VIEWPOINT

Looking Inside the Entanglement "Tube" Using Molecular Dynamics Simulations

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ABSTRACT: For 30 years, the dynamics of entangled polymers have been explained using the phenomenological "tube" model, where the "tube" represents the confining effects of surrounding chains, but the tube properties, such as its length and diameter, could only be inferred indirectly by fitting the tube model to rheological data. Now, however, molecular simulations are allowing these properties to be directly computed. The computational advances in molecular dynamics and related methods that have made this possible are here reviewed. In addition, it is discussed how new findings, such as an apparent time dependence of the tube diameter and direct observation of "hopping" of branch points along the tube, are helping to refine the tube model. © 2007 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 45: 3240–3248, 2007
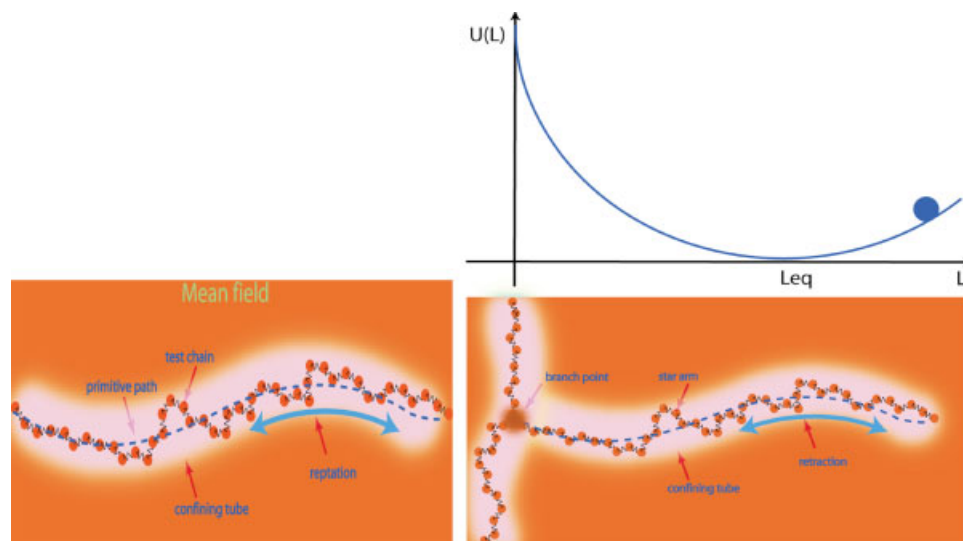**Keywords:** melt; molecular dynamics; rheology

The most important polymers, from the standpoint of sheer volume and economic impact, remain the "simple" thermoplastics. The majority of these are polyolefins (especially polyethylene and polypropylene), which annually sell at volumes of hundreds of billions of pounds, with polystyrene, polycarbonates, and a few others accounting for much of the rest. The high volumes of these is explained in part by cheap raw materials, but also by the ease with which these thermoplastics are shaped into products in high-throughput processes such as film blowing, fiber spinning, blow molding, and the like. The processing behavior is, in turn, controlled by rheology—the response of these materials in the molten state to the stresses and strains imposed by the processing environment. Hence, among the most important tasks in the field of polymer science is the creation of a reliable engineering science of polymer melt rheology, a science that can predict processing behavior of polymers

Figure 1. The tube model for (a) linear and (b) branched polymer. In (b), the graph shows the "primitive path potential" in which the polymer branch fluctuates.

from a knowledge of molecular structure, which for thermoplastics depends mainly on the molecular weight and branching distribution, as well as on the chemical makeup of the polymer, including its tacticity.

