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Definitions of entanglement spacing and time constants in the tube model

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Synopsis

Numerous papers have recently appeared in the literature presenting quantitative comparisons of experimental linear viscoelastic data to the most recent versions of "tube" models for entangled polymer melts and solutions. Since these tube models are now being used for quantitative, rather than just qualitative, predictions, it has become important that numerical prefactors for the time constants that appear in these theories be evaluated correctly using literature data for the parameters (i.e., density, plateau modulus, etc.) that go into the theories. However, in the literature two definitions of the entanglement spacing in terms of plateau modulus have been presented, and confusion between these has produced numerous errors in the recent literature. In addition, two different definitions of the "equilibration time," a fundamental time constant, have also appeared, creating additional potential for confusion. We therefore, carefully review the alternative definitions and clarify the values of the prefactors that must be used for the different definitions, in the hope of helping future authors to avoid such errors. © 2003 The Society of Rheology. [DOI: 10.1122/1.1567750]



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I. INTRODUCTION

"Tube" models are now being used more and more frequently for quantitative calculations of relaxation processes for polymers of linear, star, and more complex topologies. Unfortunately, numerous errors have appeared in these calculations due to incorrect or inconsistent use of the definitions of the key quantities, especially of the entanglement molecular weight. The objective of this note is to summarize the formulas that allow one to calculate the parameters of the reptation tube model from measured melt properties, and discuss alternative definitions of the parameters. Along the way, we will point out, and correct, some errors made in the literature in the calculation of reptation tube parameters. Finally, we will summarize the most common "canonical" lists of definitions and equations used in tube models, which we commend to those working in this field. Above all, we urge that all papers published in the future make clear which set of definitions is being used and that authors take pains to be sure they are used consistently. If authors use parameter values from tabulations in the literature (especially entanglement spacings), they should be sure that their definitions match those of the tabulator, or that they adjust the tabulated values to make them consistent with the definitions they are using.

II. TUBE PARAMETERS

The tube parameters that we calculate are τ_e , the "equilibration time;" τ_R , the Rouse orientational relaxation time; τ_d , the "disengagement time" (or "reptation time"); M_e , the "entanglement molecular weight;" a, the "tube diameter;" and Z, the "number of tube segments" per molecule. These quantities are computed via formula to be discussed below from certain measured or known quantities. These measured or known quantities include the temperature T, Boltzmann's constant k_B , and Avogadro's number N_A , from which the universal gas constant is obtained as $R = N_A k_B$. In addition, some properties of the polymer are required, including the polymer density ρ , the monomer molecular weight M_0 , the polymer molecular weight M, and the monomer-based segment length b(which is defined such that the polymer mean-square end-to-end distance is R^2 $N = Nb^2$, where $N = M/M_0$ is the number of monomers in the polymer). The radius of gyration is then given by $R_g = \sqrt{Nb^2/6}$. (Note that the universal gas constant uses the same symbol as the polymer end-to-end distance, but the former can always be recognized in that it is immediately followed by "T" for temperature.) Finally, two rheological parameters are required for calculation of the tube parameters, namely, the plateau modulus G_N^0 and the monomeric friction coefficient ζ . These two quantities have been measured for many polymer melts and are tabulated in Ferry's (1980) book, for example. Up-to-date values of the plateau modulus for many polymers can also be found in Fetters et al. (1994, 1999). As described below, values of the entanglement molecular weight M_{ρ} given by Fetters *et al.* are based on a different definition of M_{e} than those given in Ferry, and this has led to errors in published papers that we hope (by publishing this note) to prevent being propagated or repeated in the future. Also, the formulas presented below can be applied to entangled polymer solutions, if the plateau modulus and monomeric friction coefficient are adjusted from the melt values to those appropriate for entangled solutions. If swelling of the polymer due to excluded volume interactions is not completely screened out, there may be complications, however.

