	0.0	0.0	0.0	0.0	-0.15
-0.6	0.0	0.0	0.0	0.0	0.035
-0.7	0.0	0.0	0.0	0.0	0.066
-0.8	0.0	0.0	0.0	0.0	-0.026

A comparison of the dynamic modulus functions determined from the various spectra is given in Table II. Here, the square of the error relative to  $G'(\omega)_{H_i}$  is given as a function of  $\omega$ . In all cases, it is clear that  $G'(\omega)$ , at least over approximately two decades, is insensitive to the form of the assumed relaxation spectra.

In the case of real spectra, extending over many decades, the exact reproduction of the function  $G'(\omega)$  is not possible by using only one Maxwell element with constant parameters. For real polymers, Tobolsky,<sup>24</sup> using his  $X$  procedure, reduced a box spectrum extending over 6 decades into a box spectrum ranging over 2.2 decades with little effect in reproducing the measured function  $G(t)$ . In another case, Tobolsky<sup>25</sup> explained the relaxation properties of organic glasses using only one relaxation time. Meissner<sup>26</sup> has reduced a continuous spectrum over 4 decades for polyethylenes to four discrete Maxwell elements with constant parameters. We have shown that these cases of parameter reduction are not necessarily dependent on special properties of the materials (as Tobolsky believed<sup>24, 25</sup>), but reflect the general properties of operators governing memory effects in

viscoelasticity. The data as well as the numerical example show that a single time-constant is always adequate to replace at *least* one decade of the continuous spectral function.

Similar comments apply to nonlinear continuum models which retain the essential features of eqs. (4)–(7). That is, from a continuum point of view, we cannot distinguish the difference between models with very few relaxation times from those containing a large number (say 50) relaxation

TABLE II  
Error in Real Part of Dynamic Modulus Predicted from Various Spectra

$\log \omega$	$G_{H_1}'$	$(G_{H_1}' - G_{H_2}')^2$	$(G_{H_1}' - G_{H_3}')^2$	$(G_{H_1}' - G_{H_4}')^2$	$(G_{H_1}' - G_{H_5}')^2$
1.1	1.97	$0.5138 \times 10^{-5}$	$0.983 \times 10^{-5}$	$0.217 \times 10^{-4}$	$0.631 \times 10^{-4}$
1.0	1.95	$0.127 \times 10^{-4}$	$0.2440 \times 10^{-4}$	$0.425 \times 10^{-4}$	$0.615 \times 10^{-4}$
0.9	1.93	$0.312 \times 10^{-4}$	$0.601 \times 10^{-4}$	$0.768 \times 10^{-4}$	$0.588 \times 10^{-4}$
0.8	1.89	$0.757 \times 10^{-4}$	$0.146 \times 10^{-3}$	$1.23 \times 10^{-4}$	$0.547 \times 10^{-4}$
0.7	1.83	$0.179 \times 10^{-3}$	$0.351 \times 10^{-3}$	$1.65 \times 10^{-4}$	$0.476 \times 10^{-4}$
0.6	1.76	$0.413 \times 10^{-3}$	$0.822 \times 10^{-3}$	$1.73 \times 10^{-4}$	$0.345 \times 10^{-4}$
0.5	1.65	$0.905 \times 10^{-3}$	$0.184 \times 10^{-2}$	$1.316 \times 10^{-4}$	$0.161 \times 10^{-4}$
0.4	1.52	$0.183 \times 10^{-2}$	$0.389 \times 10^{-2}$	$0.656 \times 10^{-4}$	$0.254 \times 10^{-5}$
0.3	1.36	$0.331 \times 10^{-2}$	$0.752 \times 10^{-2}$	$0.168 \times 10^{-4}$	$0.194 \times 10^{-7}$
0.2	1.18	$0.504 \times 10^{-2}$	$0.127 \times 10^{-1}$	$0.0004 \times 10^{-4}$	$0.353 \times 10^{-7}$
0.1	0.998	$0.593 \times 10^{-2}$	$0.181 \times 10^{-1}$	$0.132 \times 10^{-4}$	$0.060 \times 10^{-4}$
0.0	0.811	$0.468 \times 10^{-2}$	$0.203 \times 10^{-1}$	$0.573 \times 10^{-4}$	$0.224 \times 10^{-4}$
-0.1	0.634	$0.173 \times 10^{-2}$	$0.168 \times 10^{-1}$	$1.18 \times 10^{-4}$	$0.263 \times 10^{-4}$
-0.2	0.475	$0.371 \times 10^{-5}$	$0.939 \times 10^{-2}$	$1.58 \times 10^{-4}$	$0.127 \times 10^{-4}$
-0.3	0.342	$0.143 \times 10^{-2}$	$0.293 \times 10^{-2}$	$1.51 \times 10^{-4}$	$0.199 \times 10^{-5}$
-0.4	0.237	$0.421 \times 10^{-2}$	$0.248 \times 10^{-3}$	$1.11 \times 10^{-4}$	$0.272 \times 10^{-7}$
-0.5	0.160	$0.5477 \times 10^{-2}$	$0.873 \times 10^{-4}$	$0.685 \times 10^{-4}$	$0.092 \times 10^{-5}$
-0.6	0.105	$0.470 \times 10^{-2}$	$0.413 \times 10^{-3}$	$0.370 \times 10^{-4}$	$0.071 \times 10^{-5}$
-0.7	0.068	$0.310 \times 10^{-2}$	$0.468 \times 10^{-3}$	$0.183 \times 10^{-4}$	$0.215 \times 10^{-5}$
-0.8	0.044	$0.1721 \times 10^{-2}$	$0.336 \times 10^{-3}$	$0.086 \times 10^{-4}$	$0.227 \times 10^{-5}$