Forty years ago, the rheology of polymer melts was an empirical discipline. A few "rules" of rheology were known, such as the famous 3.4 power law in the dependence of zero-shear viscosity on molecular weight for linear polymers,[1] and the much steeper, roughly exponential, dependence for star-branched polymers.[2] It was also known that such melts were highly shear thinning.[2] Causes for these behaviors were sought in the "entanglements" that long, densely concentrated, polymers were thought to have with each other, and some crude theories were bandied about in an effort to reduce the empirical observations to usable formulas. But, few entertained illusions that any deep understanding of the rheology of polymer melts or concentrated polymer solutions had been attained.

This situation began to change drastically in the 1970s. First, in 1971, de Gennes,[3] in a conceptual breakthrough, envisioned that entangled polymer chains might move through the entangling mesh of other chains by snaking primarily along their own coarse-grained random-walk contour—a process he called reptation. The coarse-grained path is now called the primitive path, and its length is proportional to, but much shorter than, the contour length of the actual chain. Using the "reptation" idea, de Gennes was able to predict that there should be a

power-law exponent of 3.0 relating the relaxation time (and also the viscosity) to molecular weight, not far from the observed 3.4 power law. Then, starting in 1978, Doi and Edwards[4] began publishing their blockbuster series of papers, and eventually a book,[5] which presented multiple specific predictions for the major linear and nonlinear rheological properties, along with pre-
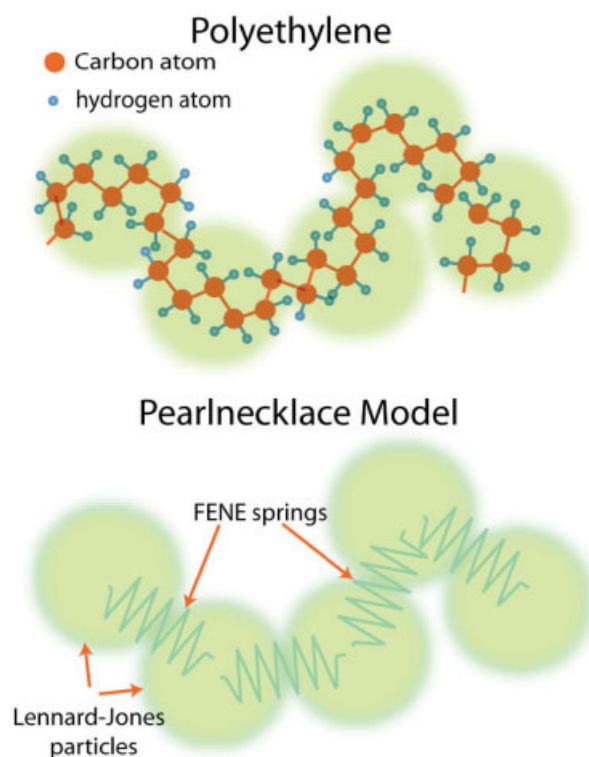
Figure 2. The coarse-grained pearl necklace model.

dictions of molecular diffusivities, and much else besides, all based on the primitive path, and the meandering worm-like volume centered on this path called the "tube," to which the chain is largely confined due to the presence of the surrounding molecules; see Figure 1(a). The diameter of the tube, which is assumed to be the same as the length of a random-walk step of the primitive path, is *a priori* unknown, and is usually obtained by fitting of a rheological quantity (the so-called "plateau modulus") to the tube model.

From this starting point, the "tube" model has gone from strength to strength, and has become the basis for the rheology not only of linear polymers, but also of ones with long-chain branching. The effects of long-chain branching are most easily contemplated for the simple "star" polymer with a single branch point, from which emanate several "arms" of equal molecular weight; see Figure 1(b). Since the branch point suppresses reptation, the arms are obliged to relax, Houdini-like, by retracting into the tube until the tip of the arm threads its way around the entanglements that are closest to the branch point, and the arm can thereby take on a completely different, relaxed, configuration. The unlikelihood of such processes occurring spontaneously is governed by a phenomenological tube primitive path "fluctuation potential" that penalizes deep retractions of the arm tip into the tube. As with reptation, the underlying idea goes back to de Gennes[6] and the first clear predictive models are due to Doi and Kuzuu.[7]

