Consistency Relations for Double-Step Strain Experiments

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ABSTRACT: Consistency relations for double-step strain deformations are formulated and applied in the evaluation of proposed constitutive models for nonlinear viscoelastic behavior. Two important double-step deformations are used to evaluate three constitutive models: the Doi–Edwards model without the independent alignment approximation, an integral viscoanelastic model, and a strain-coupling model. Comparison of the consistency relations for the Doi–Edwards and viscoanelastic models with double-step shear stress data showed that there may be important deficiencies in these models. The shear stress data were in reasonable accord with the consistency relation for the strain-coupling constitutive equation.

Introduction

Integral constitutive equations provide a useful way of describing the nonlinear viscoelastic behavior of concentrated polymer solutions and melts, and various equations of this type have been proposed. The predictive capabilities of such equations can conveniently be tested by using stress relaxation experiments. Single-step shear strain experiments can be used to classify rheological constitutive equations and to exclude extensive classes of constitutive equations from further consideration.[1-3] In a single-step shear strain experiment, an instantaneous shear strain γ_1 is imposed on a material at time $t = 0$, and the shear stress $\sigma(\gamma_1,t)$ and the first normal stress difference $N_1(\gamma_1,t)$ are measured as functions of time for $t > 0$. In addition, double-step shear strain experiments can be used to provide further information on the validity of proposed integral constitutive equations.[4-9] In a double-step shear strain experiment, a sudden strain γ_1 is imposed at $t = 0$ and a second total strain of γ_2 (a change of $\gamma_2 - \gamma_1$) is imposed at $t = t_1$. The shear stress $\sigma(\gamma_1,\gamma_2,t,t_1)$ and the first normal stress difference $N_1(\gamma_1,\gamma_2,t,t_1)$ can then be measured for $t > t_1$.

Evaluation of the predictive capabilities of various integral constitutive equations is facilitated if rheological relations that do not require assuming any special forms for the memory functions are developed for the measured stresses. The so-called Lodge–Meissner rule[10] is an example of such a rheological consistency relation for single-step experiments. In addition, the following consistency relation is valid for a K-BKZ fluid[10] for a double-step experiment:

$$\hat{\sigma}(\gamma_1,\gamma_2,t,t_1) = \sigma(\gamma_2-\gamma_1,t-t_1) + \sigma(\gamma_2,t) - \sigma(\gamma_2-\gamma_1,t) \quad (1)$$

It has been shown[4-9] using single-step and double-step strain data in eq 1 that the K-BKZ theory does not generally yield satisfactory predictions for double-step shear strain deformations. Consequently, new constitutive models have been proposed[8,11,12] in attempts to explain the double-step stress relaxation data. Since these constitutive equations presumably represent improvements over the K-BKZ model, it is of interest to determine whether their predictions are consistent with available data from double-step shear strain experiments.

The objective of this study is the formulation and application of rheological consistency relations for double-step strain deformations in the evaluation of three proposed constitutive models for nonlinear viscoelastic behavior. The three rheological constitutive models are introduced in the second section of the paper, and consistency relations for two important double-step deformations are presented in the third section of the paper. An evaluation of the three constitutive equations using some of the consistency relations is carried out in the final section of the paper.

Rheological Constitutive Equations

In this section, we present three constitutive equations which will be evaluated in this paper. The first equation is the Doi–Edwards constitutive equation without the independent alignment approximation.[8] The constitutive equation for general flow histories is very complicated,[13] but, for a double-step strain experiment, the following rheological relationship can be derived:

$$\sigma(\gamma_1,\gamma_2,t,t_1) = \sigma(\gamma_2-\gamma_1,t-t_1) + A(\beta)[\sigma(\gamma_2,t) - \sigma(\gamma_2-\gamma_1,t)] - B(\alpha_2,\beta)\sigma(\gamma_2-\gamma_1,t) \quad (2)$$

The parameters α_2 and β are functions of γ_1 and γ_2. Expressions for $A(\beta)$, $B(\alpha_2,\beta)$, α_2, and β are presented elsewhere.[6,8,9] These equations are not reproduced here because the definitions of these quantities are not important in the present context.