times. There needs to be, however, a spectral function which has a physical basis, and this needs to be determined through optimum methods based on unit operator.<sup>27,16</sup>

### APPLICATION TO WHITE-METZNER EQUATION

Although a formal procedure for separation of relaxation times is not precisely defined, it is clear that if we wish to use a one-parameter relaxation spectrum, then separation of relaxation times by at least one decade is possible. Therefore, in the following we assume that  $\tau_{i+1}$  is negligible compared to  $\tau_i$ . The limit of zero gradient will be considered followed by a generalization to larger gradients.

In the limit of zero gradient for steady shear flow, we can put from eqs. (5) and (7) (noting that the same series applies for  $\mu$  and  $\eta'$ )



$$\lim_{\gamma \rightarrow 0} \mu(\dot{\gamma}) = \sum_{p=1}^n G_p \tau_p \tag{27}$$

$$\lim_{\gamma \rightarrow 0} \frac{P_{11} - P_{22}}{\dot{\gamma}^2} = 2 \sum_{p=1}^n \tilde{G}_p \tau_p^2. \tag{28}$$

Generally, since the  $G_p$  vary only slightly (for a box spectrum they are constant), comparison of eqs. (2) and (3) with (27) and (28) gives

$$\lim_{\text{II} \rightarrow 0} \theta(0, \text{II}, 0) \cong \tau_1$$

and

$$\lim_{\text{II} \rightarrow 0} \mu(0, \text{II}, 0) \cong G_1 \tau_1$$

since  $\tau_2 \ll \tau_1$ . It should be noted that we have assumed that  $G_p = \tilde{G}_p$  or that eq. (8) is valid. If eq. (8) is valid *without* the 2, then  $\theta \simeq \tau_1/2$ . Since we have shown that the basic functions can be reproduced over approximately 2 decades with one relaxation time, it follows that in the range of independent variables,

$$\begin{aligned} \log t &\geq \log \tau_1 - 1 \\ \log 1/\omega &\geq \log \tau_1 - 1, \end{aligned} \tag{29}$$

eq. (1) with  $\theta = \tau_1 = \text{constant}$  will be satisfactory. In fact, the sums (27) and (28) are slightly larger than the first term and will be shifted toward the second relaxation time. The effect on the basic functions, however, will be entirely negligible, as illustrated by the functions  $G'(\omega)_{\text{H}_2}$  and  $G'(\omega)_{\text{H}_3}$  in Table II. In some cases, Tobolsky's data<sup>25</sup> indicate that the range of applicability of independent variable may be much larger than indicated in the preceding example.

