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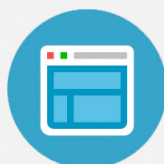
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Rheological implications of completely monotone fading memory

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Synopsis

In the constitutive equation modeling of a (linear) viscoelastic material, the “fading memory” of the relaxation modulus $G(t)$ is a fundamental concept that dates back to Boltzmann [Ann. Phys. Chem. **7**, 624 (1876)]. There have been various proposals that range from the experimental and pragmatic to the theoretical about how fading memory should be defined. However, if, as is common in the rheological literature, one assumes that $G(t)$ has the following relaxation spectrum representation: $G(t) = \int_0^\infty \exp(-t/\tau)[H(\tau)/\tau]d\tau$, $t > 0$, then it follows automatically that $G(t)$ is a completely monotone function. Such functions have quite deep mathematical properties, that, in a rheological context, spawn interesting and novel implications. For example, because the set of completely monotone functions is closed under positive linear combinations and products, it follows that the dynamics of a linear viscoelastic material, under appropriate stress–strain stimuli, will involve a simultaneous mixture of different molecular interactions. In fact, it has been established experimentally, for both binary and polydisperse polymeric systems, that the dynamics can simultaneously involve a number of different molecular interactions such as the Rouse, double reptation and/or diffusion, [W. Thimm *et al.*, J. Rheol., **44**, 429 (2000); F. Léonardi *et al.*, J. Rheol. **44**, 675 (2000)]. The properties of completely monotone functions either yield new insight into modeling of the dynamics of real polymers, or they call into question some of the key assumptions on which the current modeling is based, such as the linearity of the Boltzmann model of viscoelasticity and/or the relaxation spectrum representation for the relaxation modulus $G(t)$. If the validity of the relaxation spectrum representation is accepted, the resulting mathematical properties that follow from the complete monotonicity of $G(t)$ allows one to place the classical relaxation model of Doi and Edwards [M. Doi and S. F. Edwards, J. Chem. Soc., Faraday Trans. 2 **74**, 1789 (1978)], as a linear combination of $\exp(-t/\tau^*)$ relaxation processes, each with a characteristic relaxation time τ^* , on a more general and rigorous footing. © 2002 The Society of Rheology. [DOI: 10.1122/1.1514203]

I. INTRODUCTION

As is clear from the rheological literature, for much industrial decision making, the molecular weight distribution $w(m)$ of a polymer represents a suitable and adequate

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molecular characterization [McLeish and Larson (1998); Mead (1994)]. Consequently, there is great interest in its determination. A wide variety of methods, ranging from the direct experimental (high-performance liquid chromatography, size exclusion and triple F) to the inversion of indirect rheological measurement, is available and applied on a regular basis [Anderssen and Westcott (2000)]. Although the former are quite appropriate in the study of the structure of DNA and proteins, it is the latter class which is normally applied in the study of synthetic polymers.

Of these rheological methods, the most natural and popular are mixing rules which assume that the relationship between the (Boltzmann) relaxation modulus $G(t)$ and the molecular weight distribution $w(m)$ can be modeled as

$$G(t) = G_N^0 \left[\int_0^\infty k(t,m)w(m)dm \right]^\beta, \quad t > 0, \quad (1)$$

for some constant G_N^0 , where β denotes some real positive value which reflects the nature of the polymer dynamics under consideration, and the kernel $k(t,m)$ is chosen to reflect how the various components of $w(m)$ contribute to $G(t)$. There is extensive literature on the subject which includes work by Mead (1994), Anderssen and Mead (1998), Anderssen and Loy (2001), Thimm *et al.* (1999, 2000) and Léonardi *et al.* (2000).

The situation with $\beta = 1$ corresponds to classical single reptation, while $\beta = 2$ characterizes the dynamics of double reptation [des Cloizeaux (1988)]. This leads naturally to the idea that the parameter β represents a way of characterizing the nature of the dynamics of a polymer. This is the point of view that is adopted in this paper. At least mathematically, in terms of how one manipulates and interprets Eq. (1), one can have different forms of the dynamics. Experimentally, the challenge is to clarify and validate the extent to which it occurs in reality.

On the one hand, it is widely assumed [e.g., by Bird *et al.* (1987), p. 285] that the relaxation modulus $G(t)$ has a relaxation spectrum representation given by

$$G(t) = \int_0^\infty \exp(-t/\tau) \frac{H(\tau)}{\tau} d\tau, \quad H(\tau) \geq 0, \quad t > 0, \quad (2)$$

where $H(\tau)$ denotes the non-negative relaxation spectrum and τ the relaxation time. The advantage of this assumption is that it automatically guarantees that $G(t)$ has a “fading memory” [in the sense introduced by Boltzmann (1876)], but at the expense of constraining $G(t)$ to be a completely monotone function [Widder (1946), Anderssen and Loy (2002)]. Although other definitions have been proposed (there is a brief review in Sec. II), the completely monotone version gives one considerable mathematical machinery with which to investigate matters theoretically. The practical rheological consequences of such theoretical results are the focus of this paper.