A second constitutive model is the integral viscoanelastic model presented by Larson and Valesano.[11] This model is based on the irreversibility hypothesis of Wagner[14] and Wagner and Stephenson.[15,16] For a reversing double-step strain experiment, the shear stress is described by the following equation:

$$\sigma(\gamma_1,\gamma_2,t,t_1) = [G(t-t_1) - G(t)](\gamma_2-\gamma_1)h(\gamma_2-\gamma_1) + G(t)\gamma_2 h(\gamma_1) \quad (3)$$

The quantity $h(\gamma_1)$ is defined by using the following factored form for a single-step shear strain experiment:

$$\sigma(\gamma_1,t) = \gamma_1 G(t)h(\gamma_1) \quad (4)$$

Here, $G(t)$ is the shear stress relaxation modulus of linear viscoelasticity.

The third constitutive equation is an integral constitutive equation that, unlike the K-BKZ model, includes the effect of strain coupling on the extra stress **S**. This constitutive

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equation can be expressed as follows:[12]

$$\mathbf{S} = \int_0^\infty [\varphi_1(s,I,II) + \int_0^\infty \varphi_3\{s_1,s,I(s_1)\}\, ds_1][\mathbf{N}(s) - \mathbf{I}]\, ds + \int_0^\infty [\varphi_2(s,I,II)][\mathbf{N}^{-1}(s) - \mathbf{I}]\, ds \quad (5)$$

$$\varphi_3(s_1,s,0) = 0 \quad (6)$$

$$I = \mathrm{tr}\,[\mathbf{N} - \mathbf{I}] \quad (7)$$

$$II = {}^1/_2[I^2 - \mathrm{tr}\,(\mathbf{N} - \mathbf{I})^2] = \mathrm{tr}\,[\mathbf{N}^{-1} - \mathbf{I}] - 2\,\mathrm{tr}\,[\mathbf{N} - \mathbf{I}] \quad (8)$$

$$\mathbf{N}(s) = \mathbf{C}_t^{-1}(t-s) = \mathbf{B}_\tau(t) \quad (9)$$

$$\mathbf{N}^{-1}(s) = \mathbf{C}_t(t-s) \quad (10)$$

$$\tau = t - s \quad (11)$$

Here, t is the present time, τ is the running time, s is the backward running time, $\mathbf{C}_t(t-s)$ is the right Cauchy–Green tensor relative to time t, $\mathbf{B}_\tau(t)$ is the left Cauchy–Green tensor relative to time τ, and $\mathbf{I}$ is the identity or unit tensor. This strain-coupling constitutive equation has three scalar-valued material functions φ_1, φ_2, and φ_3. When $\varphi_3 = 0$, eq 5 reduces to the K–BKZ constitutive equation. For the K–BKZ model, it is assumed that the contribution to the extra stress at time t made by the strain at some previous time τ depends on that strain and on the elapsed time $s = t - \tau$ and not on the strain at any other time. For eq 5, however, there is strain coupling since the influence of each strain increment on the stress is not independent of other strain increments.

Consistency Relations

In this section, rheological consistency relations are developed for two important double-step deformations that are described by the following values of γ_2 after an initial step of γ_1:

$$\gamma_2 = 0 \quad (12)$$

$$\gamma_2 = \gamma_1/2 \quad (13)$$

For the case of $\gamma_2 = 0$, we consider the quantity $\Delta\sigma$, the difference between an experimental measurement or a proposed theoretical result for the shear stress and the prediction of the K–BKZ theory:

$$\Delta\sigma = \sigma(\gamma_1,0,t,t_1) - \hat{\sigma}(\gamma_1,0,t,t_1) \quad (14)$$

For the integral viscoanelastic model of Larson and Valesano,[11] eqs 1 and 3 yield

$$\Delta\sigma = 0 \quad (15)$$

so that the prediction of this model is identical with the K–BKZ result when $\gamma_2 = 0$. For the Doi–Edwards theory[8] without the independent alignment assumption, combination of eqs 1 and 2 gives the following result for a deformation with $\gamma_2 = 0$:

$$\Delta\sigma = [1 - A(\beta) - B(\alpha_2,\beta)]\sigma(-\gamma_1,t) \quad (16)$$