To extend the range of gradients expressed by eq. (29), let us suppose the total response of the fluid arises from contributions of separate fluids A and B. The elements A and B are each described by eq. (1), so that for each element

$$P_{ij}^{\text{A}} + \theta^{\text{A}} \frac{\delta P_{ij}}{\delta t} = 2\mu^{\text{A}} d_{ij} \tag{30}$$

$$P_{ij}^{\text{B}} + \theta^{\text{B}} \frac{\delta P_{ij}}{\delta t} = 2\mu^{\text{B}} d_{ij} \tag{31}$$

or for the whole

$$P_{ij}^{\text{S}} + \theta^{\text{S}} \frac{\delta P_{ij}}{\delta t} = 2\mu^{\text{S}} d_{ij}. \tag{32}$$

In eqs. (30)–(32), we can think of A and B as separate polymers which have been mixed or, in the present context, that A and B are contributions from

different parts of the spectra such that  $\tau_1 \sim \theta^A \gg \max \theta^B$  and  $\theta^B = f(\text{II,III})$ . Considering simple shear flow,

$$\frac{\delta P^S}{\delta t} = \frac{\delta P^A}{\delta t} + \frac{\delta P^B}{\delta t} \quad (33)$$

$$\mu^S = \mu^A + \mu^B. \quad (34)$$

According to the "stress-optical law,"<sup>28-30</sup> if  $\chi$  is the birefringence angle, then

$$\cot(2\chi^A) = \frac{P_{11}^A - P_{22}^A}{2P_{12}^A} \quad (35)$$

or, rearranging and using eq. (3),

$$\theta_A = \frac{\cot 2\chi^A}{\dot{\gamma}}. \quad (36)$$

Similarly, for component B and the whole system S,

$$\theta_B = \frac{\cot 2\chi^B}{\dot{\gamma}} \quad (37)$$

$$\theta_S = \frac{\cot 2\chi^S}{\dot{\gamma}}. \quad (38)$$

Because the principal stress of systems A and B are additive as vectors,<sup>30</sup> we obtain for  $\theta_S$

$$2\dot{\gamma}\theta_S = \frac{(P_{11} - P_{22})^S}{P_{12}^S} = \frac{(P_{11} - P_{22})^A + (P_{11} - P_{22})^B}{P_{12}^A + P_{12}^B}. \quad (39)$$

The geometric relation resulting in eq. (39) is shown in Figure 1, where the point S characterizes the stress state of the whole system and  $\Delta S$ ,  $\Delta B$ , and  $\Delta A$  are the principal stresses for S, B, and A, respectively. From eq. (35)–(39), it follows that

$$\theta_S = \frac{\theta_A P_{12}^A + \theta_B P_{12}^B}{P_{12}^A + P_{12}^B}. \quad (40)$$

Or, in general for a system of  $n$  components,

$$\theta_S = \frac{\sum_{i=1}^n \theta_i P_{12}^i}{\sum_{i=1}^n P_{12}^i} \quad (41)$$