Until roughly the 1990s, the tube model, outlined above, was not developed enough to account with any accuracy for polydispersity in molecular weight or branching distributions. However, over the last fifteen years, polydispersity has been successfully incorporated into a variety of tube models, through inclusion of concepts of "tube renewal" or "constraint release," which allow the tube itself to relax in response to the motions of the polymers whose entangling effects define the tube.[8] This has opened the door to use of the tube model to predict the rheology of commercial linear polymers, which are inevitably polydisperse in molecular weight. Commercial long-chain branched polymers are never simple monodisperse stars, but are polydisperse in branch length, spacing, and number per molecule. Describing the rheology of such melts requires accounting for the relaxation of "backbone" segments lying between branch points, which cannot relax by either reptation or primitive path fluctuations. Modern ideas, arising from McLeish et al.,[9,10] model backbone relaxation by a kind of "hopping" motion of the branch points, wherein each "hop" occurs whenever an arm executes a complete retraction, and is then temporarily effectively unentangled, at least near the branch point, and thus the branch point is free to move roughly a tube diameter or so along the tube containing the backbone. These ideas have proven successful in predicting the rheology of branched polymers with two or more branch points, with regular, or even irregular, branching structures.[10–12]

These successes, however, have not removed the phenomenological nature of the "tube" ansatz nor provided a firm molecular-level prediction of the phenomenological parameters of the model, which to date are still obtained by fits to rheological data.[5,13] The "tube diameter" is one of these parameters, as is (to some extent) the "dilution exponent"[14] that relates the tube diameter to the polymer concentration in a solution. Also, for branched polymers, the entropic "fluctuation potential" is in the main phenomenological, as is the "branch point diffusivity," although scaling ideas yield some relationships between these quantities and underlying physical properties of the polymers.[9,10]

A more satisfying approach would be to derive the tube model, and the properties of the "tube," such as its diameter, the fluctuation potential, dilution exponent, branch point diffusivity, and other quantities, directly from the fine-scale statics and dynamics of the polymer molecules themselves. Fortunately, skillful use of rapidly increasing computer power is now enabling this to be done. Just as de Gennes, and Doi, Edwards, and coworkers laid the foundations for the tube model, the foundations for computer simulation of entanglement dynamics were laid by Kremer et al. The first breakthrough, accomplished with Herculean effort, was the molecular dynamics simulation of entangled chains by Kremer and Grest in 1990.[15] This effort required months of time on one of the (then) fastest supercomputers in the world. Besides computational brawn, the effort also required thoughtful development of a "pearl necklace" model of a generic linear polymer;[15,16] see Figure 2. The "pearls" of the pearl necklace are repulsive Lennard-Jones beads, which are strung together by short, stiff springs, which cannot be stretched far enough apart to allow to permit a bead of another chain to squeeze
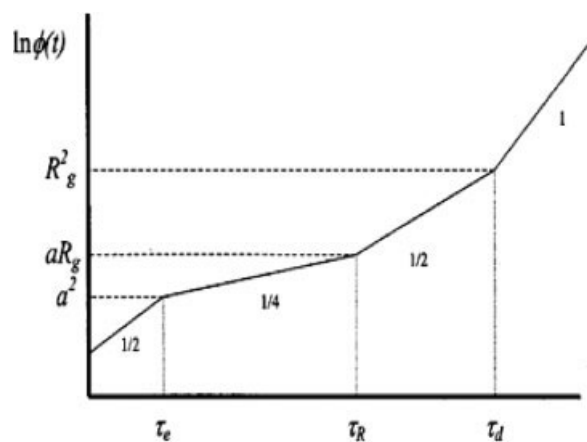
Figure 3. Log-log plot of time-dependent mean-square displacement of monomer of a long entangled chain according to the tube model. The first 1/2-power-law regime is Rouse subdiffusion of the monomer, which persists until the chain "feels" the tube at time τ_e. Then, the Rouse subdiffusion is directed along the tube, which is a random walk, leading to a combined power-law exponent of 1/4. After time τ_R, the whole chain begins moving coherently (i.e., reptates), and so the Rouse subdiffusion disappears, leaving a 1/2-power-law exponent. Finally, the chain escapes the tube at the "disengagement time" or "reptation time" τ_d, leading to ordinary center-of-mass diffusion, with power law exponent of unity.