If a series of double-step strain experiments with $\gamma_2 = 0$ is carried out for different t_1 values, then it is evident that eq 16 predicts that the value of $\Delta\sigma$ evaluated at the same time t is independent of the value of t_1 for the experiment:

$$(\partial\Delta\sigma/\partial t_1)_t = 0 \quad (17)$$

This derivative is taken with the time of observation t held constant. It should be noted here that $\Delta\sigma \to 0$ as $t_1 \to 0$ since a single-step strain experiment can of course be described perfectly by the K–BKZ theory.

A consistency relation can also be derived for eq 5, the strain-coupling model, if time–strain factorability is assumed for single-step experiments. Time–strain factorability will be valid for many materials for sufficiently small values of γ_1, and, in some cases, the separability of time and strain is valid for rather wide ranges of γ_1. From eqs 1 and 5, it is easy to deduce the result

$$\Delta\sigma = \gamma_1 \int_{t-t_1}^{t} \int_t^\infty \varphi_3(s_1,s,\gamma_1^2)\, ds_1\, ds + \gamma_1 \int_{t-t_1}^{t} \int_t^\infty \varphi_3(s,s_1,\gamma_1^2)\, ds_1\, ds \quad (18)$$

and differentiation with respect to t_1 with fixed t yields the following expression:

$$\left(\frac{\partial\Delta\sigma}{\partial t_1}\right)_{t,t_1=0} = \gamma_1 \int_t^\infty [\varphi_3(s_1,t,\gamma_1^2) + \varphi_3(t,s_1,\gamma_1^2)]\, ds_1 \quad (19)$$

For a single-step shear strain experiment, the strain-coupling model yields the expression

$$\sigma(\gamma_1,t) = \gamma_1 \int_t^\infty [\varphi_1(s,\gamma_1^2,-\gamma_1^2) - \varphi_2(s,\gamma_1^2,-\gamma_1^2) + \int_t^\infty \varphi_3(s_1,s,\gamma_1^2)\, ds_1]\, ds \quad (20)$$

and differentiation with respect to t produces the following result:

$$\frac{\partial\sigma(\gamma_1,t)}{\partial t} = -\gamma_1[\varphi_1(t,\gamma_1^2,-\gamma_1^2) - \varphi_2(t,\gamma_1^2,-\gamma_1^2) + \int_t^\infty \{\varphi_3(s_1,t,\gamma_1^2) + \varphi_3(t,s_1,\gamma_1^2)\}\, ds_1] \quad (21)$$

If time–strain factorability is valid for a material in single-step experiments, then

$$\frac{\partial\sigma(\gamma_1,t)}{\partial t} = g(\gamma_1)\frac{dG}{dt} \quad (22)$$

and eqs 21 and 22 imply that

$$\int_t^\infty \{\varphi_3(s_1,t,\gamma_1^2) + \varphi_3(t,s_1,\gamma_1^2)\}\, ds_1 = F(\gamma_1)\frac{dG}{dt} \quad (23)$$

Consequently, eq 19 can be written as follows:

$$\left(\frac{\partial\Delta\sigma}{\partial t_1}\right)_{t,t_1=0} = \gamma_1 F(\gamma_1)\frac{dG}{dt} \quad (24)$$

It is now possible to use eq 24 to derive a rheological relation by proposing that the following series of double-step strain experiments be performed. For fixed γ_1 and $\gamma_2 = 0$, shear stress data are collected for a number of values of t_1 that are sufficiently small so that extrapolation to $t_1 = 0$ is possible. It is then possible to evaluate $\Delta\sigma$ as a function of t_1 for a fixed time $t = t_A$ and also for another fixed time $t = t_B$. It follows from eq 24 that we can then arrive at the following rheological relation:

$$\frac{\left(\frac{\partial\Delta\sigma}{\partial t_1}\right)_{t_A,t_1=0}}{\left(\frac{\partial\Delta\sigma}{\partial t_1}\right)_{t_B,t_1=0}} = \frac{\left(\frac{dG}{dt}\right)_{t=t_A}}{\left(\frac{dG}{dt}\right)_{t=t_B}} \quad (25)$$

