Relating the shear-thinning curve to the molecular weight distribution in linear polymer melts

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Synopsis

The double-reptation ansatz for stress relaxation in broadly polydisperse melts of linear chains relates the molecular weight distribution \( \phi(n) \) and the dynamic viscosity \( \eta(\omega) \), and has been used to infer \( \phi(n) \) from rheological data. I show that the microscopic theory of constraint release implies the double-reptation model is valid for practical distributions \( \phi(n) \). I also provide a heuristic theoretical argument for the Cox–Merz empirical rule that the shapes of the functions \( \eta^*(\omega) \) and \( \eta(\dot{\gamma}) \) are similar, which allows the shear-thinning curve to be predicted. © 1996 Society of Rheology.

I. INTRODUCTION

A robust relation between molecular weight distribution (MWD) and the frequency-dependent viscosity \( \eta(\omega) \) or modulus \( G(\omega) \) would have useful applications in either direction. Such a relation would allow rheologists to infer molecular weight distribution from their data, perhaps with sensitivity to small admixtures of long chains superior to that of gel permeation chromatography. A relation between MWD and \( \eta(\omega) \) would also allow engineers to design a blend with a desired shear-thinning characteristic \( \eta(\dot{\gamma}) \), assuming the Cox–Merz empirical rule that the shapes of the functions \( \eta^*(\omega) \) and \( \eta(\dot{\gamma}) \) are similar [Cox and Merz (1958)].

One such relation proposed between MWD and \( \eta(\omega) \) is based on “double reptation” [Tuminello (1986); des Cloizeaux (1988), (1990a); Tsengoglou (1991)] as the mechanism of stress relaxation in polydisperse entangled linear melts. Different scientific and engineering communities have taken different views as to the validity of this approach. In the rheological community, where various versions of double reptation have been successfully used to relate rheological data to MWD for polydisperse melts [Tuminello (1986); Tuminello and Cudre-Mauroux (1991); McGrory and Tuminello (1990); Tsengoglou (1991); Wasserman and Graessley (1992); Shaw and Tuminello (1994)], less attention has been paid to the microscopic theory and the resulting conditions that must hold for such a relation to be valid. On the other hand, in the physics community considerable attention has been given to extending the successful microscopic reptation theory [Doi and Edwards (1986)] to polydisperse polymers [Doi et al. (1987)]; Rubinstein and Colby (1988); Viovy et al. (1991)] as well as branched polymers [McLeish (1988a), (1988b); McLeish and O’Connor (1992); Ball and McLeish (1989)], often with a level of detail that makes rheological modeling quite tedious. Less attention has been given to the theoretical validity of the Cox–Merz relation; rheologists tend to regard it as an empirical fact, and polymer physicists tend to view it as a suspicious coincidence.

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The goals of this paper are twofold. In Sec. II, I give arguments to bridge the gap between detailed microscopic theories of stress relaxation in polydisperse linear melts, and the simple and apparently effective approximation of double reptation. In Sec. III, I give some theoretical justification for the approximate validity of the Cox–Merz relation. Then, in Sec. IV I discuss briefly the question of "mixing rules" for the plateau modulus and microscopic relaxation times in miscible blends of chemically different polymer species.

II. DOUBLE REPTATION

To motivate the relation between $\eta(\omega)$ and the molecular weight distribution, represented as the volume fraction $\phi(n)$ of monomers on chains of length $n$, a brief review of the reptation theory [Doi and Edwards 1986] is necessary. According to the reptation theory of stress relaxation in entangled linear melts, the stress after a step strain is borne by the anisotropic alignment of the "tube" constraining the transverse motion of a given chain. The tube is defined by the temporary topological constraints of chains entangled with a given chain. On a very short time scale after a step strain, a chain is able to contract within the tube to its equilibrium length; this contraction is regarded as instantaneous within the simplest version of reptation theory, and sets an upper limit on the frequency to which this description may be applied. A chain confined to its tube is then only free to "reptate," or diffuse back and forth along the curvilinear path of its tube.

Entanglements in a melt are not permanent. When a chain involved in an entanglement that defines a portion of another chain’s tube reptates so that one of its ends slips past the entanglement, the entanglement disappears. Then the formerly constrained chain can move sideways at this point, with a displacement of roughly the distance $l_e$ between entanglements (which may be thought of as the "tube diameter"). One may say that the tube itself is able to make a small sideways motion when a constraint is released, since a new constraint will arise in due time to redefine the released portion of the tube. The consequences of this constraint release have been examined in detail by Viovy, Rubinstein, and Colby [Viovy et al. (1991)]; I will now review their results, and show how and when their picture reduces to the simpler double-reptation model, which I shall describe below.

