

On the Definitions of Entanglement Spacing and Time Constants in the Tube Model

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Abstract

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 pre-factors for the time constants that appear in these theories be evaluated correctly using literature data for the constants (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 pre-factors that must be used for the different definitions, in the hope of helping future authors to avoid such errors.

“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. Since 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 formulae 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 are being used and that authors take pains to be sure they are used consistently. Consistent use of these definitions also requires that any parameter values taken from tabulations in the literature (especially entanglement spacings) be corrected, if necessary, to account for any differences in definition between that used by whomever created the tabulation and the calculations using that parameter.

The “tube” properties 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 from certain measured or known quantities, including 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 polymer statistical segment length b (which is defined such that the polymer mean-square end-to-end distance is $R^2 = Nb^2$, where $N \equiv M/M_0$ 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, namely the plateau modulus G_N^0 and the monomeric friction coefficient ζ . These two quantities have been measured for many polymers and are tabulated in Ferry’s (1980) book, for example. Up-to-date values of the plateau modulus for many polymers can be found in Fetters, et al. (1994; 1999). As described below, values of the entanglement molecular weight M_e 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.

The various lengths in the problem are depicted in Figure 1, showing $b \ll a \ll R = \sqrt{6} R_g \ll L_{\text{tube}} \ll L$. Rather than the “statistical 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 $R^2 = N_K b_K^2$, where 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 $b_K = \frac{\sqrt{C_\infty}}{0.82\sqrt{j}}$ and N_K is related to N by $N_K = \frac{j(0.82)^2}{C_\infty} N$, where C_∞ is the “characteristic ratio” relating R^2 to the number $n = jN$ of backbone bonds and their length l by $R^2 = C_\infty n l^2$, and j is the number of carbon-carbon bonds per monomer. The factor “0.82” enters because the tetrahedral bonding angles produce a zig-zag polymer conformation when the chain is fully extended.

Formulae describing the reptation model are taken from Doi and Edwards’ (1986) book. First, we give the formulae for the polymer contribution to the stress tensor, which assumes that tube is made of straight segments of length a , which are uncorrelated before deformation (eq. 7.3 from Doi-Edwards book).

$$\sigma_{\alpha\beta}(t) = \frac{3k_B T}{b^2} \frac{n_M}{N} \sum \left\langle \frac{\partial R_{n\alpha}(t)}{\partial n} \frac{\partial R_{n\beta}(t)}{\partial n} \right\rangle \quad (1)$$

where n_M is the number of monomers per unit volume of 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 bulk polymer (no solvent), n_M is related to the polymer density and monomer molecular weight by

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

Note that a is therefore introduced strictly as a tube *persistence length* rather than as a “tube diameter”, by which it is more colloquially referred-to.

$$\sigma_{\alpha\beta}(t) = G_N^0 \psi(t)$$

. Using this expression, Doi and Edwards’ derived the stress relaxation due to reptation:

where $\psi(t)$ is well known relaxation function changing from 1 to 0, and the plateau modulus is

$$G_N^0 = \frac{4}{5} n_M \frac{b^2}{a^2} k_B T \quad (3)$$

Eq. (2) allows us to write the plateau modulus for a melt as

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

Eq. 4 is then the basic equation for obtaining the tube diameter a (which is assumed to be equal to the tube persistence length) 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 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)

$$Za^2 = Nb^2 \quad (5)$$

Combining this with Eq. (4) gives a relationship between Z and the plateau modulus:

$$G_N^0 = \frac{4}{5} \frac{\rho RT}{M_0} \frac{Z}{N} \quad (6)$$

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

$$M_e^F = \frac{\rho RT}{G_N^0} \quad (7)$$

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 arose from the result for the modulus of affine network made of strands of length M_e^F , but we note that it does not apply to entangled melt because entanglements allow chain to slip through it, unlike crosslinks. Also there is no reason to believe that the network of entanglements deforms affinely. There is in consequence no reason to expect the prefactor of unity in (7) to be particularly robust.

Another definition, used by Fetters, et al. (1984), will be discussed later. We find from Eqs. 4 and 7 that

$$a^2 = \frac{4}{5} \frac{M_e^F}{M_0} b^2 \quad (8)$$

Combining Eqs. 6 and 7, we find a very counterintuitive result

$$Z = \frac{5}{4} \frac{M}{M_e^F} \quad (9)$$

The quantity M/M_e^F is sometimes referred to as the “number of entanglements” per molecule. However, Eq. 9 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 considerable confusion in the literature, as discussed below. The fundamental reason for such confusion is probably inconsistent mixture of two alternative concepts: *entanglements* and the *tube*.