between neighboring beads on the same chain without experiencing impossibly high repulsive forces from the beads. Hence, "entanglements," or chain noncrossability, are enforced in a "natural" way, permitting their effects to emerge in the same way they do in real chains, i.e., without assuming that the chains are in a "tube" to begin with.

Work by Kremer et al.[16] revealed the characteristic "signature" of reptation, which is a 1/4-power law relating mean-square displacement of the beads with time. This 1/4-power-law diffusion is subdiffusive (i.e., has lower power-law exponent than "normal" diffusion, with its power law exponent of unity relating mean-square displacement with time) in two different ways. First, the bead is tethered to other beads, and as time goes on, feels itself bogged down by more and more of them, as their motion becomes more and more coordinated at longer times. This effect produces a square-root slow-down of diffusion in time, identical to that seen in unentangled chains, as described by the well known Rouse model and appears at the earliest times in a plot of mean-square displacement with time; see Figure 3. A second square root rela-

tionship emerges as a result of the fact that the chain's motion must be directed along the primitive path, which itself follows a random walk. Thus, the distance diffused in real space increases as the square root of the distance diffused along the tube. This source of subdiffusive behavior combines with that derived from chain connectivity (i.e., Rouse subdiffusion) to produce a net 1/4-power-law behavior of the monomer mean-square displacement with time that is distinctive to the reptation model of diffusion in a tube; see Figure 3 again. The simulations of Kremer and Grest captured this behavior, thus demonstrating the emergence of reptation from realistic monomer-scale motions. (Note, however, that reptation, as such, is the coordinated sliding of the chain as a whole, and occurs at times longer than those for which the 1/4-power-law holds, times at which the Rouse subdiffusive motion has fallen away, leaving only the 1/2-power-law resulting from coordinated motion of the whole chain along the random-walk primitive path—again see Figure 3.)

Showing the 1/4-power-law regime of chain motion required that long chains be simulated, chains too long to relax completely in the time available even on modern computers. The failure to reach complete relaxation is simply a result of the incredibly slow processes involved in reptation. Remember that the longest relaxation time scales roughly as the 3.4 power of molecular weight, implying that a mere doubling of chain length necessitates a 10-fold longer run to achieve complete relaxation. The longer chains also necessitate a large box to contain them, and the box volume scales as the cube of the linear dimension of the box, which itself scales as the square root of the chain length. Thus, "well entangled" linear chains (with more than 10 entanglements per chain) are essentially impossible to equilibrate even today. However, the signatures that the "chain is in a tube" are revealed as soon as the chain has moved far enough to "feel" the tube, and this occurs on a time scale of roughly τ_e—the so-called "equilibration time," which is roughly the longest relaxation time of a piece of chain just long enough to occupy one tube "segment"—i.e, a portion of the tube containing one primitive path step. Thus, much can be learned through direct molecular dynamics simulations on short time scales. In fact, it is at the times scales in the vicinity of τ_e that small-scale motions characteristic of simple liquids begin to give way to motions

along the tube that are characteristic of entangled polymers. If the details of this transitional process can be studied and understood through molecular dynamics simulations, then the behavior at long time scales will likely be made understandable as well. The reason for this confidence is that we already know that the tube model works well for long linear and branched chains, if only the "tube parameters" can be specified and understood. And, for the most part, these parameters characteristic of the tube are determined by processes that occur at time scales in the vicinity of τ_e, or at least, one can contrive situations where most of the important physics occurs within a decade or two in time of τ_e.