From the start, this approach assumes that an "entanglement" involves two chains; or, more precisely, that a constraint release event involves two chains, i.e., that the removal by reptation of a single chain can allow another chain to make a small sideways motion. The direct experimental evidence for this is incomplete, but one important result is that the effective plateau modulus of entangled long chains diluted by shorter chains scales roughly as the square of the long-chain volume fraction [Struglinski and Graessley (1985)]. Less direct evidence, of course, is provided by the fact that the dynamic rheology of polydisperse blends of known molecular weight distributions is consistent with the double-reptation model [Wasserman and Graessley (1992)].

Motion of entangled chains via constraint release, as described above, amounts to saying that the tube confining a chain has Rouse dynamics, with single steps taken on a time scale of the reptation time of the chains involved in the entanglements defining the tube. Consider now a blend of short and long chains, with chain lengths $N_S$ and $N_L$, respectively, and a volume fraction $\phi$ of long chains. (See Fig. 1.) We may define several time scales of interest. First of all, we have the reptation times of the short and long chains, $\tau_{rep}(N_S) = \tau_0(N_S/N(\epsilon))^3$ and $\tau_{rep}(N_L) = \tau_0(N_L/N(\epsilon))^3$, respectively, where $\tau_0$ is the Rouse time of an entanglement segment (for our purposes, a "microscopic" time) and $N(\epsilon)$ is the arclength between successive entanglements along a chain.
Next, I define the long-chain segment between successive entanglements involving another long chain. This segment has an arclength of $N_L^{(e)} = N^{(e)}/\phi$, since only a fraction $\phi$ of the entanglements along the long chain are with other long chains. The radius of gyration of this segment is $a_L = a/\phi^{1/2}$, where $a$ is the tube diameter (and hence the radius of gyration of a segment of arclength $N^{(e)}$). In other words, if only the long-chain entanglements mattered, there would be a larger tube diameter $a_L$ [called the “supertube” in Viovy et al. (1991)]. The Rouse motion via constraint release of this segment of length $N_L^{(e)}$ has a Rouse time

$$\tau_R(N_L^{(e)}) = \tau_{rep}(N_S)(N_L^{(e)})^2 = \tau_0(N_S/N^{(e)})^3 \phi^{-2}. \quad (1)$$

Corresponding to this Rouse motion, the long chain may “reptate by constraint release in the supertube”: that is, the hops of its entanglement segments $N_L^{(e)}$ by a distance $a$ on the time scale $\tau_{rep}(N_S)$ may be regarded as Rouse motion within the supertube of radius $a_L$ defined by long-chain entanglements. The corresponding “supertube reptation” time is

$$\tau_{super}(N_L) = \tau_R(N_L)(N_L^{(e)}) = \tau_0(N_S/N^{(e)})^3(N_L/N^{(e)})^3 \phi. \quad (2)$$

The ordering of these time scales depends on the values of $N_S$, $N_L$, and $\phi$. Chain conformations will relax by the fastest route available. Suppose for instance the following inequalities hold:

$$\tau_R(N_L^{(e)}) < \tau_{rep}(N_L) < \tau_{super}(N_L). \quad (3)$$

Then the long chains will execute Rouse motion within the supertube, thereby releasing the portion of stress associated with entanglements with short chains, but will ultimately release the portion of stress held by long-chain entanglements by ordinary reptation. The first of these inequalities requires that the short chains be sufficiently short and the long chains not too dilute (so that constraint release is rapid and the segment $N_L^{(e)}$ between long-chain entanglements is not so long as to give a large Rouse time):

$$\tau_R(N_L^{(e)}) < \tau_{rep}(N_L) \quad \text{if} \quad (N_S/N_L)^3 < \phi^2. \quad (4)$$

If $\phi = 1/4$, say, this implies $N_L/N_S > 2.5$, a modest requirement.

The second of these inequalities holds if

$$\tau_{rep}(N_L) < \tau_{super}(N_L) \quad \text{if} \quad 1 < \phi(N_S/N^{(e)})^3. \quad (5)$$

FIG. 1. An entangled blend of short and long chains. When the entanglements of long chains by short chains are released, the long chain is constrained only by other long chains, and may be thought of as confined to a supertube.
Assuming $\phi$ is not especially small, but that even the short chains are highly entangled ($N_S/N^{(e)} > 10$, say), reptation by constraint release is irrelevant. Thus the inequalities of Eq. (3) are relevant to moderately broad molecular weight distributions of highly entangled polymers, as I shall consider here.