and

$$\mu_S = \sum_{i=1}^n \mu_i. \quad (42)$$

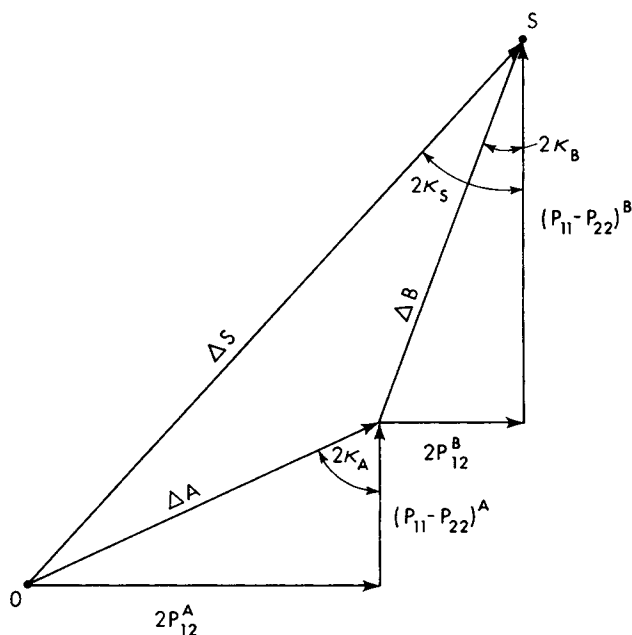


Fig. 1. Geometric relation for stress contributions:  $\Delta A$ , principal stress of system A;  $\Delta B$ , principal stress of system B;  $\Delta S$ , principal stress of entire system S.

Equation (41), expressed through the White-Metzner parameters for different noninteracting systems, is analogous to the Sadron optical rule<sup>30</sup> which was introduced by study of birefringent solutions. In general, the systems are interacting or the friction coefficient of an individual monomer unit is changed, and the relaxation times of an individual component are shifted relative to those for pure components. The shift of relaxation times observed on blending different molecular weight fractions has been studied in some detail by Ferry and Ninomya<sup>11,31,32</sup> and may be described by a shift factor of order unity. The blending laws may be of especial importance in the estimation of the elastic properties of very dilute solutions wherein it is not possible to directly measure normal forces.

Equations (41) and (42) provide a general rule for formulating the shear-dependent White-Metzner relaxation time and viscosity as separate con-

TABLE III  
Comparison of Predicted and Experimental Relaxation Times for  
Polyisobutylene Solution

$n$	$\tau_n$ , sec	$G_n \tau_n$ , poises	$\dot{\gamma}$ , sec <sup>-1</sup>	$\theta(\dot{\gamma})$ , sec	$\theta_S(\dot{\gamma})$ , sec
1	$10^{-1}$	6.1	10	$2.5 \times 10^{-2}$	$3.9 \times 10^{-2}$
2	$10^{-2}$	4.0	$10^2$	$4.6 \times 10^{-3}$	$7.1 \times 10^{-3}$
3	$10^{-3}$	1.9	$10^3$	$6.1 \times 10^{-4}$	$14.4 \times 10^{-4}$

tributions from a number of components. It is worthwhile to emphasize that these relations must be satisfied for any choice (for which  $(P_{11} - P_{22})_S = F_1(\dot{\gamma}) + \dots + F_n(\dot{\gamma})$  and  $\theta_i$  are determined from  $\theta_i = F_i/2\mu_i\dot{\gamma}^2$ ) of the component functions, including those which arise from theoretical considerations. The addition rule provides a direct relation between the viscosity function and shear dependence of the relaxation time. Again, for dilute solutions, it should be noted that eqs. (41) and (42) apply rigorously only to the polymer contribution of the stress.

The addition law can be illustrated from Tanner's data<sup>15</sup> for a 5.4% polyisobutylene cetane solution. Tanner's spectrum has been reduced (crudely) to three characteristic times  $\tau_n$ , as shown in Table III. The  $\theta(\dot{\gamma})$  is estimated directly from the published normal stresses using eq. (3) or equivalently eq. (1), and  $\theta_S$  has been determined using eq. (41). In view of the crude reduction of parameters, the agreement with  $\theta$  determined from the normal stress measurements is rather good. Better agreement can be obtained by a slight shift of the relaxation times to coincide with the peaks in the spectra determined by Tanner.