But, to study long chains, even at short times, the chains must be well equilibrated, i.e., their conformations must be those of a system that has been able to relax for a time longer than the longest relaxation time. But, as mentioned, this time is inaccessible to simulations for the well-entangled chains we are most interested. To resolve this problem, again it was Kremer and coworkers[17] who developed methods of rapidly equilibrating long chains. To do so, Auhl et al.[17] simply followed Flory in noting that on long length scales, the configurations of long polymers are simply random walks, with effective random-walk step size set by bond angle and local packing constraints. Thus, even for isolated chains one can readily generate arbitrarily long chains whose configurations on the longest length scales are those of the melt state. It remains then to pack these together and relax out the overlapping-bead configurations over a short time scale in a way that does not then introduce distortions at the long length scales that one has avoided by the initial construction of the chains. Kremer and coworkers figured out a way to do this, through a chain-packing algorithm that uses a combination of translations and rotations of chains with fixed configuration, so as to make monomer density as uniform as possible, followed by a short molecular dynamics run wherein the bead repulsions are gradually turned on, to remove the bead overlaps. Auhl et al.[17] developed this algorithm, sometimes called the "slow-push-off" method for long linear chains. Our group found a way to apply this to star-branched polymers,[18] which are even more hopeless of relaxing by brute force, owing to their exponential dependence of relaxation time on chain length.

Armed with these tools, the physics underlying the tube model is now being revealed. A key element of the tube model is obviously the tube itself, along with its centerline, the primitive path. Again, it was Kremer and coworkers who made the first dramatic breakthrough in calculating directly the primitive path from computer simulations of the pearl necklace model.[19] To determine the set of primitive paths from their simulations, Everaers et al.[19] simply start from an equilibrated melt and at some point in time instantaneously freeze in place all chain ends. They then turn off the excluded-volume repulsions between beads on the same polymer while leaving them in place between beads on differing polymers. The chains then tend to shrink their contour length under the action of the spring forces connecting neighboring beads, and this tendency is increased by steadily "cooling" the system to dampen Brownian motion and leave the chains with no recourse but to shrink their contour lengths to the "shortest possible" paths, subject to the constraints that the chain ends are fixed and the chains cannot pass through each other. The result is a "network" of "primitive paths," pulled tight against each other, as shown in Figure 4. Everaers et al. showed that the average length of these primitive paths, and the random-walk step size one infers from this average length, are consistent with the plateau modulus one "measures" in simulations of this melt, thus validating the formula derived from the tube model.