The left-hand side of eq 25 can be evaluated by using the above series of double-step strain experiments, and the right-hand side of eq 25 can be evaluated by using linear relaxation data for the material under consideration. The strain-coupling constitutive equation will be consistent with the double-step relaxation data only if eq 25 is satisfied by the measured shear stress data. Consequently, eq 25 is a rheological consistency relation that can be used to check the validity of eq 5. The functions φ_1, φ_2, and φ_3 are not evaluated, and only single-step and double-step shear stress data are needed to check the consistency of the data with the proposed model.

Another interesting consistency relation that can be easily derived from eq 5, the strain-coupling constitutive equation, is the following result for the ratio of normal and shear stresses for the double-step strain experiment with $\gamma_2 = 0$:

$$\frac{N_1(\gamma_1,0,t,t_1)}{\sigma(\gamma_1,0,t,t_1)} = -\gamma_1 \tag{26}$$

This result, which is independent of t and t_1, is of course very similar to the Lodge–Meissner rule[10] for single-step strain experiments. Equation 26 is also valid for the K-BKZ model, and, indeed, Osaki et al.[6] have reported that eq 26 is valid for a simple fluid. Any constitutive equation that is a special case of a simple fluid (like eq 5, for example) must then of course yield eq 26 as a relationship between the stresses measured for a double-step strain experiment with $\gamma_2 = 0$.

For a deformation with $\gamma_2 = \gamma_1/2$, the first normal stress difference for the strain-coupling model, eq 5, can be expressed as follows:

$$N_1\left(\gamma_1,\frac{\gamma_1}{2},t,t_1\right) = \int_{t-t_1}^{\infty}\left[\varphi_1\left(s,\frac{\gamma_1^2}{4},-\frac{\gamma_1^2}{4}\right) - \varphi_2\left(s,\frac{\gamma_1^2}{4},-\frac{\gamma_1^2}{4}\right)\right]\frac{\gamma_1^2}{4}\,ds + \int_{t-t_1}^{\infty}\int_{t-t_1}^{\infty}\varphi_3\left(s_1,s,\frac{\gamma_1^2}{4}\right)\frac{\gamma_1^2}{4}\,ds_1\,ds \tag{27}$$

Also, for a single-step deformation with a step of $\gamma_1/2$, the first normal stress difference at $t - t_1$ for the strain-coupling model is simply

$$N_1\left(\frac{\gamma_1}{2},t-t_1\right) = \int_{t-t_1}^{\infty}\left[\varphi_1\left(s,\frac{\gamma_1^2}{4},-\frac{\gamma_1^2}{4}\right) - \varphi_2\left(s,\frac{\gamma_1^2}{4},-\frac{\gamma_1^2}{4}\right)\right]\frac{\gamma_1^2}{4}\,ds + \int_{t-t_1}^{\infty}\int_{t-t_1}^{\infty}\varphi_3\left(s_1,s,\frac{\gamma_1^2}{4}\right)\frac{\gamma_1^2}{4}\,ds_1\,ds \tag{28}$$

Clearly, from eqs 27 and 28, it follows that

$$N_1\left(\gamma_1,\frac{\gamma_1}{2},t,t_1\right) = N_1\left(\frac{\gamma_1}{2},t-t_1\right) \tag{29}$$

and the normal stress response for a double-step strain experiment with $\gamma_2 = \gamma_1/2$ is equal to the normal stress response for a single-step experiment with a step of magnitude $\gamma_1/2$. Furthermore, this normal stress response is dependent only on $t - t_1$ and hence is independent of the duration of the first step. This result is identical with the result derived by McKenna and Zapas for the K-BKZ theory[17] and for a modified form of the K-BKZ theory.[18] In addition, Bruker[19] has shown that a similar result can be derived for the K-BKZ fluid for a triple-step strain experiment. The derivation here shows that this interesting normal stress prediction is valid also for the strain-coupling constitutive equation.