As mentioned briefly above, the inequalities Eq. (3) have consequences for stress relaxation. Immediately following a step strain of small amplitude $\gamma$, the stress is as given by the rubbery plateau modulus $G$ of the entangled polymer melt, which is a material parameter independent of molecular weight or distribution $\phi(n)$: the stress is simply $\sigma = G \gamma$. In a blend of long and short chains for which Eq. (3) is satisfied, the stress then relaxes as follows. First, the stress held by the short chains relaxes in a time $t_s$. In fact, a few constraint-release steps are very efficient at relaxing the anisotropy in the direction of that portion of the tube. So one may crudely speak of the stress associated with entanglements between long and short chains as completely relaxed whenever the shorter of the two chains defining the entanglement is able to reptate its free end past the entanglement. This is the simple description is correct. I will derive below a condition on the molecular weight distribution such that these inequalities hold; for now, I will assume a double-reptation shorthand of double reptation. I will derive below a condition on the molecular weight $\phi(n)$: the stress is simply $\sigma = G \gamma$. In a blend of long and short chains for which Eq. (3) is satisfied, the stress then relaxes as follows. First, the stress held by the short chains relaxes in a time $t_s$. In fact, a few constraint-release steps are very efficient at relaxing the anisotropy in the direction of that portion of the tube. So one may crudely speak of the stress associated with entanglements between long and short chains as relaxing on the time scale $\tau_{rep}(N_S)$. To see this, recall that the stress relaxation function for the Rouse model is [Doi and Edwards (1986)]

$$\psi_R(t) = \sum_{\rho = 1}^{\rho_{\text{max}}} \exp(-t/\tau_R).$$

Each of the $\rho_{\text{max}} = (N/N^{(e)})$ Rouse modes bear an equal amount of the stress initially, but the high-$\rho$ modes decay very quickly. Defining a microscopic time $\tau_0$ by $\tau_R = \rho_{\text{max}}^2 \tau_0$, the upper-half of the modes ($\rho$ between $\rho_{\text{max}}/2$ and $\rho_{\text{max}}$) relax in a time $t = 4 \tau_0$. Thus a finite fraction of the stress after a step strain relaxes in a few time steps $\tau_0$. Only a small fraction of order $N^{(e)}/N$ of the stress survives to relax in the Rouse time.

Thus, in a crude approximation, one may regard the stress associated with a given entanglement as completely relaxed whenever the shorter of the two chains defining the entanglement is able to reptate its free end past the entanglement. This is the simple double-reptation picture of des Cloizeaux [des Cloizeaux(1988), (1990a), (1990b)], which ignores the connectivity of the long chains (i.e., the lower Rouse modes). I have argued that this double-reptation picture is sensible when the inequality Eq. (3) holds.

Now consider a polydisperse melt, modeled as a discrete set of molecular weights $\{n_1, n_2, n_3, \ldots\}$ with volume fractions $\{\phi_1, \phi_2, \phi_3, \ldots\}$. One may consider a hierarchy of relaxation events, with reptation of the chains of length $n_j$ releasing constraints on the chains of length $n_k$ with $k \geq j + 1$, and dilating the tube diameter from $a_j = a/(\Sigma_k \geq j \phi_k)^{1/2}$ to $a_{j+1}$ similarly defined. As long as the inequalities analogous to Eq. (3) continue to hold between successive molecular weights, one may speak in the shorthand of double reptation. I will derive below a condition on the molecular weight distribution such that these inequalities hold; for now, I will assume a double-reptation description is correct.

Within the double-reptation picture [des Cloizeaux (1988), (1990a)], the survival probability $\Psi(t)$ of an entanglement in a polydisperse melt depends on a volume-fraction weighted average of the likelihood that either of the two chains defining the entanglement
is able to reptate past. Let \(\psi(t/\tau_{\text{rep}}(n))\) be the probability that a chain of length \(n\) has not yet reptated past one of its entanglements; then the survival probability of an entanglement becomes

\[
\Psi(t) = \left[ \int_0^\infty d\phi(n)\psi(t/\tau_{\text{rep}}(n)) \right]^2.
\]

Detailed calculations within the reptation theory for monodisperse linear melts [Doi and Edwards (1986)] show that the function \(\psi(x)\) is essentially a single exponential, \(\psi(x) \approx \exp(-x)\). Des Cloizeaux has proposed corrections to this expression to take account of contour-length fluctuations of a chain within its tube, which may allow constraint release to occur without reptation of the chain [des Cloizeaux (1990b)]. Such corrections become less important in the limit that all chains are highly entangled, since the amplitude of contour-length fluctuations is only a finite number of entanglement lengths regardless of the molecular weight of the chain.

The expression Eq. (7) was proposed as the form of stress relaxation by des Cloizeaux, and in various equivalent forms by several authors [Tuminello (1986); Tsenoglou (1991)]. This is, as described above, a considerably simplified version of the microscopic theory of constraint release developed by Viovy et al. (1991), the simplification being that the stress carried by an entanglement point is regarded as completely relaxed after a few constraint-release events. The justification for this simplification are inequalities analogous to Eq. (3), which I shall now derive for the case of continuous polydispersity.