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):

$$\tau_R = \frac{\zeta N^2 b^2}{3\pi^2 k_B T} \quad (10)$$

Note that the terminal *stress* relaxation time of the Rouse model is a factor of two 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 re-written as

$$\tau_R = \frac{\zeta Z^2 a^4}{3\pi^2 k_B T b^2} \quad (11)$$

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:

$$\tau_e = \frac{\zeta a^4}{3\pi^2 k_B T b^2} = \left(\frac{4}{5}\right)^2 \left(\frac{M_e^F}{M_0}\right)^2 \frac{\zeta b^2}{3\pi^2 k_B T} \quad (12)$$

where Eq. 8 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. 12, once τ_e is specified for a given polymer at a given temperature, the Rouse time τ_R is then given by simply:

$$\tau_R = Z^2 \tau_e = \left(\frac{5}{4}\right)^2 \left(\frac{M}{M_e^F}\right)^2 \tau_e \quad (13)$$

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

$$\tau_d = \frac{\zeta N^3 b^4}{\pi^2 k_B T a^2} = 3Z^3 \tau_e \quad (14)$$

The above formulae 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 experimental 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 blending together different chain architectures.

An alternative definition of the “equilibrium” time has been used frequently by Milner, McLeish, and coworkers (see, for example, Milner and McLeish, 1997), which chooses 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 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

$$\tau_e^{MM} = \left(\frac{5}{4}\right)^2 \frac{\zeta a^4}{3\pi^2 k_B T b^2} = \left(\frac{M_e^F}{M_o}\right)^2 \frac{\zeta b^2}{3\pi^2 k_B T} \quad (15)$$

We therefore obtain

$$\tau_R = \left(\frac{4}{5}\right)^2 Z^2 \tau_e^{MM} = \left(\frac{M}{M_e^F}\right)^2 \tau_e^{MM} \quad (16)$$

and

$$\tau_d = \frac{\zeta N^3 b^4}{\pi^2 k_B T a^2} = \frac{15}{4} \left(\frac{M}{M_e^F}\right)^3 \tau_e^{MM} \quad (17)$$

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. 7. 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. 7, producing a value of M_e only $4/5$ as large as that of Ferry. We will refer to this as the “G definition,” which is given by

$$M_e^G \equiv \frac{4}{5} \frac{\rho RT}{G_N^0} \quad (18)$$

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). So, we use a superscript “G” for this second definition to distinguish it from the “F” used for the first definition, which is due to Ferry. The “G” definition results in $Z = M/M_e^G$, which removes factors of 4/5 from the formulae for the relaxation times, avoiding a source of possible error. This also means that M_e^G has a simple physical meaning of number of monomers in one tube segment, so that the concept of entanglement is not necessary in any of “G” definition. However, one must then re-compute and re-tabulate the values of M_e , which has been done by Fetters, et al. (1994). While intended to simplify matters, this re-tabulation has led to further errors, because some authors have used values of M_e from Fetters et al., but have employed the Ferry definition of M_e in theoretical calculations. (An example of this error occurs in Milner and McLeish 1997). This causes only rather small 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.* Thus, in summary, using the “G” definition for the entanglement molecular weight, the formulae for the tube model are:

$$Z = \frac{M}{M_e^G} \quad (19)$$

$$\tau_e = \frac{\zeta a^4}{3\pi^2 k_B T b^2} = \left(\frac{M_e^G}{M_0} \right)^2 \frac{\zeta b^2}{3\pi^2 k_B T} \quad (20)$$

$$\tau_R = Z^2 \tau_e = \left(\frac{M}{M_e^G} \right)^2 \tau_e \quad (21)$$

$$\tau_d = \frac{\zeta N^3 b^4}{\pi^2 k_B T a^2} = 3Z^3 \tau_e = 3 \left(\frac{M}{M_e^G} \right)^3 \tau_e \quad (22)$$

