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Note: A simple picture of subdiffusive polymer motion from stochastic simulations

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Entangled polymer solutions and melts exhibit unusual frictional properties. In the entanglement limit self-diffusion coefficient of long flexible polymers decays with the second power of chain length and viscosity increases with 3–3.5 power of chain length.[1] It is very difficult to provide detailed molecular-level explanation of the entanglement effect.[2] Perhaps, the problem of many entangled polymer chains is the most complex multibody issue of classical physics. There are different approaches to polymer melt dynamics. Some of these recognize hydrodynamic interactions as a dominant term, while topological constraints for polymer chains are assumed as a secondary factor.[3,4] Other theories consider the topological constraints as the most important factors controlling polymer dynamics. Herman and co-workers describe polymer dynamics in melts, as a lateral sliding of a chain along other[5,6] chains until complete mutual disentanglement. Despite the success in explaining the power-laws for viscosity, the model has some limitations. First of all, memory effects are ignored, that is, polymer segments are treated independently. Also, each entanglement/obstacle is treated as a separate entity, which is certainly a simplification of the memory effect problem. In addition to that, correlated motions of segments are addressed within the framework of renormalized Rouse-chain theory,[7] without calling any topological entanglements in advance. This approach leads to the generalized Langevin equation characterized by distinct memory kernels describing local and nonlocal segment correlations[8–10] or to the Smoluchowski equation in which the segments' mobility is treated as a stochastic variable.[11] Both models describe the polymer segments motion at a microscopic level. An interesting alternative is to solve the integrodifferential equation for the chain relaxation with a sophisticated kernel function.[12] The design of the kernel function is based on a mesoscopic description of the polymer melt. These theories explain some experimental data, although the description of the crossover between the Rouse and non-Rouse behavior is not satisfactory. Obviously, within the scope of a short note we cannot review all theoretical concepts of the polymer melt dynamics. Here we focus just on the interpretation of the observed single segment autocorrelation function.

The most popular theory of entangled polymers is the reptation theory by De Gennes.[13] According to this theory a long polymer chain moves in a fluctuating tube imposed by entanglement with other chains. The theory assumes that the overall shape of such a tube resembles the Gaussian random coil and that the main component of motion of polymer segments follows the contour of the tube. The reptation theory explains approximately the scaling of the diffusion coefficient and viscosity with the polymer length. There are however some problems with the interpretation of experimental findings by the reptation theory. The critical polymer length for the onset of reptation is different for diffusion coefficient and viscosity measurements. Moreover, cyclic (ring) polymers in noncatenated solution diffuse about two times faster than linear polymers of the same length.[14] According to the reptation theory ring polymers should not diffuse at all, or at least their diffusion should be much slower than that observed. Similar conclusion was made by Phillies under the assumptions of nonpower-law behavior of self-diffusion in many systems.[3]

On the microscopic level, the reptation theory predicts that the mean-square displacement of polymer segments on a time scale shorter than the longest relaxation time of the polymer chain follows $t^{1/4}$ scaling with time.[13] In many publications concerning computer simulation of multichain systems, the presence of such a regime (with a slope of 0.25 or intermediate between 0.25 and 0.5) for the polymer segment time autocorrelation function has been interpreted as a proof of the reptation concept.[15–20] In the past, we performed stochastic simulations of polymer motion in a coarse-grained model of long entangled polymers.[21,22] These simulations clearly indicated that the $t^{1/4}$ scaling of the monomer autocorrelation function does not mean necessarily a reptationlike type of motion. Analysis of time evolution of averaged chain contours, in the melt, demonstrated that the long chains do not follow the tube motion, although for polymer matrix, such a motion can emerge as a dominant one.[22] In melts lateral motion dominated. Obviously, for very short times a series of chain snapshots may look like a tube. Such picture reflects the very local chain motion, without "reptationlike" sliding along the hypothetical tube. Inspired by these simulations Skolnick *et al.*[23,24] proposed a very simple single-chain theory of subdiffusive polymer dynamics. The theory assumed Rouse-like local motion of model polymers with two types of monomers: conventional Rouse segments and high friction segments, corresponding to entanglement constraints from other chains. In fact, the introduction of high friction for some segments is not an analog of the cage effect of correlated liquids. The reason for that is the low concentration and the random distribution of these slow-moving segments, while all instantaneous contacts are neglected.[23,24] Also, the distance scale of such slow motion in polymers is much larger than for cage effects. Macroscopic predictions derived from such an analytical