Consider the chains of molecular weight \(n_i\) and \(n_{i+1}\) in a discretely polydisperse melt. Constraint release by reptation of the chains of length \(n_i\) in a time \(\tau_i = \tau_{\text{rep}}(n_i)\) allows the tubes of the chains of length \(n_{i+1}\) to make a Rouse jump of distance \(a_i\) (the tube diameter of the time scale \(\tau_i\)). The arclength between entanglements effective on the time scale \(\tau_i\) is likewise \(N_i^{(e)} = N_i^{(e)}/\Phi_i\), where \(\Phi_i = \sum_j N_j^{(e)}\) is the volume fraction of material on chains with length \(n_i\) or longer. The tube diameter \(a_i\) is given by \(a_i = a_i/\Phi_i^{1/2}\). The diameter of the supertube confining the chains of length \(n_{i+1}\) is correspondingly \(a_{i+1}\). The Rouse time is an entanglement segment of the chains of length \(n_{i+1}\), which has arclength \(N_i^{(e)}\), is [see Eq. (1)]

\[
\tau_{\text{rep}}(N_i^{(e)}) = \tau_{\text{rep}}(n_i)(N_i^{(e)}/N_i^{(e)})^2.
\]

Requiring that this time be shorter than the reptation time \(\tau_{\text{rep}}(n_{i+1})\) of the chains of length \(n_{i+1}\) leads to the condition

\[
(\Phi_i/\Phi_{i+1})^2 < (n_{i+1}/n_i)^3.
\]

Taking the limit of a continuous distribution of chain lengths, in which

\[
\Phi(n) = \int_n^\infty dn' \phi(n'),
\]

one obtains the final requirement on the integrated molecular weight distribution:

\[
\frac{\partial \log \Phi}{\partial \log n} > -\frac{3}{2}.
\]

For any distribution, this condition eventually fails; since \(\Phi(n)\) begins at unity for \(n = 0\) and decreases to zero as \(n\) increases, its slope on a log–log plot starts out as zero and becomes arbitrarily negative. Physically, sufficiently long chains are so rare that their tubes dilate so much that the constraint-release Rouse time of their entanglement segments exceeds their reptation time. For the most-probable distribution [Flory (1953)].
with a ratio of weight-averaged to number-averaged molecular weight \( M_W/M_N = 2 \) (see Fig. 2), this occurs for \( n/\bar{n} > 2.186 \).

As Eq. (11) fails, some of the stress borne by entanglements between very long and somewhat shorter chains persists until the very long chains reptate away, violating the double-reptation approximation. Because the double-reptation approximation always assumes that this stress relaxes on the short-chain reptation time, double reptation always overestimates the amount of stress relaxed after a given time.

The requirement that “supertube reptation” remain irrelevantly slow is (see Eq. (2))

\[
\tau_{\text{rep}}(n_i)(n_{i+1}/N_i^{(e)})^2(n_{i+1}/N_{i+1}^{(e)}) > \tau_{\text{rep}}(n_{i+1}),
\]

which we may write as

\[
(\Phi_{i+1}/\Phi_i)(n_i/N_i^{(e)})^3 > 1.
\]

Ignoring the modest factor of the ratio \( \Phi_{i+1}/\Phi_i \), this amounts to saying that the chains at each level of the hierarchy remain self-entangled. This condition also fails for sufficiently long chains, but typically for much longer chains than the limit imposed by Eq. (3) if \( n/\bar{n} \) is large. For the most-probable distribution of Eq. (12), with \( n = 100N^{(e)} \), Eq. (14) fails for \( n/\bar{n} > 9.1 \).

Consider once more the stress relaxation in a polydisperse melt after a small step strain of magnitude \( \gamma \). Immediately following the step strain, the stress is as given by the rubbery plateau modulus \( G \) of the entangled polymer melt, which is a material parameter independent of molecular weight or \( \phi(n) \): the stress is simply \( \sigma = G\gamma \). When the double-reptation approximation is valid, the stress as a function of time following a small step strain becomes simply [des Cloizeaux (1988a,b)]

\[
\sigma(t) = G\gamma\psi(t).
\]

The stress relaxation following a step strain is sufficient to determine the frequency-dependent viscosity \( \eta(\omega) \), because an arbitrary strain history can be decomposed into a time sequence of step strains. Equivalently, the strain rate \( \dot{\gamma}(t) \) may be thought of as a time sequence of delta functions. Superposition of the resulting stresses gives the relation

\[
\phi^w(n;\bar{n}) = \frac{n}{\bar{n}} \exp(-n/\bar{n}),
\]

Fig. 2. The volume fraction \( \phi(n) \) of monomers belonging to chains of length \( n \) (in units of \( \bar{n} \)), for the most-probable distribution.
Fourier transformation, and defining $s \sim v \sigma(t) = \int_{-\infty}^{t} dt' \mathcal{J}(t') G(t-t')$.