### NONVISCOMETRIC FLOW

Owing to the possibility of parameter reduction, we can comment briefly on the form of material functions for elongational flow by a consideration of molecular arguments. In elongation flow, the kinematics are defined by

$$\begin{aligned}v_1 &= d_{11} \cdot x_1 \\v_2 &= (-d_{11}/2)x_2 \\v_3 &= (-d_{11}/2)x_3\end{aligned}\tag{43}$$

and the second and third invariants of  $\mathbf{d}$  are

$$\begin{aligned}\text{II}_d &= \frac{3}{4} \dot{\gamma}^2 \\ \text{III}_d &= \frac{1}{4} \dot{\gamma}^3.\end{aligned}\tag{44}$$

For the elongational viscosity defined as the total stress in the axial direction divided by the deformation rate, eq. (1) predicts

$$\eta_e = \frac{3\mu(\text{II}, \text{III})}{[1 + \theta(\text{II}, \text{III})d_{11}][1 - 2\theta(\text{II}, \text{III})d_{11}]}\tag{45}$$

In eq. (45), no information is given as to how the parameters  $\theta$  and  $\mu$  depend on the second and third invariants in elongational flow. As a first approximation, these have been assumed equal to the function determined in simple shear, and dependence on the third invariant therefore was neglected.<sup>6,7</sup> Alternatively, if we assume contributions from a number of

Maxwell elements (characterized through constant parameters and built on molecular notions), then the elongational viscosity may be written as<sup>11,33</sup>

$$\bar{\eta}_e = \sum_{i=1}^n \frac{3\eta_i}{(1 + \tau_i d_{11})(1 - 2\tau_i d_{11})} \tag{46}$$

in which  $\tau_i$  and  $\eta_i$  are constants. In shear flow, the most elementary dependence on the second invariant of the contribution to solution viscosity of each Maxwell element has been shown in a number of instances to be (see, for example, refs. 11 and 34)

$$\mu_i = \frac{\eta_i}{1 + 4\tau_i^2 \cdot \text{II}} \tag{47}$$

Thus, in the viscosity function of the White-Metzner equation, the relevant viscosity function which is consistent with simple molecular arguments is

$$\mu(\text{II,III}) = \sum_{i=1}^n \mu_i = \sum_{i=1}^n \frac{\eta_i}{1 + 4\theta_i^2 \text{II}} f_i(\text{III}) \tag{48}$$

where we insert  $f(\text{III})$  to account for the possibility of  $\mu$  depending in the third invariant. The function  $f_i(\text{III})$  has not been considered experimentally; however, we require  $f_i(0) = 1$ . Furthermore, it is clear from eq. (46) that the dominant contribution to  $\bar{\eta}_e$  is always from the longest relaxation time. Previous calculations based on a molecular model<sup>35</sup> where the sudden increase in elongation viscosity was observed to be in the area of the first relaxation time are in agreement with this. In the area of longest relaxation time (in fact, for at least the first decade), we have shown that a single constant  $\theta$  in the White-Metzner equation is sufficient to portray the viscoelastic functions. Therefore, applying eqs. (30) and (31), say as an approximation, where  $A$  reflects longest relaxation time and using eq. (48) for the viscosity function,

$$\eta_i = \frac{\frac{3 \eta_A}{1 + 4\theta_A^2 \text{II}} \cdot f_A(\text{III})}{(1 + \theta_A d_{11})(1 - 2\theta_A d_{11})} + \frac{\frac{3 \eta_B}{1 + 4\theta_B^2 \text{II}} \cdot f_B(\text{III})}{(1 + \theta_B d_{11})(1 - 2\theta_B d_{11})} \tag{49}$$