III. EXPERIMENTAL CONSIDERATIONS

In addition to the issues discussed here involving tube-model definitions, completely separate issues arise in determining the plateau modulus and the monomeric friction coefficient experimentally, and in estimating, and correcting for, errors in these measurements. In principle, the plateau modulus G_N^0 can be determined from data on entangled melts, usually from the value of G' in the plateau region, for example at the minimum of G'', or from an integral of G'' over frequency. In practice, however, the value of G_N^0 obtained in this way depends on the frequency at which G' is evaluated, or from the upper limit of the frequency integration of G'', and can depend on polymer molecular weight, in apparent contradiction to the tube model. However, as was shown in Likhtman and McLeish (2002), the tube theory, when contour length fluctuations and constraint release are properly incorporated, does predict a weak dependence of the apparent plateau of G' on molecular weight as approximately $Z^{0.1-0.15}$, which saturates to reasonable accuracy between about Z = 150 and 1000. Thus, in principle, the tube model itself, when all relevant relaxation processes are included, could be used to "correct" the value of G_N^0 obtained from experiments. While these corrections might be rather small, they affect the value of the entanglement molecular weight that is inferred from G_N^0 , which can have a large effect on the predictions of the rheology of branched polymers, in particular. We also note that corrections to G_N^0 inferred from G' values are even more important for entangled polymer solutions, which in general have fewer entanglements per molecule, and therefore, larger effects on G_N^0 due to contour length fluctuations, than do melts. For the monomeric friction coefficient ζ , there are also difficulties obtaining values that are accurate in the plateau and terminal regions for entangled melts. More complete discussion of these issues can be found in Ferry (1980), in Plazek et al. (1979), in Raju et al. (1981), and in Likhtman and McLeish (2002).

IV. LENGTH SCALES

The various length scales in the problem are depicted in Fig. 1, showing $b \le a \le R = \sqrt{6R_g} \le L_{\text{tube}} \le L$. Rather than the "monomer-based segment length" b as defined above, sometimes the "Kuhn" step length b_K is used, which follows a formula for the mean-square end-to-end length similar to that of b, namely, $R^2 = N_K b_K^2$. Here, N_K is the "number of Kuhn steps" rather than the number of monomers, and the number of Kuhn steps is defined so that $N_K b_K = L$, the total polymer length. For synthetic polymers with a carbon backbone, the "Kuhn step length" is related to b by $b_K = b\sqrt{C_\infty}/0.82\sqrt{j}$ and N_K is related to N by $N_K = [j(0.82)^2/C_\infty]N$, where C_∞ is the "characteristic ratio" relating R^2 to the number n = jN of backbone bonds and their length ℓ by $R^2 = C_\infty n \ell^2$, and j is the number of carbon–carbon bonds per monomer. Values for C_∞ are tabulated in Flory (1989) and Fetters *et al.* (1994). The factor "0.82" enters because the tetrahedral bonding angles produce a zig-zag polymer conformation when the chain is fully extended.

V. FORMULAS FROM DOI AND EDWARDS' (1986) BOOK

We adopt formulas describing the reptation model directly from Doi and Edwards' (1986) book. Within the classical Doi–Edwards theory, as described in this book, the linear shear stress relaxation modulus G(t) is the product of the plateau modulus G_N^0 and a time-dependent function $\psi(t)$ that relaxes from unity to zero with time t after a small

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b << a << R << L_{tube} << L

FIG. 1. Illustration of tube model, and the various length scales of the polymer chain and the tube. The blow up shows a small section of the polymer, modeled as a freely jointed chain. Here, *b* is the monomer-based segment length, a the tube diameter (which is equivalent to the tube persistence length), *R* the root-mean-square end-to-end vector, L_{tube} the path length of the tube, and *L* the fully extended chain length.

step strain; i.e., $G(t) = G_N^0 \psi(t)$. In Eq. (7.128) of Doi and Edwards' book, the relationship between the tube diameter a and the plateau modulus G_N^0 is given as

$$G_N^0 = \frac{4}{5} n_M \frac{b^2}{a^2} k_B T,$$
 (1)

where n_M is the number of monomers per unit volume of the sample. In Doi and Edwards' book, this quantity (n_M) is given the symbol "*c*," but the symbol "*c*" has a well-established use as the mass concentration of polymer, and so here we introduce a different symbol for the number of monomers per unit volume. For a polymer melt (no solvent), n_M is related to the polymer density and monomer molecular weight by

$$n_M = \frac{\rho N_A}{M_0}.$$
 (2)

This allows us to write the plateau modulus for a melt as

$$G_N^0 = \frac{4}{5} \frac{\rho RT}{M_0} \frac{b^2}{a^2}.$$
 (3)

Equation (3) is then the basic equation for obtaining the tube diameter a from the plateau modulus G_N^0 . A similar formula is given as Eq. (7.51) by Doi and Edwards, but their formula is only an approximate scaling relationship and does not include the factor 4/5.