On the other hand, in work by Thimm *et al.* (1999), the idea has been exploited of using $G(t)$ as the link concept which allows one to construct the following types of relationship between $w(m)$ and $H(\tau)$:

$$\int_0^\infty \exp(-t/\tau) \frac{H(\tau)}{\tau} d\tau = G_N^0 \left[\int_0^\infty k(t,m)w(m)dm \right]^\beta. \quad (3)$$

Before this equation can be exploited to define the molecular weight distribution $w(m)$ as a function of the relaxation spectrum $H(\tau)$, it is necessary to specify the function $\tau = \tau(m)$ that defines how the relaxation time τ depends on the molecular weight m . This is normally taken to be

$$\tau(m) = Km^\alpha,$$

where the constants K and α are independent of the nature of the dynamics that occur. However, this aspect will not be pursued further in this paper.

This equivalencing, which will be referred to as the relaxation time spectrum and molecular weight distribution (RTSMWD) relationship, has allowed Thimm *et al.* (1999, 2000) to derive various expressions between $w(m)$ and $H(\tau)$ and to put the study of the mixing rules, Eq. (1), on a more formal footing.

However, the fact that the right-hand side of Eq. (3) has become, on the basis of the form of the left-hand side, a completely monotone function has not been fully exploited theoretically and rheologically. The theoretical properties of this relationship have been examined in some detail in Anderssen and Loy (2002). The purpose of this paper is an examination of their rheological consequences.

The paper is organized in the following manner. Section II contains a review of the concept of fading memory, and, thereby, brings together a summary of the different definitions that have been proposed and published. Theoretical rheological consequences of the complete monotonicity assumption are examined Sec. III. The inversion of the RTSMWD relationship, for single and double reptation as well as for values of $\beta > 2$, is discussed in Sec. IV. Some circumstantial experimental evidence that supports the hypothesis that polymer dynamics can simultaneously involve a number of different molecular interactions is examined in Sec. V.

II. CONCEPT OF FADING MEMORY

As explained in various rheological texts, appropriate conditions must be imposed on $G(t)$ in order to guarantee that the associated Boltzmann constitutive relationship for linear viscoelastic materials,

$$\sigma(t) = \int_{-\infty}^t G(t-\tau)\dot{\gamma}(\tau)d\tau, \quad (4)$$

makes sense physically. Here, $\sigma(t)$ denotes the stress corresponding to the given strain rate $\dot{\gamma}(t)$. In particular, following Boltzmann (1876), $G(t)$ is said to have “fading memory,” if changes in the past have less effect now than equivalent more recent changes.

In work of Thimm *et al.* (1999, 2000) and in most related work, the fact that $G(t)$ must have fading memory has not been a central issue. The assumption, either explicitly or tacitly, that $G(t)$ has the relaxation spectrum representation of Eq. (2), automatically guarantees that an appropriate form for the Boltzmann fading memory has been invoked. However, this in turn imposes regularity conditions on any subsequent manipulations of $G(t)$ such as the formulation of mixing rules as in Eq. (1). As is clear from the literature, there is no universal definition of fading memory. A wide variety of views prevail that are summarized as follows.

A. Purely mechanical

This is the point of view which is supported most strongly by rheological pragmatists. They assert that one only requires a set of conditions [such as $G(t)$, $-dG(t)/dt$ and $d^2G(t)/d^2t$ being non-negative] which guarantee that the related physical concepts of work, dissipation etc. respect the conservation of energy and related principles [Akyildiz *et al.* (1990)]. Although such conditions guarantee sensible physics, there is no guarantee that other conditions should not have been included in order to fully model the physics of

the polymer dynamics. For example, rheologically, these limited conditions are not sufficient to draw a distinction between polymers and other materials. Mathematically, a more general condition, which includes the above conditions (either explicitly or implicitly), can sometimes assist in the theoretical analysis. In addition, the purely mechanical approaches rule out the possibility of assuming that $G(t)$ has the relaxation spectrum representation, Eq. (2). To assume otherwise would contradict the goal of defining fading memory in terms of purely physical concepts.