As before, if we assume that  $\theta_A \gg \theta_B$ , the first term in eq. (49) is dominant. Thus, if we compare with eq. (46), it is seen that

$$\theta_A \rightarrow \tau_1 = \text{const}$$

and

$$\frac{\eta_A}{1 + 4\theta_A^2 \text{II}} \cdot f_A(\text{III}) \rightarrow \eta_1 = \text{const}$$

or that the proper parameters in the White-Metzner equation for elongational flow are simply the zero shear viscosity and first relaxation time of the material. Therefore, using eq. (44), we find

$$f_1(\text{III}) = 1 + 3\tau_1^2(4\text{III})^{2/3} \tag{50}$$

Equation (50) gives an explicit dependence of viscosity on the third invariant which is consistent with molecular arguments and would appear to be valid for use with the White-Metzner equation. From a molecular point of view, we are in effect noting that if the elongation viscosity of one element increases indefinitely, then the elongation viscosity of the entire solution must increase indefinitely.

The importance of separating the polymer contribution to the shearing and normal stresses in determination of  $\theta$  and  $\mu$  can be emphasized by considering eqs. (38) and (49). In eq. (49) it is clear that large elongation viscosities occur if  $2\theta_A d_{11}$  approaches unity. Thus, in eq. (38) the limiting birefringence angle is approximately  $31^\circ$ . Available data<sup>28,36</sup> based on the total stress of the solution, not just the polymer contribution, indicate that at high shear rates the birefringence angle becomes a constant,  $\chi_c$ , which is characteristic of the solution, or equivalently that  $2\theta\dot{\gamma} = \text{constant}$ . Now, if  $\chi_c > 31^\circ$ , the limit of  $2\theta\dot{\gamma} \sim \text{unity}$  would be exceeded at the appropriate deformation rate in elongation flow while, if the constant  $\chi_c < 31^\circ$ , the material would never have  $2\theta\dot{\gamma}$  approaching unity. This is not the case if one considers only the polymer contribution to the birefringence, eqs. (36) or (37). It has been shown<sup>35</sup> that in the area of gradient equal to the reciprocal of the first relaxation time, the curves for  $(P_{12})_{\text{pol}}$  and  $(P_{11} - P_{22})_{\text{pol}}$  cross, and for larger gradients,  $(P_{12})_{\text{pol}}$  is always less than  $(P_{11} - P_{22})_{\text{pol}}$  or that  $2\theta\dot{\gamma} > \text{unity}$ . That is, if we use only the polymer contribution to stresses in determining  $\theta$ , an infinite elongation viscosity will be predicted for all solutions. This is consistent with the molecular arguments where it was observed that only one of the Maxwell elements needs to have a critical stretch rate for the whole solution to show an infinite elongation viscosity. Gordon<sup>37</sup> has observed similar effects where there appears to be a certain molecular weight below which one would never observe a critical elongation viscosity. Gordon, although considering only the polymer contribution to  $P_{12}$ , has neglected to remove the solvent contribution to  $P_{11} - P_{22}$ .

## CONCLUSIONS

In the most elementary case, the relaxation times  $\theta_i$  in eq. (41) have been shown to coincide with the constant time parameters  $\tau_i = \theta_i$ . It follows that the White-Metzner parameter  $\theta_S$  can then be connected directly to the linear viscoelastic spectra and use can be made of the extensive linear viscoelastic data to show how  $\theta_S$  depends on concentration, temperature, etc.

In elongation flow, the dependence of  $\theta_S$  and  $\mu_S$  on the third invariant was proposed. Effectively, the proposed function forces the shear viscosity part of the elongation viscosity to be independent of the rate of elongation. In this regard it is important to emphasize the difference between elongation and shear flows at a molecular level. In shear flow, each molecule is deformed in a harmonic fashion while rotation takes place. In steady elongation, the particle assumes a steady position and is subject to a steady force which determines the elongation. The differences in the

character of these two flows expressed through dependences on the second and third invariants, therefore, will probably depend on the rotation or vorticity of the flow.