We note also that Eq. (3) holds only for flexible polymers, for which the tube persistence length is equal to the tube diameter; i.e., for polymers that are already a random walk even when their lengths are no larger than that corresponding to a single tube segment.

We next obtain the number of tube segments in a polymer of molecular weight M. The number of tube segments Z is chosen so that the random walk describing the tube conformation has the same mean-square end-to-end length as the real polymer. This implies that [see Doi and Edwards, Eq. (6.20)]

$$Za^2 = Nb^2. (4)$$

Combining this with Eq. (3) gives a relationship between Z and the plateau modulus:

$$G_N^0 = \frac{4}{5} \frac{\rho RT Z}{M_0} \frac{Z}{N}.$$
(5)

Doi and Edwards also give a formula for M_e , the molecular weight between entanglements, as [Doi and Edwards, Eq. (7.52)]

$$M_e^F = \frac{\rho RT}{G_N^0},\tag{6}$$

where we have superscripted the entanglement molecular weight M_e with "F" to indicate that this is Ferry's definition [see Ferry (1980)], which is used in Doi and Edwards' book. This definition was motivated by the relationship between the molecular weight between cross links and the modulus of a classical rubber network, which follows a formula completely analogous to Eq. (6). Since early theories viewed entangled melts as "temporary" rubber networks [Green and Tobolsky (1946); Lodge (1968)], this definition seemed appropriate. However, the Doi–Edwards tube model differs from "temporary network" models in that it permits sliding of chains along tubes, which quickly relaxes some stress that would be retained if entanglement points really acted like cross links that do not permit such sliding motions. Thus, in view of the reduced stress predicted by the tube model, it seemed to Fetters *et al.* (1994) that a slightly different definition of the entanglement molecular weight would be more appropriate, and this definition will be discussed later. Using the Ferry definition, we find from Eqs. (3) and (6)

$$a^{2} = \frac{4}{5} \frac{M_{e}^{F}}{M_{0}} b^{2}.$$
 (7)

Combining Eqs. (5) and (6), we find that

$$Z = \frac{5}{4} \frac{M}{M_{\rho}^F}.$$
(8)

The quantity M/M_e^F is sometimes referred to as the "number of entanglements" per molecule. However, Eq. (8) shows that this is not quite equal to the number of tube segments per molecule, but rather Z is 25% larger than M/M_e^F . This difference has caused confusion in the literature, as discussed below.

The Rouse *rotational* relaxation time τ_R is given by a formula that is independent of the tube model [Doi and Edwards, Eq. (4.37)]:

$$\tau_R = \frac{\zeta N^2 b^2}{3\pi^2 k_B T}.$$
(9)

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Note that the terminal *stress* relaxation time of the Rouse model is a factor of 2 smaller than this value of the rotational relaxation time τ_R ; see the parenthetical comment at the top of page 115 of Doi and Edwards. The above equation can be rewritten as

$$\tau_R = \frac{\zeta Z^2 a^4}{3\pi^2 k_R T b^2}.\tag{10}$$

It is now convenient to define a molecular-weight-independent relaxation time scale, by setting Z = 1 in Eq. (10), giving the *equilibration time* τ_e , which is the Rouse relaxation time of a chain of length equal to one tube segment:

$$\tau_e = \frac{\zeta a^4}{3\pi^2 k_B T b^2} = \left(\frac{4}{5}\right)^2 \left(\frac{M_e^F}{M_0}\right)^2 \frac{\zeta b^2}{3\pi^2 k_B T},$$
(11)

where Eq. 7 has been used to get the second equality. This choice for the definition of the equilibration time makes the formula 6.106 in Doi and Edwards, which was intended as a scaling relationship, into the precise definition of τ_e . Using Eq. 11, once τ_e is specified for a given polymer at a given temperature, the Rouse time τ_R is then given by simply:

$$\tau_R = Z^2 \tau_e = \left(\frac{5}{4}\right)^2 \left(\frac{M}{M_e^F}\right)^2 \tau_e \tag{12}$$