(16)

Fourier transformation, and defining $\sigma(\omega) = -i \omega \gamma(\omega) \eta(\omega)$, gives

$\eta(\omega) = G \Psi(\omega)$.

(17)

As the function $\Psi(t)$ is essentially a sum of exponentials, it is simple to Fourier transform; one obtains

$\eta(\omega) = G \int_{0}^{\infty} dn \int_{0}^{\infty} dn' \phi(n) \phi(n') \left[ \frac{1}{\tau(n)} + \frac{1}{\tau(n')} - i \omega \right]^{-1}$.

(18)

Since even a factor of 2 in $n$ changes $\tau(n)$ by a factor of 8, for distributions at all polydisperse the factor $1/\tau(n) + 1/\tau(n')$ can be replaced by the larger of the two terms, giving

$\eta(\omega) \approx 2G \int_{0}^{\infty} dn \frac{\phi(n) \tau(n)}{1-i\omega \tau(n)} \int_{n}^{\infty} dn' \phi(n')$.

(19)

The double-reptation result in the form of Eq. (19) has been used successfully by several authors [Tsenoglou (1991); Wasserman and Graessley (1992)] to relate rheological data to molecular weight distribution, for commercial polydisperse samples and also for “artificial” polydisperse samples made by solution blending many different monodisperse samples of different molecular weights [Wasserman and Graessley (1992)]. The stability of the numerical inversion of rheological data into a molecular-weight distribution has been discussed by several authors [Shaw and Tuminello (1994); Mead (1994)]. Note also that for narrow distributions $\phi(n)$ Eq. (19) reduces appropriately to a single Maxwell relaxation function $\tau/(1-i\omega \tau)$.

As a simple example of the applicability of Eq. (19), Fig. 3 displays a log–log plot of $\eta'(\omega)$ and $\eta''(\omega)$ for a commercial polyethylene sample made with a single-site catalyst [and hence with a most-probable molecular weight distribution Eq. (12)], compared to the results from Eq. (19), with two adjustable parameters $G = 1.44$ MPa and $\tau_{\text{rep}}(\bar{n}) = 6.52 \times 10^{-4}$ s. Note that even a sample with a most-probable MWD (which is a narrow distribution by commercial standards) has a broad range of time scales, and that the shape of $\eta'(\omega)$ is clearly distinguishable from a single relaxation-time shape of the form $1/[1+(\omega \tau)^{2}]$. The theoretical approach of this paper depends at several points on the
range of time scales being sufficiently broad, but even the most-probable distribution is sufficiently broad in this sense for present purposes.

For practical calculations (such as the solid curve in Fig. 3), it suffices to evaluate the integral over the molecular weight appearing in Eq. (19) as an integral over $\log(n/\bar{n})$ with a rather coarse step size, in effect including only a sequence of molecular weights such as $\{\bar{n}/4, \bar{n}/2\sqrt{2}, \bar{n}/2, \bar{n}, \sqrt{2}\bar{n}, 2\bar{n}, 2\sqrt{2}\bar{n}, 4\bar{n}\}$. This results in about two time scales per decade in frequency [since $\tau(n) \sim n^3$, a factor of 2 in molecular weight implies a factor of 8 in frequency]. For the most-probable distribution, the weighting function appearing in Eq. (19) is

$$\tau(n)\phi(n)\int_n^{\infty} dn' \phi(n') = (n/\bar{n})^3(1+n/\bar{n})\exp(-2n/\bar{n}). \tag{20}$$

The weighting function and the corresponding log-spaced sampling points are shown in Fig. 4.

Observe that the most severe test of the double-reptation approximation is the zero-frequency viscosity, since it depends on the integral of the stress relaxation function, and small amounts of stress surviving for a long time make a large contribution. (For instance, the viscosity of a Rouse model is dominated by the few lowest Rouse modes, which carry proportionately very little stress, but persist a long time.) Taking the zero-frequency limit of Eq. (19), one obtains

$$\eta_0 = 2G\int_0^{\infty} dn\tau(n)\phi(n)\int_n^{\infty} dn' \phi(n'). \tag{21}$$

One may ask how much of this expression for $\eta_0$ comes from values of $n$ such that Eq. (11) holds. For the most-probable distribution, which is the narrowest distribution one would ever expect to use in this context, about one-third of the contribution to Eq. (21) for $\eta_0$ comes from molecular weights that strictly satisfy Eq. (11)

As described briefly above, the description leading to Eq. (19) holds for time scales greater than the time required after a step strain for contraction of a chain within its tube to its equilibrium length. This time is the usual Rouse time $\tau_R = \tau_0(N/N(e))^2$, and is much shorter for a long entangled chain than the reptation time $\tau_{rep} = \tau_0(N/N(e))^3$. The Rouse and reptation times are of the same order for a chain of length $N \sim N(e)$, which
defines the minimum length of chain for which this description applies. Hence Eq. (19) only applies for frequencies less than \( \tau_0^{-1} \), which is roughly speaking the reptation time for a chain of length \( N(e) \).