B. Rheological

This is the point of view adopted by rheologists working with mixing rules. From the tabulation, given by Maier *et al.* (1998), of models proposed by various authors for the kernel $k(m, t)$ of Eq. (1), it can be seen that, except for the Tuminello kernel, fading memory corresponds to assuming that the dominant behavior of $k(t, m)$ takes the form $\exp[-t/\tau(m)]$. The proof for the des Cloizeaux kernel is a little more complicated, but it, too, is completely monotone. The advantage of this approach is the practicality of such mixing rules, which have been validated theoretically [Anderssen and Mead (1998); Anderssen and Loy (2001)] and experimentally [Maier *et al.* (1998); Thimm *et al.* (1999, 2000)]. However, whether or not $G(t)$ is a complete monotone now depends on the value of β [in Eq. (1)]. Integer powers of completely monotone functions are completely monotone. Fractional powers are completely monotone only under special circumstances [Anderssen and Loy (2002)]. Consequently, one can only invoke the relaxation spectrum representation of Eq. (2) for $G(t)$ for special values of β . Unlike the purely mechanical approach to fading memory, this approach allows the possibility of distinguishing between polymers and other materials. The classical example is the Doi–Edwards reptation theory of polymer dynamics [Doi and Edwards (1978)] which yields a natural rationale for $k(m, t)$ to have $\exp(-t/\tau(m))$ -type behavior. An independent example was given by McLeish (1992) who, as a result of modeling the disentanglement of highly polydisperse polymers, proposed a framework that leads to the following model for $k(m, t)$ [Thimm (2002)]:

$$\exp\left(-2\left[\int_0^t\left\{\frac{G(t')}{G_N^0}\right\}^{1/2} dt'\right] / \tau(m)\right).$$

This function is only completely monotone for a restricted class of $G(t)$.

C. Response functional histories

Here we summarize the various definitions invoked in theoretical investigations of linear viscoelasticity. A complete explanation is outside the scope of the current discussion, but a comprehensive summary can be found in work by Fabrizio and Morro (1992). In a nutshell, it is assumed that fading memory behavior can be modeled by a monotone decreasing and suitably smooth function $G(t)$. Consequently, complete monotonicity would be a special case. Again, the need to draw a clear distinction between the behavior of polymers and other materials is not specifically addressed. In addition, it rules out the possibility of $G(t)$ having the relaxation spectrum representation of Eq. (2), unless greater regularity is invoked.

D. Complete monotonicity

The strongest assumption about fading memory appears to date back to Day (1970), and assumes that $G(t)$ is a completely monotone function, namely,

$$(-1)^n \frac{d^n G(t)}{dt^n} \geq 0, \quad n \geq 0, \quad t > 0.$$

Bernstein's theorem [Widder (1946), p. 160] shows this is equivalent to

$$G(t) = \int_0^\infty \exp(-ts) d\mu(s) \tag{5}$$

for some positive measure μ on $(0, \infty)$ such that the integral converges for all $t > 0$.

It follows from this result that any completely monotone function is the restriction to the positive half line $(0, \infty)$ of a function analytic in the right half plane. It is this fact which gives the concept of complete monotonicity its specialized structure and explains why the definition is not as innocuous as it initially appears.

The simple change of variable $s = 1/\tau$ in Eq. (2) yields

$$G(t) = \int_0^\infty \exp(-ts) \frac{H(1/s)}{s} ds.$$

This is, of course, a particular form of Eq. (5), which thereby establishes complete monotonicity of the relaxation spectrum representation. This definition has two key advantages. On the one hand, it yields a structure which can be exploited mathematically to prove potentially useful rheologically results. On the other hand, it allows polymeric considerations to be built into the modeling. For example, the probabilistic concept of infinite divisibility, which is related to an important subset of completely monotone functions, can be utilized to construct molecular models of polymers [Montroll and Bendler (1984); Bendler (1984)], as distinct from other materials. In addition, as shown by Beris and Edwards (1993), thermodynamic compatibility is an immediate consequence of complete monotonicity.

Consequently, the purpose of this paper is an examination of the consequences of assuming that fading memory is modeled as a completely monotone $G(t)$ and the resulting rheological implications.

The examination below is independent of the analysis contained in the work of Day (1970). Among other things, Day (1970) proved that $G(t)$ is completely monotone if and only if the work done on retraced paths is increased by delay. In addition, Day (1970) established conditions under which this result extends to nonlinear viscoelasticity. Subsequently, Del Piero and Deseri (1995) extended this result to the multidimensional case. They also established, under suitable regularity, that the work done in every closed path in stress-strain space is non-negative, if and only if the multidimensional relaxation modulus $\mathbf{G}(t)$ is of exponential type, namely,

$$\mathbf{G}(t) = \mathbf{A} + \mathbf{B} \exp[t\mathbf{H}(t)],$$

where \mathbf{A} , \mathbf{B} and \mathbf{H} are fourth order tensors, and all the eigenvalues of \mathbf{H} , the eigenspaces of which are not contained in the null space of \mathbf{B} , have negative real parts. The if and only if nature of these results shows just how critical physical assumptions are in restricting the allowable behavior of $\mathbf{G}(t)$. This again calls into question the purely mechanical approach to fading memory discussed above.

The if and only if nature of Day's (1970) result is a challenge in that, if one assumes the complete monotonicity of $G(t)$, then one must automatically allow for the fact that "work is always increased by delay on retraced paths."