Finally, we obtain a formula for the reptation disengagement time τ_d (without fluctuation correction) from Eq. 6.19 of Doi and Edwards:

$$\tau_d = \frac{\zeta N^3 b^4}{\pi^2 k_B T a^2} = 3Z^3 \tau_e \tag{13}$$

The above formulas permit calculation of all the tube-model parameters from standard polymer properties tabulated in Ferry (1980) and Fetters *et al.* (1994). We note, however, that the Ferry tabulation of the monomeric friction coefficient ζ is based on data from the transition region, and might not be very accurate for calculation of slow relaxation processes. Many authors, therefore, feel justified in adjusting τ_e to obtain the best agreement with linear viscoelastic data for entangled polymers. Adjustment of this one parameter still leaves plenty of room for rigorous testing of the tube model since τ_e must in principle be held fixed when varying molecular weight, chain architecture, or in blending together different chain architectures.

VI. ALTERNATIVE DEFINITIONS

An alternative definition of the "equilibration" time has been used frequently by Milner, McLeish, and co-workers [see, for example, Milner and McLeish (1997)], who choose it to be the Rouse time of an entanglement segment of molecular weight M_e^F , rather than of a tube segment. Thus, the Milner–McLeish (MM) equilibration time is larger by a factor of $(5/4)^2$ than that given above. Superscripting this choice of τ_e with "MM," we have

$$\tau_{e}^{\rm MM} = \left(\frac{5}{4}\right)^{2} \frac{\zeta a^{4}}{3\pi^{2}k_{B}Tb^{2}} = \left(\frac{M_{e}^{F}}{M_{o}}\right)^{2} \frac{\zeta b^{2}}{3\pi^{2}k_{B}T}.$$
 (14)

We therefore obtain

$$\tau_R = \left(\frac{4}{5}\right)^2 Z^2 \tau_e^{\text{MM}} = \left(\frac{M}{M_e^F}\right)^2 \tau_e^{\text{MM}},\tag{15}$$

and

$$\tau_d = \frac{\zeta N^3 b^4}{\pi^2 k_B T a^2} = \frac{15}{4} \left(\frac{M}{M_e^F}\right)^3 \tau_e^{\rm MM}.$$
 (16)

Much confusion and many errors in the literature have been produced because of the differing definitions of M_e and τ_e , and because of the factor of 4/5 that appears in many places in the above equations. The key problem is that the number of tube segments Z is not equal to the molecular weight divided by the entanglement molecular weight if one uses the Ferry definition, given as M_e^F in Eq. (6). Thus, Pattamaprom *et al.* (2000) have made errors of 4/5 or powers thereof, in their calculations of the tube diameter, and the reptation time, owing to their (incorrect) assumption that Z is equal to M/M_e^F . To avoid this problem, Fetters *et al.* (1994) incorporate the "pesky factor" of 4/5 into the definition of M_e in Eq. (6), producing a value of M_e that is only 4/5 as large as that of Ferry. We will refer to this as the "G definition," which is given by

$$M_{e}^{G} = \frac{4}{5} \frac{\rho RT}{G_{N}^{0}}.$$
 (17)