The corresponding expression for the real part of the complex modulus \( G(\omega) \), when a slight further approximation is made, is particularly convenient for extracting the molecular weight distribution \( \phi(n) \) from rheological data [Tuminello (1986); McGrory and Tuminello (1990)]. Recalling that \( G(\omega) = -i \omega \eta(\omega) \), one obtains

\[
G'(\omega) = 2G \int_{0}^{\infty} dn \phi(n) \frac{[\omega \tau(n)]^2}{1 + [\omega \tau(n)]^2} \left[ \int_{n}^{\infty} dn' \phi(n') \right].
\]

(22)

Again assuming that the molecular weight distribution is not overly narrow, the frequency-dependent factor in the above equation reduces essentially to a theta function \( \Theta[\omega \tau(n) - 1] \), which gives a lower bound to the integral \( \int dn \). A slight rearrangement then gives

\[
G'(\omega) \approx G \left[ \int_{\omega \tau(n) = 1}^{\infty} dn \phi(n) \right]^2.
\]

(23)

This relation has been used to infer the partial integral of \( \phi(n) \) from the square root of \( G'(\omega) \) [Tuminello (1986)], or equivalently from data on stress relaxation after a step strain \( G(t) \) [McGrory and Tuminello (1990)]. This equation was proposed directly [Tuminello (1986)], before the double-reptation ansatz [des Cloizeaux (1988)], with an argument similar in spirit to the argument leading to Eq. (19): at a frequency \( \omega \), the “active” entanglements capable of bearing elastic stress and thus contributing to the elastic modulus at a frequency \( \omega \) are those that are unable to relax on the time scale \( \omega^{-1} \). This fraction is precisely \( \left[ \int_{\omega \tau(n) = 1}^{\infty} dn \phi(n) \right]^2 \), the square of the probability of a chain defining an entanglement being unable to relax on the time scale \( \omega^{-1} \), since two chains define an entanglement.

III. THE COX–MERZ RULE

One is often interested in relating the molecular weight distribution not to the frequency-dependent rheology \( \eta(\omega) \), but instead to the shear-rate-dependent rheology \( \eta(\dot{\gamma}) \). There is a well-known empirical correlation called the Cox–Merz rule [Cox and Merz (1958)] that the shapes of \( \eta(\omega) \) and \( \eta(\dot{\gamma}) \) are quite similar for a variety of circumstances, including polydisperse melts of linear chains. Here, I provide an argument for the approximate validity of the Cox–Merz rule for polydisperse linear chains, which requires first a brief review of the origin of shear thinning in linear melts.

It is conceptually convenient to approximate a shear flow with a constant strain rate \( \dot{\gamma} \) roughly as a sequence of step stains \( d\gamma \) separated in time by some convenient interval \( dt \), during which the chains may relax. For a monodisperse linear melt, the appropriate time step \( dt \) is the reptation time \( \tau_{\text{rep}} \), since within a reptation time the stress associated with the anisotropic tube of a chin is completely relaxed as the chain explores a new tube. The constant stress level \( \sigma \) corresponding to the constant strain rate \( \dot{\gamma} \) then is roughly the time average of the stress level during the interval \( dt \) between successive step strains.

Recall that within the reptation picture [Doi and Edwards (1986)], following a step strain a chain is able to retract along its own tube to its equilibrium length in a time of the order of the Rouse time \( \tau_R \), which is nearly instantaneous on the scale of the reptation time \( \tau_{\text{rep}} \). This retraction occurs because the tube length tends to increase during the affine step strain. For larger strain rates, the step strain amplitude \( d\gamma \) is larger (it becomes
of order unity when \( \dot{\gamma}_\text{rep} \sim 1 \), and the increase in tube length immediately following the step strain is correspondingly larger.

When the chain inside the tube contracts to its equilibrium contour length, the stress associated with the portion of the tube no longer occupied is relaxed. The stress level immediately following the step strain is roughly \( \sigma(t = 0^+) = Gd\gamma \), since the melt responds like a rubber network on short time scales. The stress level following chain retraction (i.e., at a time \( \tau_R \) after the step strain \( d\gamma \)) is then

\[
\sigma(t = \tau_R) = h(d\gamma)Gd\gamma,
\]

where \( h(\gamma) \) is called the nonlinear damping function, which we shall crudely estimate below.