III. THEORETICAL RHEOLOGICAL IMPLICATIONS

As explained above, the relaxation modulus $G(t)$, defined in Eq. (2), is *completely monotone*. Pragmatically, the importance of this result is that one only needs to derive a positive estimate of $H(\tau)$, from given rheological measurements, in order to guarantee that $G(t)$, defined by Eq. (2), has fading memory. In addition, Eq. (2) yields a formal characterization of the concept of a relaxation spectrum $H(\tau)$ of a polymer in terms of the kernel $G(t)$ which characterizes the Boltzmann constitutive relationship for (linear) viscoelasticity.

Anderssen and Loy (2001, 2002) have examined, in some detail, the properties of completely monotone functions and their implications for Eq. (3). It follows from that work that, for a suitable choice of the N , $G(t)$ can have the following structure:

$$G(t) = \sum_{r=1}^N \alpha_r G_r(t), \quad G_r(t) = \int_0^{\infty} \exp(-g_r(t)/\tau) \frac{H_r(\tau)}{\tau} d\tau, \quad (6)$$

$$\alpha_r > 0, \quad g_r(t) \geq 0, \quad H_r(\tau) \geq 0,$$

where $g_r(t)$, and $H_r(\tau)$ denote, respectively, the r th contribution of the nature of the fading memory and the relaxation spectrum. On the basis of the mixing rule formalism of Eq. (1), one can define the components $G_r(t)$ as having the following form:

$$G_r(t) = G_N^0 \left(\int_0^{\infty} k_r(m) \exp[-f_r(t)/\tau_r(m)] w_r(m) dm \right)^r, \quad (7)$$

where $k_r(m)$ denotes some continuous, non-negative, bounded function of m , which can change as the level r changes, $w_r(m)$ the r th contribution to the molecular weight distribution $w(m)$, $f_r(t)$ the nature of the fading memory appropriate to the behavior of this molecular weight component, $\tau_r(m)$ the relaxation time dependence on the molecular weight m , which can also change as the level r changes, and, finally, G_N^0 the plateau modulus.

Note 1. Mathematically, the meaning of the r th contribution is unambiguously defined in terms of the definition of $G_r(t)$ in Eqs. (6) and (7). Rheologically, for $r = 1$ and 2, one has the well-accepted concepts of single and double reptation. How one decides, rheologically, to interpret triple and higher levels of molecular interaction will determine the usefulness and applicability of the decomposition, Eqs. (6). A detailed examination is outside the scope of this paper.

Note 2. The function t in the exponential terms $\exp(-t/\tau)$ has been replaced by more general $g_r(t)$ and $f_r(t)$. As explained by Anderssen and Loy (2002), the complete monotonicity of $G(t)$ will be preserved, provided that both $dg_r(t)/dt$ and $df_r(t)/dt$ are positive and completely monotone [a fact also noted by Grinshpan *et al.* (2000)]. This generalization is closely related to the probabilistic concept of infinite divisibility and is discussed below.

Note 3. In Eqs. (6), the decomposition was chosen to reflect the dynamical characteristics of the polymer under investigation. This decomposition is not unique and should be chosen in the most appropriate form, when the need arises. As illustrated, for example, in Eq. (4) in the work of Thimm *et al.* (2000), as well as in the classical delta function decompositions, even the relaxation spectrum in Eq. (2) can be reformulated as the sum of suitable component relaxation spectra with each having a different completely mono-

tone characterization. Since $\exp(-t/\tau)$ has fading memory, Eq. (2) can be viewed as defining $G(t)$ to be a weighted averaging of the “elementary” fading memory functions $\exp(-t/\tau)$.

Caveat. Mathematically, there is no inconsistency between Eqs. (2) and (6), because they define equivalent representations of completely monotone functions. Consequently, one can be folded into the other as the need arises. Rheologically, however, the matter is more delicate. For a given polymer, the existence of these different representations for $G(t)$ imply that it may not be correct, without further investigation, to assume that the underlying dynamics are simply determined by Eq. (2). Within the polymer context, there is a need to determine what the appropriate version of Eqs. (6) should be.

The key rheological consequences of this model are the following.

- (i) The dynamics of a complex polymer flow can involve some simultaneous combination of molecular interactions.
- (ii) The various molecular interactions involved in the dynamics of a complex polymer flow will combine linearly, through their respective relaxation moduli, in proportion to their relative activity. From a practical perspective, this model generates the need to estimate these proportional activities.
- (iii) The nature of the fading memory associated with each of the molecular interactions and encapsulated in terms of the choice of the $f_r(t)$ can be different. In many ways, it is this fact which gives a new dimension to the modeling of polymer dynamics in terms of the underlying molecular interactions.
- (iv) The relaxation time dependence on the molecular weight can change from one type of molecular interaction to the next.
- (v) It is not necessary to assume that, for a particular stress–strain stimulus, the fading memory associated with the relaxation spectrum is the same as that connected with the molecular weight distribution. Even for a polymer that only involves a single type of molecular interaction (such as single or double reptation), this result has significant consequences. Among other things, it implies that, for such situations, the RTSMWD will take the form