The "G" definition of the entanglement spacing has been attributed to Graessley (1980); however, the formula in this paper by Graessley relates G_N^0 to the number of tube segments (here, Z), not to M_e . Thus, to our knowledge, the first to propose the definition in Eq. (17) for M_e is Fetters *et al.* (1994). Nevertheless, we use a superscript "G" for this second definition to distinguish it from the "F" used for Ferry's definition, although without intending to ascribe attribution to Graessley. The "G" definition results in Z $= M/M_{\rho}^{G}$, which removes factors of 4/5 from the formulas for the relaxation times, avoiding a source of possible error. However, one must then recompute and retabulate the values of M_e , which has been done by Fetters et al. (1994). While intended to simplify matters, this retabulation has led to further errors, because some authors have used values of M_{ρ} from Fetters *et al.*, but have employed the Ferry definition of M_{ρ} in theoretical calculations. [An example of this error occurs in Milner and McLeish (1997)]. This causes only rather modest errors for linear polymers, where small powers of 4/5 end up erroneously included or omitted, but for star polymers, the errors are large, since the quantity M/M_e appears inside an exponential function for the relaxation time or viscosity.

Therefore, authors must take pains to make sure that the literature value of M_e used in their calculations was determined using the appropriate definition, or is corrected to account for any difference in definition. The appropriate tube-model formulas that are consistent with these different definitions, are summarized in Table I.

Finally, we note that other expressions are affected by the definitions of M_e and of τ_e , such as the equation for the "early time" primitive path fluctuations of a star arm (or of a linear polymer thought of as a "two-arm star"), discussed by Milner and McLeish (1997). Milner and McLeish give the formula for this time as

$$\tau_{\text{early}}(s) = \frac{225\pi^3}{256} \left(\frac{M}{M_e^F}\right)^4 \tau_e^{\text{MM}} s^4,$$
(18)

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	G definitions (Fetters <i>et al.</i>) Based on Eq. (17) for M_e and Eq. (19) for τ_e	F definitions (Ferry) Based on Eq. (22) for M_e and Eq. (19) for τ_e	MM definitions (Milner-McLeish) Based on Eq. (22) for M_e and Eq. (14) for τ_e
<i>M_e</i> entanglement molecular weight	$M_e^G = \frac{4}{5} \frac{\rho RT}{G_N^0}$	$M_e^F \equiv \frac{\rho RT}{G_N^0}$	$M_e^F \equiv \frac{\rho RT}{G_N^0}$
Z number of tube segments	$Z = \frac{M}{M_e^G}$	$Z = \frac{5}{4} \frac{M}{M_e^F}$	$Z = \frac{5}{4} \frac{M}{M_e^F}$
$ au_e$ equilibration time	$\tau_e = \left(\frac{M_e^G}{M_0}\right)^2 \frac{\zeta b^2}{3\pi^2 k_B T}$	$\tau_e = {\left(\frac{4}{5}\right)^2} {\left(\frac{M_e^F}{M_0}\right)^2} \frac{\zeta b^2}{3\pi^2 k_B T}$	$\tau_e^{\rm MM} = \left(\frac{M_e^F}{M_0}\right)^2 \frac{\zeta b^2}{3 \pi^2 k_B T}$
$ au_R$ Rouse rotational time	$\tau_R = Z^2 \tau_e$	$\tau_R = Z^2 \tau_e$	$\tau_R = \left(\frac{4}{5}\right)^2 Z^2 \tau_e^{\rm MM}$
$ au_d$ reptation time	$\tau_d = 3Z^3 \tau_e$	$\tau_d = 3Z^3 \tau_e$	$\tau_d = 3 \left(\frac{4}{5}\right)^2 Z^3 \tau_e^{\rm MM}$
$\tau_{\text{early}}(s)$ early-time arm	$\tau_{\text{early}}(s) = \frac{9\pi^3}{16}$	$\tau_{\text{early}}(s) = \frac{5625\pi^3}{4096}$	$\tau_{\text{early}}(s) = \frac{225\pi^3}{256}$
fluctuation time	$ imes \left(rac{M}{M_e^G} ight)^4 au_e s^4$	$\times \left(\frac{M}{M_e^F}\right)^4 \tau_e s^4$	$ imes \left(rac{M}{M_e^F} ight)^4 au_e^{ m MM} s^4$

TABLE I. Summary of the alternative definitions of tube parameters.