On the other hand, the Ferry definition of M_e , namely $M_e^F \equiv \frac{\rho RT}{G_N^0}$ (Eq. 6) leads to

$$Z = \frac{5}{4} \frac{M}{M_e^F} \quad (23)$$

$$\tau_e = \frac{\zeta a^4}{3\pi^2 k_B T b^2} = \left(\frac{4}{5}\right)^2 \left(\frac{M_e^F}{M_0}\right)^2 \frac{\zeta b^2}{3\pi^2 k_B T} \quad (24)$$

$$\tau_R = Z^2 \tau_e = \left(\frac{5}{4}\right)^2 \left(\frac{M}{M_e^F}\right)^2 \tau_e \quad (25)$$

$$\tau_d = \frac{\zeta N^3 b^4}{\pi^2 k_B T a^2} = 3Z^3 \tau_e = 3\left(\frac{5}{4}\right)^3 \left(\frac{M}{M_e^F}\right)^3 \tau_e \quad (26)$$

(Ron: do we really need to list these out all again here – why not just refer to the box at the end)

If the “Milner-McLeish” definition of τ_e is used, then the factor of $(4/5)^2$ is missing from Eq. 23, and, correspondingly, two powers of $5/4$ are dropped from the formulae for τ_r and τ_d in Eqs. 24 and 25.

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

$$\tau_{early}(s) = \frac{225\pi^3}{256} \left(\frac{M}{M_e^F}\right)^4 \tau_e^{MM} s^4 \quad (27)$$

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, for a “two-arm star.” We note that it was shown (Likhtman and McLeish, 2002) that the concept of average local relaxation time is in fact *not* applicable to small times $t < \tau_R$ (since the local relaxation of orientation is not a single exponential near the chain end) and therefore the prefactor in eq. (26) does not have much meaning. We still mention it here because of its wide use as an approximate formulae.

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. 12, we obtain

$$\tau_{early}(s) = \frac{9\pi^3}{16} \left(\frac{M}{M_e^G} \right)^4 \tau_e s^4 = \frac{5625\pi^3}{4096} \left(\frac{M}{M_e^F} \right)^4 \tau_e s^4 \quad (28)$$

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 1, 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

$$\tau_{late}(s) = \left(\frac{2\pi^5}{15} \right)^{1/2} \left(\frac{M}{M_e^F} \right)^{3/2} \tau_e^{MM} \frac{\exp(U_{eff}(s))}{\left[s^2(1-s)^{2\alpha} + \left(\left(\frac{4M_e^F}{15M} \right) (1+\alpha) \right)^{2\alpha/(1+\alpha)} \Gamma^{-2} \left(\frac{1}{\alpha+1} \right) \right]^{1/2}} \quad (29)$$

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

$$U_{eff}(s) = \frac{15M}{4M_e^F} \frac{1 - (1-s)^{\alpha+1} [1 + (1+\alpha)s]}{(1+\alpha)(2+\alpha)} \quad (30)$$

Here α is the “dilution exponent” of Milner and McLeish, which has been assigned the values either of 4/3 or unity. $\Gamma(x)$ is the “gamma function,” which in Eq. 30 is raised to the -2 power. An error of a factor of two was introduced into Eq. 30 by Milner and McLeish (1998), but corrected in Frischknecht, et al. (2002; see their footnote 24). However one missprint has been carried persistently from one paper to another, which is in factor of s^2 in denominator of eq. (30): it must multiply only the first term in brackets.

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:

$$\tau_{late}(s) = \left(\frac{\pi^5}{6}\right)^{1/2} \left(\frac{M}{M_e G}\right)^{3/2} \tau_e \frac{\exp(U_{eff}(s))}{\left[s^2 (1-s)^{2\alpha} + \left(\left(\frac{M_e G}{3M}\right)(1+\alpha)\right)^{2\alpha/(\alpha+1)} \Gamma^{-2}\left(\frac{1}{\alpha+1}\right) \right]^{1/2}} \quad (31)$$

and

$$U_{eff}(s) = \frac{3M}{2M_e G} \frac{1 - (1-s)^{\alpha+1} [1 + (1+\alpha)s]}{(1+\alpha)(2+\alpha)} \quad (32)$$