In the next section, some of the above rheological relations are used to critically evaluate the three constitutive equations presented in the second section of the paper.

Results and Discussion

In this section, it is shown that double-step shear stress data for a deformation with $\gamma_2 = 0$ provide a convenient and critical test of the three constitutive equations described above. Double-step shear stress data from two investigations[5,9] are used to carry out the evaluation of these constitutive equations. Shear stress measurements for diethyl phthalate–polystyrene[5] and dibutyl phthalate–polystyrene[9] solutions clearly show significant deviations between the data for double-step deformations with $\gamma_2 = 0$ and the predictions of the K-BKZ model. Consequently, from eq 15 it is evident that the integral viscoanelastic model does not give good predictions for the shear stress in a double-step deformation with $\gamma_2 = 0$. This is an important shortcoming of this theory, although Larson and Valesano[11] have shown that good results are obtained with $\gamma_1 = 5$ and $\gamma_2 = 4$.

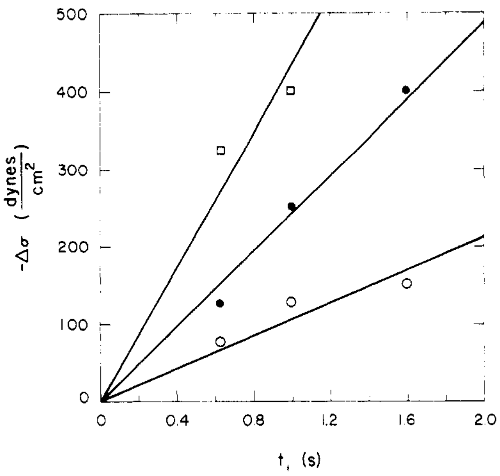

Figure 1. Dependence of $\Delta\sigma$ on t_1 for the dibutyl phthalate–polystyrene system with $\gamma_1 = 4$ and $\gamma_2 = 0$ for three values of t: 2.5 s (□), 4.0 s (●), and 6.3 s (○).

Table I
Evaluation of Eq 25 for the Dibutyl Phthalate–Polystyrene System

t_A, s	t_B, s	left-hand side of eq 25	right-hand side of eq 25
2.5	6.3	4.2	4.9
2.5	4.0	1.8	2.0
4.0	6.3	2.4	2.4

Values of $\Delta\sigma$ for the dibutyl phthalate–polystyrene system[9] with $\gamma_1 = 4$ and $\gamma_2 = 0$ are plotted versus t_1 in Figure 1 for three values of t, the time of measurement. It is clear that $\Delta\sigma$ for fixed t *does* depend on t_1 so that eq 17 is not satisfied. This observation casts some doubt on the ability of the Doi–Edwards theory to provide an adequate description of the double-step experiment. The data in Figure 1 can also be used to check on the validity of eq 25, the consistency relation for the strain-coupling model. The straight lines in Figure 1 are least-squares lines through the origin, and they can be used to evaluate $\partial\Delta\sigma/\partial t_1$ at $t_1 = 0$. The results of this calculation coupled with data for $G(t)$ for the polymeric fluid of interest can then be used to evaluate the left-hand and right-hand sides of eq 25. A summary of this evaluation is presented in Table I. The data in this table show that eq 25 is satisfied reasonably well, and, hence, the double-step stress relaxation data are consistent with the predictions of the strain-coupling constitutive equation. It should be noted, however, that there are some deviations from time–strain factorability for $\gamma_1 \geqq 4$ for the dibutyl phthalate–polystyrene single-step data.[9] Hence, in the strictest sense, eq 25 should not be applied to the double-step data for $\gamma_1 = 4$ and $\gamma_2 = 0$. However, the deviations from factorability at this strain level are modest, so that utilization of eq 25 should still provide a reasonable test of the consistency of the model with the shear stress data.