The estimation of  $\theta_s$  from birefringence measurements is possible through eqs. (33)–(41) and, since these are connected directly to structural characteristics of the material, may provide an important tool in connecting continuum and molecular models.

### Appendix

Equation (26) is a more general form of eq. (18) in which the possible error of matrix  $E_1$  is expressed in eq. (26b) and provides a means for estimation of how  $\Delta g$  or  $CE_1$  contribute to  $\Delta G$ .

We, in fact, solve the equation

$$E_1 \cdot G^* = g^* \tag{A-1}$$

where

$$g = g^* + \Delta g \tag{A-2}$$

$$G = \Delta G + G^* \tag{A-3}$$

From eqs. (9b) and (A-1) we have

$$(I - C) \cdot E_1 G^* = g^* \tag{A-4}$$

$$E_1 G^* = (I - C)^{-1} g^* = (I + C + C^2 + \dots) g + (I + C + C^2 + \dots) \Delta g, \tag{A-5}$$

and through rearrangement of eq. (A-5) in terms of the norms,

$$\begin{aligned} \frac{\|\Delta G\|}{\|G\|} &= \frac{\|g\|}{\|G\|} \cdot \|E_1^{-1}\| \cdot \frac{\|(C + C^2 + \dots)g + (I + C + \dots)\Delta g\|}{\|g\|} \\ &\leq \frac{\|g\|}{\|G\|} \cdot \|E_1^{-1}\| \left\{ \frac{q}{1 - q} + \frac{1}{1 - q} \cdot \frac{\|\Delta g\|}{\|g\|} \right\}, \tag{A-6} \end{aligned}$$

which is eq. (26).

### List of Symbols

- $c$  = empirically determined constant (approx. unity)
- $\bar{c}$  = constant
- $d$  = deformation rate tensor
- $g, g'$  = discrete (matrix) representation of relaxation modulus and real part of dynamic modulus, respectively
- $\Delta g$  = "error," or "change," in relaxation modulus
- $q$  = norm of matrix  $C$
- $t$  = time
- $v_i$  = velocity
- $x_i$  = coordinate directions
- $\|x\|$  = norm of matrix  $x$
- $A$  = general quadratic matrix
- $C$  = "error" matrix
- $E_1$  = matrix of exponential functions (see 9a)

$E_2, E_3$	= corresponding matrices for relation of real part of dynamic modulus and real part of dynamical viscosity to discrete relaxation spectra
$G(t)$	= linear relaxation modulus
$G'(\omega)$	= real part of dynamic modulus
$\Delta G$	= "error," or possible change, in discrete relaxation spectra
$G_p$	= modulus which characterizes spring stiffness of linear viscoelastic Maxwell model
$H(\log \tau)$	= continuous logarithmic relaxation spectrum
$I$	= unit matrix
$P$	= deviatoric stress tensor
$P_{11} - P_{22}$	= first normal stress difference (1 indicates flow direction, 2 indicates direction of shear)
II,III	= second and third invariants of shear rate tensor
$\dot{\gamma}$	= velocity gradient
$\frac{\delta}{\delta t}$	= Oldroyd convected derivative
$\delta(t - \tau)$	= Dirac delta function
$\eta'(\omega)$	= real part of dynamic viscosity
$\eta_{el}$	= elongation viscosity of White-Metzner model, eq. (45)
$\bar{\eta}_{el}$	= elongation viscosity of model which is built on molecular motion
$\theta$	= relaxation time of White-Metzner equation
$\lambda$	= eigenvalue of matrix $A$
$\mu$	= the viscosity parameter of White-Metzner equation
$\nu$	= parameter defined through eq. (18)
$\tau$	= continuous relaxation time
$\tau_p$	= constant relaxation time of $p$ th Maxwell element
$\psi_j$	= functions that are possible representations of the relaxation modulus $G(t)$
$\chi$	= birefringence angle
$\omega$	= angular frequency

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Received June 14, 1971

Revised September 21, 1971