$$\int_0^\infty \exp(-g_r(t)/\tau) \frac{H_r(\tau)}{\tau} d\tau = G_N^0 \left[\int_0^\infty k_r(m) \exp(-f_r(t)/\tau_r(m)) w_r(m) dm \right]^r, \quad (8)$$

for an appropriate positive integer value of r . Theoretically, it is convenient to work with Eqs. (6) and (7) in the form of

$$G(t) = \sum_{r=1}^R G_N^0 \left(\int_0^\infty k_r(m) \exp[-g_r(t)/\tau_r(m)] w_r(m) dm \right)^r, \quad (9)$$

where R denotes the highest level of molecular interaction occurring. It is implicitly assumed that each of the molecular weight components $w_r(m)$ will be zero outside some bounded interval $[m_r, M_r]$. If such information were taken explicitly into account, then the general structure of a mixing rule, Eq. (9), would take the form of

$$G(t) = \sum_{r=1}^R G_N^0 \left(\int_{m_r}^{M_r} k_r(m) \exp[-g_r(t)/\tau_r(m)] w_r(m) dm \right)^r, \quad (10)$$

where there will be overlapping of the intervals $[m_r, M_r]$ in situations where some form of simultaneous molecular interaction occurs. The explicit nature of Eq. (10) is important in an experimental and rheological context since the meaning of the lower and upper

bounds m_r and M_r , respectively, will relate to the type of polymer being studied and the stress–strain response being stimulated.

Caveat. It does not follow from Eq. (9) that the total molecular weight distribution $w(m)$ of a polymer is the sum of the individual components $w_r(\bar{m})$, namely,

$$w(m) = \frac{\sum_{r=1}^R w_r(m)}{\sum_{r=1}^R \int_0^\infty w_r(\bar{m}) d\bar{m}}. \quad (11)$$

In fact, unless one invokes some condition like that in Eq. (11) as the appropriate way in which to combine the molecular weight components $w_r(m)$, it follows from Eq. (9) that the same polymer could contribute to two or more independent levels of molecular interaction. From the work of Thimm *et al.* (2000) and of Léonardi *et al.* (2000), as well as that of other authors, one has direct proof that this occurs in complicated flows that involve polymers with complex geometries.

IV. PRACTICAL RHEOLOGICAL IMPLICATIONS

A number of authors [Léonardi *et al.* (2000); Benallal *et al.* (1993); Carrot and Guillet (1997); Carrot *et al.* (1996); Lin (1984)] have observed that the relaxation modulus $G(t)$ can be rewritten as the sum of component relaxation moduli, which individually identify different relaxation processes postulated to be occurring in the dynamics of a polymer during flow and deformation. As explained by Benallal *et al.* (1993), as well as by other authors subsequently, the basis for such a decomposition dates back to the original work on reptation by Doi and Edwards (1978). For example, these relaxation components are often explained and justified in terms of the relaxation motion induced by reptation, diffusion and Rouse dynamics. Specifically, in the work of Léonardi *et al.* (2000), a decomposition of the following form is proposed:

$$G(t) = G_C(t) + G_B(t) + G_A(t) + G_{HF}(t), \quad (12)$$

where these components correspond, respectively, to the relaxation associated with reptation diffusion, Rouse relaxation of the whole chain, Rouse relaxation between two entanglement points and the glassy behavior of the chain. Theoretically, one is simply exploiting the fact that, under appropriate circumstances, $G(t)$ can be written as a sum of the sums of exponentials of the form

$$G_0^N \sum_k a_k \exp(-tk^2/\tau^*), \quad (13)$$

where the a_k denote constants, and the value of the relaxation time τ^* is chosen to distinguish between the various relaxation processes believed to be occurring. Rheologically, this agrees and fits naturally with the meaning and interpretation of the concept of relaxation time, and represents an appropriate way in which to distinguish between different relaxation processes.

On the one hand, this approach represents a way of performing the decomposition, Eqs. (6). It is clearly a viable strategy for simple forms of polymer dynamics. This is reflected in the success with which it, and even simpler versions that involve only a single sum of exponentials, Eq. (13), has been able to model the dominant features in polymer dynamics. Its major limitation is the assumption that a single sum of exponentials, Eq. (13) (with a single relaxation time), is all that is required to model each of the individual dynamics that occur in a polymer during flow and deformation.

On the other hand, it illustrates, relative to the more comprehensive form of Eqs. (6), the shortcoming of the assumption that $G(t)$ is simply the sum of sums of exponentials of the form of Eq. (13). This assumption forces the unrealistic assumption that the fading memory, up to the values of relaxation times τ^* , is identical for the different relaxation processes involved in polymer dynamics. Clearly, on stating the matter as emphatically as this, and in light of the deliberations above, this is not likely to be the situation, except under special circumstances.