This result, published in the journal *Science*, spurred a "cottage industry" of workers developing alternative methods of deriving primitive paths.[21–25] Our group's own foray into this area began with the effort of a graduate student, Sachin Shanbhag, to derive not just the average primitive path length, but the whole distribution of primitive paths, from which the primitive path "fluctuation potential" can be derived.[21] This work, developed initially for a lattice polymer model that permits huge ensembles of primitive paths to be generated, yielded a primitive path potential that is roughly consistent with the "classical" potential used in the standard tube model. However, further work using real-space molecular dynamics simulations with the pearl necklace model revealed that this gratifying result only emerges for a modified version of the "cooling" method of Everaers et al. in which the spring forces used to shrink the chains is replaced by a constant spring tension that mini-
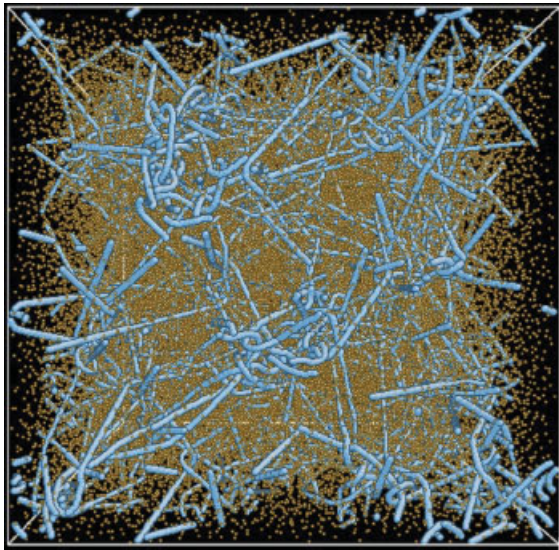
Figure 4. Network of "primitive paths" (paths) determined by the "cooling method" from a dense melt of pearl necklace chains (orange). (Figure from Larson et al.,[20] AIChE J). [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]
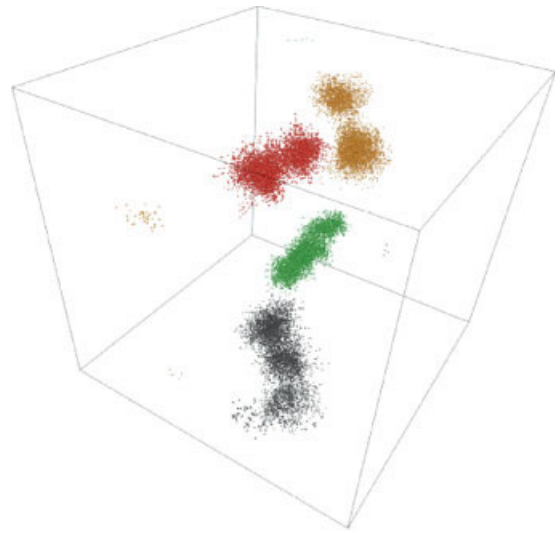
Figure 6. (Left): Scatter plot of locations of branch point for four different polymers, each designated with a different color, selected from a box containing 200 chains. Each branch point is initially confined to a roughly spherical volume of diameter corresponding to the tube diameter, but then "hops" to a different region when the short branch retracts, releasing its entanglement constraints, before becoming confined again (from Zhou and Larson,[27] Macromolecules). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
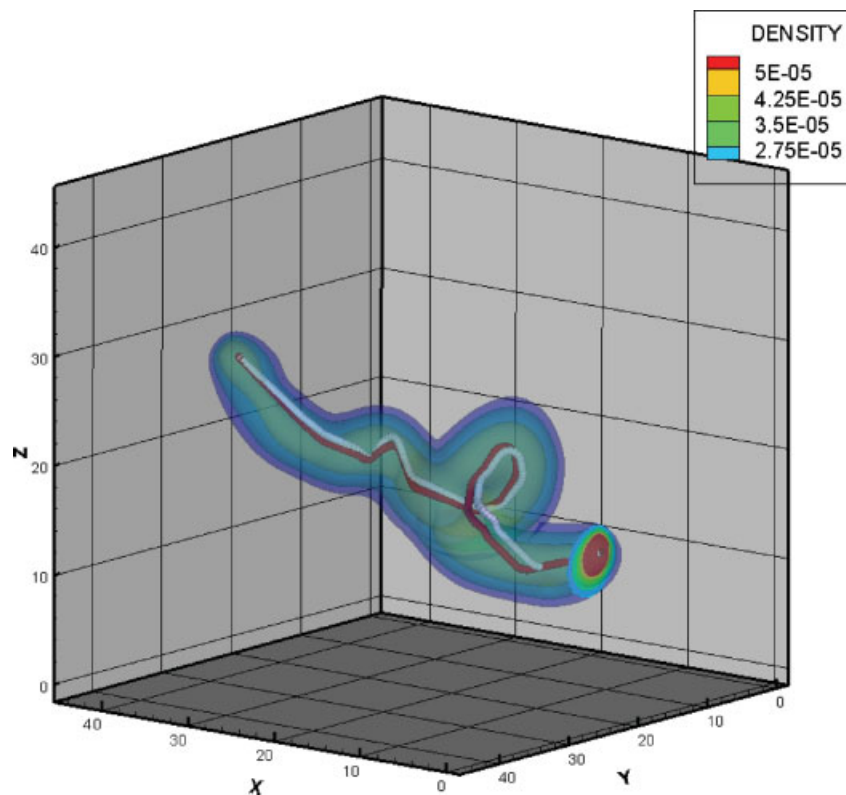
Figure 5. The monomer "bead" density contour map, determined by direct "tube sampling." The primitive paths determined by two different cooling methods (red and white lines) are both near the center of the "tube" as determined by direct sampling of bead density (from Zhou and Larson,[26] Macromolecules). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