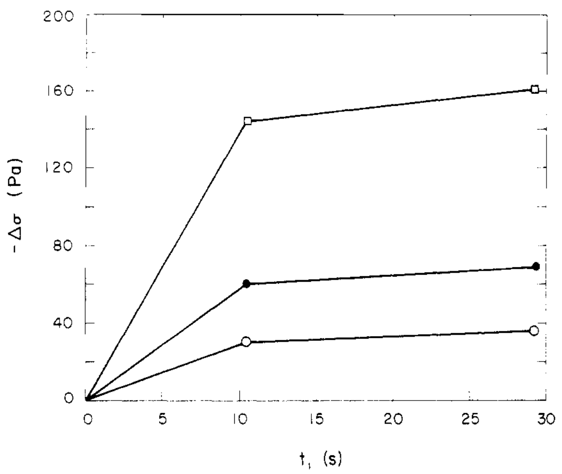

Figure 2. Dependence of $\Delta\sigma$ on t_1 for the diethyl phthalate–polystyrene system with $\gamma_1 = 11.6$ and $\gamma_2 = 0$ for three values of t: 59.3 s (□), 99.3 s (●), and 129.3 s (○).

Table II
Evaluation of Eq 25 for the Diethyl Phthalate–Polystyrene System

t_A, s	t_B, s	left-hand side of eq 25	right-hand side of eq 25
59.3	129.3	4.7	4.6
59.3	99.3	2.4	2.8
99.3	129.3	1.9	1.6

The double-step shear stress data of Osaki and Kurata[5] for the diethyl phthalate–polystyrene system for $\gamma_1 = 11.6$ and $\gamma_2 = 0$ can also be used to check the validity of eqs 17 and 25. Values of $\Delta\sigma$ for this system are plotted versus t_1 in Figure 2 for three values of t, the time of measurement. The value of $\Delta\sigma = 0$ at $t_1 = 0$ is also included in this figure. Again, it appears that $\Delta\sigma$ for fixed t depends on t_1, and, again, eq 17 is not satisfied. Unfortunately, it is not possible to carry out an accurate assessment of the validity of eq 25 because sufficiently small values of t_1 were not included in the data set. However, a rough estimate of $\partial\Delta\sigma/\partial t_1$ at $t_1 = 0$ can be obtained by using the slope of the straight line from the origin to the first data point for each value of t. The results of this approximate calculation can be combined with $G(t)$ data to provide values for the left-hand and right-hand sides of eq 25. A summary of this evaluation is presented in Table II, and it is evident that eq 25 is again satisfied reasonably well, even with the uncertainty in the initial slope.

The above evaluation of the three constitutive equations using double-step shear stress data with $\gamma_2 = 0$ shows that there may be important deficiencies in the Doi–Edwards model and in the integral viscoanelastic model. On the other hand, the fact that the shear stress data are in reasonable accord with the consistency relation for the strain-coupling model indicates that this model deserves further scrutiny. Additional comparisons using more double-step data and start-up, cessation, and finite amplitude oscillatory data are needed to assess the ability of this model to provide an adequate description of nonlinear viscoelasticity.

Normal stress data for a double-step deformation with $\gamma_2 = \gamma_1/2$ are needed to check on the validity of eq 29, a relation that is valid for both K–BKZ and strain-coupling models. Unfortunately, however, there are not many double-step normal stress data sets available because of the difficulty in making accurate normal stress measurements. McKenna and Zapas[18] have shown that eq 29 is satisfied for polymeric materials that are not generally described by the K–BKZ model. This result suggests that constitutive equations that are improvements to the K–BKZ model should still satisfy eq 29, as is the case for the strain-coupling model. More normal stress data for double-step experiments are needed to assess the general validity of eq 29 for materials whose rheological behavior is not generally described by the K–BKZ model.

Finally, it is important to emphasize that eq 25, one of the consistency relations for the strain-coupling model, is valid only when time–strain factorability is applicable for single-step experiments for a particular material. The separability of time and strain is valid for many materials for small values of γ_1, and the range over which the separability assumption is valid is of course dependent on the particular system being studied.[5,9,20] For example, for the dibutyl phthalate–polystyrene system referred to above, time–strain factorability is valid up to $\gamma_1 = 4$, whereas for the diethyl phthalate–polystyrene system, time–strain factorability is valid at least up to $\gamma_1 = 11.6$. In other cases,[5] departures from time–strain factorability are noted even for relatively low strains.

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