This leads naturally to the conclusion that one should allow for the possibility that a more appropriate model for the moduli of the different relaxation components is given by the $G_r(t)$ in Eq. (6). This leaves open the interesting question of whether one should work directly with the exact expression for $G_r(t)$ in Eq. (6), or use some alternative explicit encapsulation. In the study of bone rheology, Sasaki *et al.* (1993) proposed, in the spirit of Eqs. (6), a five-parameter $(A_1, A_2, \tau_1, \tau_2, \beta)$ model for the relaxation modulus which involved two independent relaxation components, namely,

$$G(t) = A_1 \exp\left[-\left(\frac{t}{\tau_1}\right)^\beta\right] + A_2 \exp\left(-\frac{t}{\tau_2}\right), \quad 0 < \beta \leq 1. \quad (14)$$

The first function $\exp[-(t/\tau)^\beta]$ on the right-hand side of Eq. (14) is the Kohlrausch (stretched exponential) function, which has been utilized extensively to model the relaxation of glassy states of various materials [cf. Rambousky *et al.* (1996); Ngai and Roland (2002); de Gennes (2002)]. Because it takes the form $\exp[-\theta(t)]$ with the derivative of $\theta(t)$ (viz., $t^{\beta-1}$, $0 < \beta \leq 1$) completely monotone [cf. Grinsphan *et al.* (2000); Anderssen and Loy (2002)], the Kohlrausch function is the Laplace transform of an infinitely divisible probability distribution. This automatically guarantees the complete monotonicity for the above expression for $G(t)$. In addition, because it is the characteristic function (Fourier transform) of a Lévy (stable) distribution, it can be given a molecular-type interpretation [Montroll and Bendler (1984)]. A discussion of the relevance of such interpretations to the polymer dynamics context is outside the scope of this paper. Except for the recent paper of de Gennes (2002), it appears to be a matter that has not been given the attention that it deserves. What is clear, however, is that the Kohlrausch function has the type of compact structure, as well as generality and flexibility, that can be used to characterize the specific relaxation that occurs in a component-by-component decomposition of the relaxation behavior of a polymer. Furthermore, because positive linear combinations of Kohlrausch functions are completely monotone, its utilization in this manner automatically guarantees that the resulting relaxation modulus will be completely monotone.

V. ON THE INVERSION OF THE RTSMWD RELATIONSHIP

Once the structure of a component $G_r(t)$ has been determined, one can then turn to recovering information about the molecular weight distribution $w_r(m)$ of those components of the polymer that contribute to the $G_r(t)$ dynamics. This brings one back to the problem of inverting some appropriate form of Eq. (8).

The situation where r takes values of 1 and 2 was examined by Thimm *et al.* (1999, 2000) for a much simpler form of Eq. (8) [in particular, $g_r(t) = f_r(t) = t$]. For the more general situation in which r is an integer, Eq. (8) was solved by Anderssen and Loy (2002). For $r = 1$, they essentially obtained the same result as Thimm *et al.* (1999), but, for $r = 2$, they obtained a new result. In addition, they indicated how, inductively, one could construct the solution for $r \geq 3$.

A methodology like that discussed by Maier *et al.* (1998) could be used to assess whether there is a dominant or a mixture of reptation activity in a particular polymer dynamical situation. When one estimates the value of r from given data, r will tend to assume a noninteger value. It is then a matter of interpreting whether the resulting estimate of r corresponds to an integer value of r that identifies a dominant reptation behavior, or a noninteger value that identifies a mixture.

Together, the recent work of Léonardi *et al.* (2000), Thimm *et al.* (2000) and Anderssen and Loy (2002) lay the foundation for the construction of a general ansatz for the recovery of the molecular weight distribution from oscillatory shear data. The essential steps are

- (i) perform an oscillatory shear measurement on the polymer under investigation;
- (ii) construct the relaxation spectrum of the polymer from the oscillatory shear measurements;
- (iii) decompose the spectrum into the sum of individual components that can be associated with separate rheological processes, such as is implicit in the decompositions of Eqs. (6) and (12);
- (iv) determine the relaxation modulus for each of these components;
- (v) for each of these relaxation moduli formulate and solve some appropriate model of the associated mixing rule;
- (vi) for each of these individual relaxation moduli construct the associated molecular weight distribution component; and
- (vii) aggregate these components to determine the required molecular weight distribution.

Except for steps (iii), (v) and (vii), each of these steps is straightforward. In the case of step (iii), it is necessary to decide how the decomposition should be formulated. Any choice, as implied by the above deliberations, must be based on a sum of completely monotone functions each of which has an appropriate rheological interpretation. As the above analysis shows, if one considers the full generality of the molecular weight distribution problem, as encapsulated in Eq. (8), then one must allow for the possibility that the fading memory of the individual relaxation moduli $G_r(t)$ may have different types of behavior.