mizes not the spring energy but the total length of all primitive paths.[22] The original "cooling" procedure of Everaers et al. yields a fluctuation potential that is much steeper than the classical one, and that, if correct, would badly upset the current tube models in use for predicting the rheology of branched polymers. While the width of the distribution of primitive paths turns out to be very sensitive to the cooling procedure used, the mean primitive path length is almost the same for cooling that minimizes total primitive path length as it is for cooling that minimizes spring energy.

The sensitivity of the distribution of primitive paths to the method used to generate them calls attention to a problem with these methods in general. Namely, the primitive path is a concept rooted in equilibrium polymer dynamics. However, cooling procedures, with chain ends held fixed, can disrupt the structure of the melt, with unknown consequences for the properties of the primitive paths. Ideally, one would wish to derive the primitive paths from an equilibrium process that allows chains to explore their environment without the artificial disturbances produced by holding chain ends or by cooling. In principle, one can do this by "tube sampling," in which one simply bins the locations of the beads during a run under equilibrium conditions (i.e., with no cooling). An early version of this is already present in the original simulations of Kremer and Grest,[15] in which the contours of a single chain taken at various times were superimposed on each other, revealing a "tube-like" bundle of configurations, and confirming that the chain was exploring a tube-like region. Another example is shown in Figure 5, where the bead density is color coded, showing that the "tube" is defined by a continuous monomer density field, with high monomer density along the centerline of the tube, and gradually diminishing monomer density toward the edge. This monomer density field was generated without cooling, although the chain ends were held fixed to prevent the chain from escaping the tube during the time the bead densities were accumulated.[26] However, the conditions applied at the chain ends will become less and less important when longer chains are used, since for very long chains, the "tube" can be thoroughly explored during a time of order τ_e, and which can therefore be made much smaller than the time τ_d required for the chain to escape the tube. The latter time scales as $\tau_d \propto Z^3 \tau_e$, where Z is the number of steps in the primitive path, which grows large for long chains. Thus, "tube sampling" is potentially a viable way to determine the properties of the tube under equilibrium conditions.

One problem, however, is to determine the primitive path from the bead density map. One needs a one-dimensional coordinate along the tube onto which to map the bead density, and thereby find the line of maximum monomer density along the tube. Zhou and Larson[26] resolved this issue by using "primitive paths" determined by a cooling method, and mapping bead coordinates onto this path, allowing bead distances orthogonal to this "primitive path" to be determined and their cross-sectional density to be determined. This procedure involved starting at one chain end, and mapping beads to the closest primitive path location that is also near the position to which neighboring beads were mapped. The need to "march" starting at a chain end arises because the primitive path has loops, such as that shown in Figure 5. For a bead on the "inside" of a loop, it is not *a priori* clear where on the loop the bead should be mapped, i.e., where along the primitive path the bead resides. However, by marching along the primitive path, one can map the bead to a part of the primitive path that is close to where the neighboring bead was just mapped. In this way, the continuity of the chain, and of the mapping of the chain coordinates to the primitive path, can resolve the ambiguity posed by the presence of the loops. In future work, it should be possible to determine whether a procedure such as this is robust by performing the "march" twice, once from each end of the chain. The beads should obviously be mapped to the same, or nearly the same, positions along the primitive path, no matter which chain end is used to initiate the process.