which is taken from Eq. (13) of the Milner–McLeish (1997) paper, combined with their relationship for the Rouse time in terms of their definition of the equilibration time. The parameter s is the fractional distance from the tip of the star arm (s = 0) to the branch point (s = 1), or to the center of the linear molecule, which is a "two-arm" star. This result can be converted into the G definition of the entanglement spacing, but we must also note the difference in definitions of τ_e . That is, if we change to the definition of τ_e in Eq. (11), we obtain

$$\tau_{\text{early}}(s) = \frac{9\pi^3}{16} \left(\frac{M}{M_e^G}\right)^4 \tau_e s^4 = \frac{5625\pi^3}{4096} \left(\frac{M}{M_e^F}\right)^4 \tau_e s^4.$$
(19)

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The G definition of M_e avoids the bulky prefactors (225/256 or 5625/4096) arising from a square or a fourth power of 5/4 [Likhtman and McLeish (2002)].

The alternative definitions are summarized in Table I, under the headings "G definitions," which are followed in a recent paper by Likhtman and McLeish (2002); "F definitions," which are based on the Ferry definition of M_e and the definition of τ_e used in Doi and Edwards; and the "MM definitions," which are followed in the equations in Milner and McLeish (1997).

We note that the "late-time" fluctuation time is also affected by the definitions of the entanglement spacing and of the equilibration time. The Milner–McLeish (1997) theory for this relaxation time, in the case of monodisperse star polymers, is

$$\tau_{\text{late}}(s) = \left(\frac{2\pi^5}{15}\right)^{1/2} \left(\frac{M}{M_e^F}\right)^{3/2} \\ \times \tau_e^{\text{MM}} \frac{\exp[U_{\text{eff}}(s)]}{\left\{s^2(1-s)^{2\alpha} + \left[\left(\frac{4M_e^F}{15M}\right)(1+\alpha)\right]^{2\alpha/(\alpha+1)}\Gamma^{-2}\left(\frac{1}{\alpha+1}\right)\right\}^{1/2}, \quad (20)$$

where $U_{\rm eff}$ is the effective potential, given by

$$U_{\rm eff}(s) = \frac{15M}{4M_e^F} \frac{1 - (1 - s)^{\alpha + 1} [1 + (1 + \alpha)s]}{(1 + \alpha)(2 + \alpha)}.$$
 (21)

Here, α is the "dilution exponent" of Milner and McLeish, which has been assigned the values either of 4/3 or unity. $\Gamma()$ is the "gamma function," which in Eq. (20) is raised to the -2 power. An error of a factor of 2 was introduced into Eq. (20) by Milner and McLeish (1998), but corrected in Frischknecht *et al.* (2002; see their footnote 24). One missprint that has been carried from paper to paper is a factor of s^2 that has multiplied both terms in the denominator of Eq. (20), rather than only the first term, as given correctly above.

The above pair of equations uses the MM set of definitions for M_e and τ_e . When converted to the G definitions, these equations yield:

$$\tau_{\text{late}}(s) = \left(\frac{\pi^5}{6}\right)^{1/2} \left(\frac{M}{M_e^G}\right)^{3/2} \tau_e \frac{\exp[U_{\text{eff}}(s)]}{\left\{s^2(1-s)^{2\alpha} + \left[\left(\frac{M_e^G}{3M}\right)(1+\alpha)\right]^{2\alpha/(\alpha+1)} \Gamma^{-2}\left(\frac{1}{\alpha+1}\right)\right\}^{1/2},$$
(22)

and

$$U_{\rm eff}(s) = \frac{3M}{M_e^G} \frac{1 - (1 - s)^{\alpha + 1} [1 + (1 + \alpha)s]}{(1 + \alpha)(2 + \alpha)}.$$
 (23)

VII. SUMMARY

Recent refinements of the "tube model" for entangled polymer rheology have led to attempts to compare quantitatively various versions of the model with experimental data in both the linear and nonlinear regimes. Since many of these comparisons have been marred by errors and inconsistencies in use of the definitions of the tube parameters, we have here presented the most commonly used definitions, which we have labeled the G, the F, and the MM sets. We urge workers in this area in the future to use one of these

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three sets, but by all means to identify their definitions clearly and to avoid inconsistencies in their use. To that end, we have tried to identify the common pitfalls.

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