For step (v), the choices are numerous and include the suggestions of Léonardi *et al.* (2000), Thimm *et al.* (1999, 2000) and Anderssen and Loy (2002), as well as the suggestions contained in the papers that these authors reference. However, it is important to recognize that the point being made here is that determination of the molecular weight distribution should be solved on the component-by-component basis as determined in step (iii). Many of the earlier authors have assumed, even though they acknowledge the importance and relevance of the decomposition determined at step (iii), that the sum of the relaxation moduli of the components is all that must be inverted to determine the molecular weight distribution. As explained in some detail above, the mathematics of complete monotonicity is far more general than this, and, thereby, leaves open the possibility that each component determined in step (iii) requires a separate model for the determination of the associated molecular weight distribution.

As an example of this component-by-component strategy, consider the situation of double reptation when $r = 2$ and assume that $g_r(t) = t$. Equation (8) now takes the form

$$\int_0^\infty \exp(-t/\tau) \frac{H_2(\tau)}{\tau} d\tau = G_N^0 \left(\int_0^\infty k_2(m) \exp[-t/\tau_2(m)] w_2(m) dm \right)^2. \quad (15)$$

Anderssen and Loy [(2002); Eq. (30)] have established that it can be solved to yield

$$\int_0^\infty \exp(-tp) \frac{\tilde{H}_2(p)}{p} dp = G_N^0 \int_0^\infty \exp(-tp) \left[\int_0^p F(q,p-q) \tilde{w}_2(q) \tilde{w}_2(p-q) dq \right] dp, \quad (16)$$

where

$$F(q,z) = \frac{\tilde{k}_2(q) \tilde{k}_2(z)}{q^2 z^2 \tilde{\tau}'_2(q) \tilde{\tau}'_2(z)}, \quad \tilde{\tau}'_2(z) = \frac{d\tilde{\tau}_2(z)}{dz}, \quad (17)$$

and where the change of variable $p = 1/\tau_2$ has been introduced, with $m = \phi_2(p)$ defining the inverse relationship, such that $\tilde{H}_2(p) = H_2\{\tau_2[\phi_2(p)]\}$, $\tilde{\tau}'_2(p) = \tau'_2[\phi_2(p)]$, $\tilde{k}_2(p) = k_2[\phi_2(p)]$, and $\tilde{w}_2(p) = w_2[\phi_2(p)]$.

Consequently, this result can be utilized to perform the inversion of Eq. (8) for double reptation. The results given by Anderessen and Loy (2002) about Eq. (8) are much more general than indicated above and can be used as the starting point for the solution of higher levels of molecular interaction than double reptation.

Step (vii) highlights quite a deep matter. In fact, its resolution may lead to a better understanding of polymer dynamics, as well as to how the relationship between the relaxation modulus and the molecular weight distribution of a polymer should be modeled. Currently, it represents a somewhat open question in that it implies that, in full generality, some parts of a polymer network can contribute simultaneously to more than one relaxation modulus component.

It was already mentioned that the more general types of fading memory, ones that have been invoked in this paper, have a connection to the probabilistic concept of infinite divisibility. From a rheological perspective, the advantage of this concept is that it gives a rigorous framework in which to introduce the possibility of a mixing rule, Eq. (3), with the value of β not necessarily an integer. However, detailed discussion is beyond the scope of this paper.

VI. CIRCUMSTANTIAL EXPERIMENTAL EVIDENCE

The rheological significance of the above results can be explained and illustrated in a number of independent ways.

- (a) Rheologically, the formulation of the model, Eqs. (6)–(9), demands that one first know something about the nature of the dynamics occurring within the particular polymer being studied in terms of the experiment being performed, whether oscillatory shear or elongational extension.
- (b) The earlier mixing rules, based on either single or double reptation, are not in conflict with the form of Eqs. (6)–(9). They simply represent situations where it was assumed that one form of reptation dominated the dynamics with respect to all other possibilities. The papers of Mead (1994) and of Maier *et al.* (1998) fall into this category.
- (c) In a number of earlier investigations of mixing rules [cf. Thimm *et al.* (1999, 2000) and Léonardi *et al.* (2000)], the model, Eqs. (6)–(9), has been utilized implicitly. For various rheological reasons, the relaxation spectrum $H(\tau)$ was decomposed into appropriate spectral components, which were then analyzed separately in terms of the contributions they made to the molecular weight distribution. In particular, it is of interest to note that Thimm *et al.* (2000) found that, when they removed the

Rouse component from their estimate of the relaxation spectrum for the Maier *et al.* (1998) data, the value of the level of the dynamics, which had not been constrained to be an integer, was found to be approximately equal to 2. This establishes, in terms of the model considered by Thimm *et al.* (2000), that, for the Maier *et al.* (1998) data, the dominant behavior of the non-Rouse component of the dynamics is double reptation. This is validation of the position that one can only successfully deconvolve mixing rules once one has a clear *a priori* understanding about the nature of the molecular dynamics occurring in the rheological experiment being performed to determine the relaxation modulus.