It is also important to define these essential parameters from experimental point of view. We have already shown that the definition of the elementary time τ_e is theory-dependent: if it is defined from high frequency Rouse spectrum of unentangled short chains, one needs some assumptions about glass transition dependence on the chain length. If τ_e is defined from fitting the spectrum of entangled polymers, the result will be strongly model dependent. The situation with the experimental definition of the plateau modulus is better but not perfect. The most reliable and well-defined route to determination of G_N^0 from experiment is to take the value of G' in the plateau region, for example at the minimum of G'' , for an extremely entangled polymer, with at least 100-200 entanglements. In practice however this is not always possible and people define the plateau modulus for each sample, and then argue that it can be molecular weight dependent. This however strongly contradicts all theoretical assumptions of tube models, that the entanglement molecular weight is set by the local packing propensity of the polymer chain. 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 $Z=1000$ (we reiterate that this is true for a *constant* value for the parameter called the plateau modulus and given the notation G_N^0). Figure 9 of this reference shows this gentle saturation for several assumptions of the strength of constraint release. That for a wide range of molecular weights the experimentally-apparent plateau modulus is smaller than the high-molecular weight limit is particularly important for the experimental determination of plateau modulus dependence on concentration in polymer solutions, because these are never extremely strongly entangled. We suggest that *the plateau modulus should be determined by fitting linear spectra with the full theory for the linear viscoelastic response at each concentration, rather than obtained by some empirical definition evaluated at a restricted range or point of the spectrum.*

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Table 1 Summary of the alternative definitions of tube parameters

	G Definitions (Fetters et al.) 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
M_e Entanglement molecular weight	$M_e^G \equiv \frac{4}{5} \frac{\rho RT}{G_N^0}$	$M_e^F \equiv \frac{\rho RT}{G_N^0}$	$M_e^F \equiv \frac{\rho RT}{G_N^0}$
Z Number of tube segments	$Z = \frac{M}{M_e^G}$	$Z = \frac{5}{4} \frac{M}{M_e^F}$	$Z = \frac{5}{4} \frac{M}{M_e^F}$
τ_e Equilibration time	$\tau_e = \left(\frac{M_e^G}{M_0} \right)^2 \frac{\zeta b^2}{3\pi^2 k_B}$	$\tau_e = \left(\frac{4}{5} \right)^2 \left(\frac{M_e^F}{M_0} \right)^2 \frac{\zeta b^2}{3\pi^2 k_B}$	$\tau_e^{MM} = \left(\frac{M_e^F}{M_0} \right)^2 \frac{\zeta b^2}{3\pi^2 k_B}$
τ_r Rouse rotational time	$\tau_r = Z^2 \tau_e$	$\tau_r = Z^2 \tau_e$	$\tau_r = \left(\frac{4}{5} \right)^2 Z^2 \tau_e^{MM}$
τ_d Reptation time	$\tau_d = 3Z^3 \tau_e$	$\tau_d = 3Z^3 \tau_e$	$\tau_d = 3 \left(\frac{4}{5} \right)^2 Z^3 \tau_e^{MM}$
$\tau_{early}(s)$ Early-time arm fluctuation time	$\tau_{early}(s) = \frac{9\pi^3}{16} \left(\frac{M}{M_e^G} \right)$	$\tau_{early}(s) = \frac{5625\pi^3}{4096} \left(\frac{M}{M_e^F} \right)$	$\tau_{early}(s) = \frac{225\pi^3}{256} \left(\frac{M}{M_e^F} \right)$

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References

Doi M, Edwards SF “The theory of polymer dynamics,” Oxford University Press, Oxford (1986).

Ferry JD “Viscoelastic Properties of Polymers,” Third Ed., John Wiley & Sons, New York (1980).

Fetters LJ, Lohse DJ, Richter D, Witten TA, Zirkel A, “Connection between polymer molecular weight, density, chain dimensions, and melt viscoelastic properties,” *Macromolecules*, 27:4639-4647 (1994).

Fetters LJ, Lohse DJ, Graessley WW “Chain dimensions and entanglement spacings in dense macromolecular systems,” *J Polym Sci, Polym Phys Ed.* 37:1023-1033 (1999).

Frischknecht AL, Milner ST, Pryke A, Young RN, Hawkins R, McLeish TCB, “Rheology of three-arm asymmetric star polymer melts,” *Macromolecules* 35:4801-4820 (2002).

Graessley WW, “Some phenomenological consequences of the Doi-Edwards theory of viscoelasticity,” *J Polym Sci; Polym Phys Ed* 18:27-34.

Likhtman AE, McLeish TCB “Quantitative theory for linear dynamics of linear entangled polymers,” *Macromolecules* 2002, 35, 6332-6343.

Milner ST, McLeish TCB “Parameter-free theory for stress relaxation in star polymer melts,” *Macromolecules* 30:2159-2166 (1997).