Note also, that since the beads are projected onto a primitive path that was produced by "cooling," the projection procedure inherits the ambiguity of the cooling process. It should be possible to reduce or eliminate this uncertainty by finding the path of maximum bead density, once the projection onto the initial "primitive path" has been carried out. This locus of maximum density then can be taken as a "revised" primitive path to be used in a second round of bead projection, this time projecting onto the "revised" primitive path. Iteration should hopefully lead to a converged primitive path that

does not change on further iterations. It should be possible to check that the converged path is insensitive to the starting path by using different approximate starting paths, produced for example, by different cooling methods, or other methods. Thus, while there is work ahead, it appears that there is no longer any obviously insurmountable hurdle to extracting both the primitive path and the bead density distribution normal to that primitive path.

While truly converged primitive paths have not yet been demonstrated, it has already been shown that the bead density is usually maximized near the primitive paths determined by a cooling method—see Figure 5—which indicates that the these paths are usually already close to the "correct" ones. (However, the shortest and longest paths are sensitive to the method used to generate them, since the width of the primitive path distribution is sensitive to the cooling method.) A bead density determined from an admittedly still imperfect projection method has been obtained by our group[26] and used to determine the "confinement potential" that keeps the chain within the tube. The confining potential appears to be very "soft"—i.e., it is roughly a harmonic potential near the primitive path, but rolls over into a soft long-range potential at larger distances from the primitive path. Moreover, the potential becomes even softer at longer times.[26] Evidently, as time progresses, the chain finds ways of occasionally wandering ever farther from the primitive path. If these results hold up for longer chains, the conclusion will be that the tube diameter appropriate at times around τ_e is significantly smaller than the tube diameter that prevails at longer times when reptation is active. This tentative conclusion carries practical implications for how tube models ought to be used that we will touch on briefly in the next paragraph.

As a final illustration of the power of molecular dynamics simulations to explore the underpinnings of the tube model, we consider briefly the case of branched polymers. For star polymers in which all arms are of equal length, relaxation occurs essentially entirely by branch fluctuations, and the branch point is confined to a region whose diameter is roughly that of the tube. However, for an "asymmetric" three-arm star, for which one of the arms is very much shorter than the other two, the short arm will relax very much faster than either of the other two, and when it relaxes, current "tube theory" predicts that the branch point can "hop" roughly one tube diameter along the tube confining the two long arms. This "hopping" motion has now been observed directly in simulations of asymmetric star polymers;[27] see Figure 6. Moreover, the rate at which "hops" occur appears to be directly correlated with the time required for the short arm to completely relax its configuration, as predicted by the theory alluded to at the beginning of this article. In fact, at long time scales, the simulation results can be modeled by replacing the short arm by a large frictional "bead" whose friction is proportional to the relaxation time of the arm. Thus, at long time scales, the "backbone" made up of the two arms constitutes an effectively "linear" polymer containing a "fat" bead whose drag represents the resistance to motion presented by the short dangling arm. This picture of how branch-point relaxation controls the long-time motion of a polymer backbone is consistent with the theory developed by McLeish et al.[9,10] and now in active use to predict the rheology of polymers with one or more long-chain branches.[11,12] Moreover, the observation that the tube is effectively "thinner" at time scales near τ_e than it is at longer times is also consistent with both the molecular dynamics simulations of asymmetric stars, and with experimental rheological data on such molecules.[28] To account for this effect in a phenomenological tube model of polymer rheology, one would need to allow the tube diameter to increase somewhat as the time scale increases from τ_e to larger times. Thus, such simulations are not only confirming some assumptions of the tube model that have long been in use in practical rheological theories, but are suggesting ways in which those models might be modified to make their predictions more accurate. Much more can now be learned from these simulations, and some exciting days are surely in store for the field of entangled polymer dynamics and rheology. Truly an old "tube" can still be taught new tricks.

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