Following retraction, the remaining stress relaxes by reptation, leading to a time dependence following the step strain of \( \sigma(t) \sim G \). Putting \( d\gamma = \dot{\gamma}_\text{rep} \) and using Eq. (24), the time-averaged stress is approximately

\[
\sigma(\dot{\gamma}) \approx G\tau_\text{rep}h(\dot{\gamma}_\text{rep})\dot{\gamma}
\]

or

\[
\eta(\dot{\gamma}) \approx G\tau_\text{rep}h(\dot{\gamma}_\text{rep}).
\]

The fraction of stress quickly lost by retraction by the fractional increase in tube length, and hence \( h(\gamma) \), can be estimated as follows [Doi and Edwards (1986); Larson (1988)]. A unit-length piece of an originally isotropic tube, with tangent vector \( \hat{n} \), is affinely deformed by a deformation gradient \( E \) to become \( n' = E \cdot \hat{n} \). The vector \( n' \) is no longer a unit vector; its length squared is \( n'^2 = \hat{n} \cdot E^T \cdot E \cdot \hat{n} \). The mean squared length of the segment, upon averaging over the initial orientation \( \hat{n} \), has increased from unity to a value

\[
\bar{l}^2 = \langle \hat{n} \cdot E^T \cdot E \cdot \hat{n} \rangle = \frac{1}{3} \text{tr}(E^T \cdot E).
\]

For simple shear step strains, the deformation tensor \( E \) is

\[
E = \begin{bmatrix} 1 & \gamma & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}.
\]

Hence the root-mean-squared tube length increases by a factor of \( (1 + \gamma^2/3)^{1/2} \) immediately after the step strain. If the retraction process results in a tube of the original length, only a fraction \( (1 + \gamma^2/3)^{-1/2} \) of the original deformed tube, and hence of the stress \( \sigma(0^+) \), will remain after a time \( \tau_R \). Thus this simple picture suggests

\[
h(\gamma) = (1 + \gamma^2/3)^{-1/2}.
\]

Note that in the limit of large step strain amplitudes \( d\gamma \), the relation Eq. (24) becomes simply \( \sigma(\tau_R) \sim \sqrt{3}G \), independent of the amplitude \( d\gamma \). From Eq. (25), the stress \( \sigma(\dot{\gamma}) \) is linear for small shear rates, and reaches a plateau value of the order of \( G \) for \( \gamma \tau_\text{rep} \) much larger than unity. The viscosity \( \eta(\dot{\gamma}) \) correspondingly is constant for small shear rates, and then decreases as \( G/\dot{\gamma} \) for large shear rates. The precise shear-thinning power law is a delicate theoretical question [Doi and Edwards (1986)], and Eq. (28) should not be regarded as more than heuristic. (In particular, the orienting effect of the step shear strain on the tube has not been correctly represented in the above argument, so that the asymptotic behavior \( h(\gamma \gg 1) \sim 1/\gamma \) is fortuitous.)
Now consider what should be the shear-thinning curve \( \eta(\dot{\gamma}) \) for a polydisperse linear-chain melt. Within the double-reptation picture, the relaxation time for each entanglement segment is a stochastic variable, depending on essentially the length of the shorter of the two chains defining the entanglement. Thus for each entanglement, the appropriate time-step \( dt \) and hence the step-strain amplitude \( d\gamma \) at a given strain rate \( \dot{\gamma} \) are stochastic. This leads to the expression

\[
\eta(\dot{\gamma}) = 2G \int_0^\infty d\tau_{\text{rep}}(n) \phi(n) h[\dot{\gamma}\tau_{\text{rep}}(n)] \left[ \int_n^\infty d\tau' \phi(n') \right].
\]

(29)

Now consider the absolute value \( \eta^*(\omega) \) of the complex viscosity \( \eta(\omega) \) from Eq. (19). I approximate as follows:

\[
\eta^*(\omega) \approx 2G \int_0^\infty d\tau_{\text{rep}}(n) \frac{\tau(n)\phi(n)}{1+[\omega\tau(n)]^{2/12}} \left[ \int_n^\infty d\tau' \phi(n') \right].
\]

(30)

This is evidently of the same form as \( \eta(\dot{\gamma}) \) given by Eq. (29) with \( h(\dot{\gamma}) \) given by Eq. (28) and \( \omega \to \dot{\gamma}/\sqrt{3} \). The Cox–Merz rule is then justified if it can be shown why Eq. (30) is a good approximation.