Milner ST, McLeish TCB, “Arm-length dependence of stress relaxation in star polymer melts.” *Macromolecules* 31: 7479-7482 (1998).

Pattamaprom C, Larson RG, Van Dyke TJ “Quantitative predictions of linear viscoelastic rheological properties of entangled polymers,” *Rheol Acta* 39:517-531 (2000).

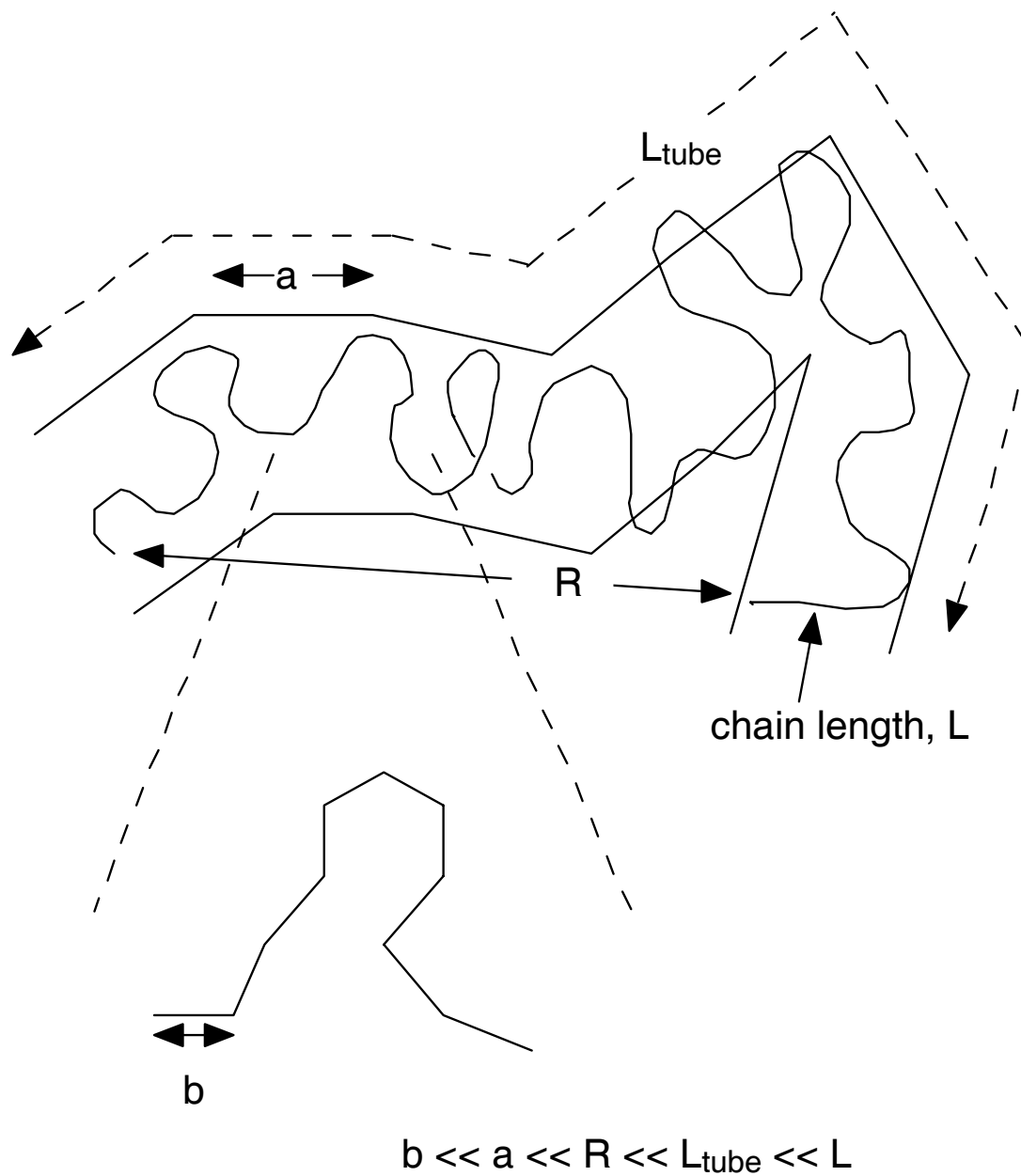


Fig. 1. Illustration of tube model, and the various length scales of the polymer chain and the tube. The blow-up shows a small section of the polymer, modeled as a freely-jointed chain.