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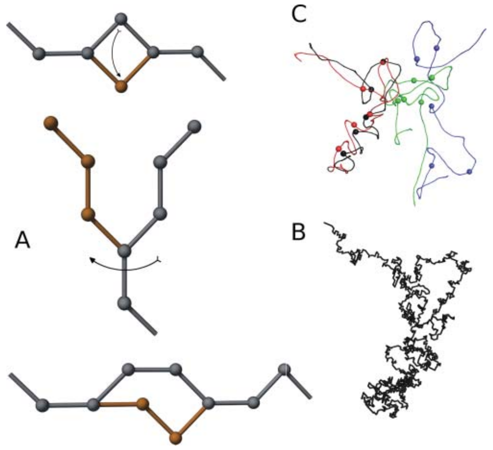

FIG. 1. Conformational updating of model chain. (a) Two-bond kinks, chain end rotations and three-bond random permutations. (b) Snapshot of lattice chain. (c) Smoothened chains contours at t = 0, t = 8.0 × 10^4 (left side, nearly overlapping), t = 1.2 × 10^6, and t = 5.4 × 10^6 (right side), with slow moving beads marked as heavy circles.

model were equivalent to predictions of the reptation theory, although the microscopic picture was qualitatively different: the local motion of the model chain was isotropic.

In this note we describe very simple simulations showing that the $t^{1/4}$ regime does not require reptationlike motion (or any spatially restrained motion, like in Herman's work[5]). The basic assumptions are the same as in Skolnick's theory,[23,24] though the results of simulations are free of any additional approximations, except statistical (small) inaccuracies of the Monte Carlo dynamics. Additionally, the simulations are for a "real" chain, with excluded volume and without chain contour crossing (the Rouse chain is a "phantom" chain).

The model chain, composed of N segments, is restricted to the face-centered simple cubic lattice (coordination number z = 12). Stochastic dynamics of the chain are simulated via a long series of local random micromodifications. Conformational updates (Fig. 1) include two-bond kinks, three-bond random permutations, and flips of the end segments. An arbitrary time unit corresponds to one attempt at local moves per chain segment on an average. It is assumed that some of the chain segments (for simplicity uniformly spaced along the chain) mimic entanglement points, and therefore should move slower. The local kinks for these slow segments are attempted with frequency p in respect to the frequency of kinks of "regular" segments. In the simulations reported below N = 1200, the number of slow segments is n = 5 and p = 0.001. Figure 1(c) shows an example of smoothened chain contours at t = 0, t = 8.0 × 10^4, t = 1.2 × 10^6, and t = 5.4 × 10^6, with slow moving beads marked as heavy circles. It is evident that the slow segments move slower than the regular segments and that the motion lateral to the chain contour dominates. Figure 2 shows the single bead time autocorrelation function in log–log coordinates. A line with slope 1/4 is drawn for comparison.

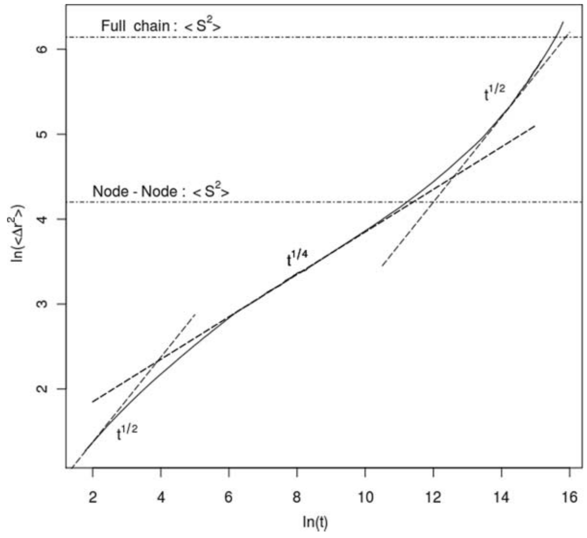

FIG. 2. Single bead autocorrelation function (mean-square displacement) in log–log time scale. The lines with slope 1/4, and 1/2 are given for reference. Dotted and dashed lines mark subchain (between two subsequent heavy, slow-moving, beads) and full chain mean-square radii of gyration.

In other simulations with larger values of parameter p the slope is different (larger). The assumed p value mimics the higher apparent friction coefficient, resulting from dragging other chains of a length equal to the length of the probe chain in the entangled system. The results of the simulation presented here clearly demonstrate that the existence of the $t^{1/4}$ regime for the autocorrelation function does not does necessarily indicate the topologically restrained, along the chain contour, mode of motion. Subdiffusive motion with the $t^{1/4}$ regime emerges due to the different mobility of chain segments. The illustration given in this note suggests that the concept of "tube" is not necessary for the mechanistic explanation of dynamic properties of entangled polymer solutions and melts.

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