First, note that for \( \omega \to 0 \) or \( \omega \to \infty \), \( \eta(\omega) \) is purely real or purely imaginary, and Eq. (30) becomes exact. Next, consider that for a broad distribution of times \( \tau(n) \), the integral \( \int dt \) of Eq. (19) may be regarded as the sum of two terms, \( \int_n^\infty \tau(n)\omega = 1dn \) approximately real and \( \int_n^\infty \tau(n)\omega = 1dn \) approximately imaginary. Now for any complex number \( z = z_r + iz_i \) the inequality \( |z| \leq |z_r| + |z_i| \) is satisfied, but if \( z_r \) is real and \( z_i \) imaginary (as the subscripts imply), the approximation \( |z| \approx |z_r| + |z_i| \) is never wrong by more than a factor of \( \sqrt{2} \) (when \( |z_i| = |z_r| \)).

Hence one obtains a serviceable approximation to \( \eta^*(\omega) \) by breaking the integral of Eq. (19) at \( n : \tau(n)\omega = 1 \), taking the modulus of each part (one nearly real, the other nearly imaginary anyhow) and adding the results together—in other words, replacing \( 1/[1-i\omega\tau(n)] \to 1/[1+(\omega\tau(n))^{2/12}] \) as in Eq. (30).

Admittedly, the argument leading to Eq. (28) for the damping function \( h(\gamma) \) is only heuristic; however, if Eq. (29) holds but with a different form for \( h(\dot{\gamma}) \), the Cox–Merz relation is still approximately valid. The reason is that any sensible \( h(\gamma) \) has the property that it is essentially unity for \( \gamma \ll 1 \), and decreases as some power law thereafter. As in the discussion following Eq. (22), one may regard \( h(\gamma) \) and \( 1/[1+(\omega\tau)^{2/12}] \) both as approximately theta functions, when considering sums over broad molecular-weight distributions, and log–log plots of \( \eta^*(\omega) \) and \( \eta(\dot{\gamma}) \). Thus the Cox–Merz relation is approximately valid if the lifetime of an entanglement segment determines whether it has “shear-thinned away.”

IV. CONCLUSIONS

It appears from previous studies in the rheological literature [Tuminello (1986); Tuminello and Cudré-Mauroux (1991); Wasserman and Graessley (1992)] that the double-reptation ansatz, proposed by several authors [Tuminello (1986); des Cloizeaux (1988); Tsengoglou (1991)] is a reasonable description of the stress relaxation in entangled melts of polydisperse linear polymers. In particular, there is striking agreement between double-reptation predictions and the experimental stress relaxation in “artificially polydisperse” melts, solution blended from many monodisperse components [Wasserman and Graessley (1992)], once corrections are made for the stress relaxation due to contour-length fluctuations of moderately entangled chains [des Cloizeaux (1990b); Wasserman...
and Graessley (1992)]. These contour length fluctuations become less significant for highly entangled polymers, giving rise to the nearly single-exponential Doi–Edwards expression [Doi and Edwards (1986)] for the rate of constraint release events involving a chain of a given molecular weight, and the simple expressions reproduced in this paper.

In an independent strain of theoretical work, a detailed microscopic model has been given to describe the effects of constraint release on stress relaxation in polymer melts composed of chains of two different molecular weights [Rubinstein and Colby (1988); Viovy et al. (1991)]. In this microscopic model, the effect of constraint release is not to instantly relax all stress associated with a given entanglement, but to permit Rouse-like motion of entangled chains, with a hopping time of the order of the reptation time of the entangling chain, and a hopping distance of the order of the tube diameter. In contrast, the double-reptation ansatz takes the highly simplified view that the stress associated with a given entanglement disappears completely when the constraint is released by the reptation of one of the two chains defining the entanglement.

I have shown in this paper how the double-reptation ansatz arise as a serviceable approximation to the microscopic constraint release model when certain inequalities regarding various time scales are satisfied. Specifically, when the constraint-release Rouse time of a segment between long-chain entanglements is shorter than the reptation time of a long chain in the melt, the stress relaxation via short-chain constraint release in a bidisperse melt will effectively eliminate the stress held by entanglements between short and long chains on a time scale of the order of the short-chain reptation time, as is assumed by the double-reptation ansatz. This inequality breaks down if the long chains are too dilute or too short. As long as the inequality holds, a hierarchy of relaxation processes can be envisioned between increasingly long and dilute chains in a discretely polydisperse melt. I have presented a generalization to the polydisperse case of the inequalities required for double reptation to be a serviceable approximation, which indicates how far out into the high molecular-weight tail of the distribution a double-reptation description can be used.

I have also presented a somewhat heuristic but rather general argument for the Cox–Merz relation, which states that the shapes of the modulus of the complex dynamical viscosity as a function of frequency $\eta^*(\omega)$, and the shear-rate-dependent steady nonlinear viscosity $\eta(\dot{\gamma})$, are similar. The argument depends on the notion that essentially only those molecular weights with reptation times shorter than the inverse shear rate will contribute effectively to the viscosity at that shear rate. The Cox–Merz relation is widely used by practical rheologists, but has not heretofore received theoretical defense in terms of the successful microscopic models of entangled chains.

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