- (d) An appropriate strategy by which to investigate the nature of the decomposition being examined is to investigate the effect on $G_r(t)$ when $w_r(m)$ is a delta function centered at m_0 [viz., $\delta(m - m_0)$]. In fact, one obtains, for the measured values $\hat{G}_r(t)$ of $G_r(t)$ from an oscillatory shear experiment with a monodisperse polymer [upon substitution of $w_r(m) = \delta(m - m_0)$], that

$$\hat{G}_r(t) = G_N^0 [k_r(m_0)]^r \exp[-rg_r(t)/\tau_r(m_0)]. \quad (18)$$

There are various ways in which this result can be deconvolved to yield information about the nature of the polymer dynamics occurring. For example, if one assumes that $k_r(m) \equiv 1$, that r is known, and that one has independent estimates of G_N^0 and $\tau_r(m_0)$, then Eq. (18) can be solved for $g_r(t)$ to yield

$$g_r(t) = -\tau_r(m_0) \ln[\hat{G}_r(t)/G_N^0]/r. \quad (19)$$

Having obtained an estimate for $g_r(t)$, it could, for example, be utilized to improve the current estimate of $\tau_r(m)$, and the process continues iteratively until a satisfactory solution is obtained. It is interesting to recall that, historically and currently, it is assumed that $g_r(t) = t$, which forces the unjustified assumption that the value of $G_r(t)$ that results from an oscillatory shear experiment with a monodisperse polymer must take the form $\hat{G}_r(t) = G_N^0 \exp[-rt/\tau_r(m_0)]$. Consequently, the above strategy yields a more comprehensive method for exploiting the information contained in the $G_r(t)$ determined in an oscillatory shear experiment with a polymer of known molecular weight distribution.

It is clear that there are various ways in which the measured values of the relaxation modulus that correspond to oscillatory shear experiments performed on combinations of monodisperse polymers can be exploited to recover various aspects of the model, Eq. (8). Having obtained an estimate for $g_r(t)$, such as that in Eq. (19), one can fit it using various models. One possibility would be to fit it with the model t^β , with $0 < \beta < 1$, because that would bring one back to use of the Kohlrausch function as a basic building block in modeling of the relaxation modulus.

VII. CONCLUSIONS

As mentioned in the Synopsis, the theoretical validity of the generalized mixing rule proposed by Anderssen and Loy (2001) is based on the assumption that the fading memory of the relaxation modulus $G(t)$ is a completely monotone function. As discussed above, this leads naturally to the viewpoint that the dynamics of a polymer should be modeled as a simultaneous combination of various types of molecular interactions (e.g., Rouse, various forms of reptation, etc.). The resulting model, Eq. (9), yields a framework for the generalization of the classical approach of Doi and Edwards (1978), Léonardi *et al.* (2000), Benallal *et al.* (1993), Carrot and Gullet (1997), Lin (1984) and of others, of decomposing $G(t)$ into a linear combination of $\exp(-t/\tau^*)$ relaxation processes. This

generalization also places, on a more formal and rigorous footing, the use of the Kohlrausch (stretched exponential) function in modeling of relaxation processes [cf. Sasaki *et al.* (1993); de Gennes (2002)]. Furthermore, it potentially represents a framework in which to resolve issues connected with modeling of the dynamics of highly polydisperse polymers [Thimm *et al.* (2000) Eq. (20); Carrot and Gullet (1997); Montfort *et al.* (1984)].

Because the existence of simultaneous molecular interactions of various types has already been established [Thimm *et al.* (2000); Léonardi *et al.* (2000)], the above theory lays the foundation for the recovery of molecular weight information from relaxation spectrum estimates. In addition, the possibility arises that polymer dynamics could be modeled in terms of a fractional mixing rule, Eq. (3), but at the expense of invoking the even stronger assumption that the relaxation modulus $G(t)$ is the Laplace transform of an infinitely divisible measure. It is interesting that the formulation of a mixing rule with a noninteger value for β requires one to invoke even stronger assumptions about the behavior of $G(t)$ than complete monotonicity.

A detailed discussion of the rheological significance of Eq. (16) is outside the scope of this paper. However, its importance should not be underestimated because it indicates how double reptation dynamics can be equivalenced back to a type of single reptation behavior with the role of the molecular weight distribution being taken by convolution of the associated molecular weight distributions involved in the double reptation dynamics. This explicitly illustrates the utility of the complete monotonicity assumptions in that it allows the same polymer to assume different dynamical configurations depending on the circumstances.

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