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Microscopic de…nition of polymer entanglements

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Abstract

The dynamics of polymer melts and concentrated solutions is notoriously slow due to the fact that long polymer

-7(m)5(u)-16(l)-7(a)-14(t)-11(i)-13(v)-14(m)16(s)-396(a)-13(f)-394(w)8(e)-13(l)-7(l)-8(-)-9(e)-13(n)13(t)-11(a)-14(n)-16(g)-13(l)-8(e)-13(d)-400(l)-8(i)-7(n)-16(e

where W_i are independent vector Wiener processes.

Despite the simplicity of such approximation, the Rouse model compares relatively well with molecular dynamics (MD) simulations [1],[2] and experiments [3],[4]. For example, the viscosity scales linearly with molecular weight and stress relaxation function scales as $G(t) \quad \frac{V}{k_B T} h_{xy}(t) \; _{xy}(0)i \quad t^{1=2}$, where is the stress tensor and V is volume.

The agreement with the Rouse model breaks dramatically when the molecular weight exceeds some critical value M_c. This is clearly observed in both MD and experiment. For example, the stress relaxation function $G(t)$ slows down and eventually develops a plateau, and the terminal time and viscosity start to grow with molecular weight as $N^{3:5}$ or so. These deviations from the Rouse model are generally believed to be caused by entanglements, or by the constraint that polymer chains can not cross each other. For long chain this constraint becomes signi…cant and the e¤ect of other

contacts between the mean paths of different chains. We will define entanglements as such persistent contacts between the mean paths. Section 3 will introduce contact maps for chain pairs and a way to analyze such maps. In section 4 we will develop numerical algorithms to extract quantitative information about entanglements, and in section 5 we shall present the results of these algorithms applied to MD trajectories of well entangled chains. Section 6 will list the conclusions and the outlook.

2 Mean paths

It is clear that both entanglements and tube pictures predict existence of long lived contacts between different chains. However, it is not easy to detect such contacts. Indeed, in a usual modest simulation with $N_c = 100$ chains of length $N = 100$ for 10^7 time steps one has to process information about 10^{11} possible contacts even if the only information one is interested in is whether chain i is in contact with chain j or not. If one does process this information, one has to decide what to call a persistent contact. Chain positions are subject to rapid fluctuations and thus contacts between the chains appear and disappear rapidly. Thus, any analysis of such contact information is bound to be probabilistic, i.e. one can ask what is the probability of two chains to be in contact at time t providing they were in contact at time 0. One can not however assert whether these two contacts constitute the same entanglement or not. Such contact analysis was performed in ref.[7] for instantaneous chain coordinates. An approach based on an average interaction energy between non-bonded monomers was utilized in ref.[8] to visualize persistent contacts.

We note that contact probability information is not very useful to calibrate the tube or the slip-spring models. These models operate with survival probabilities, i.e. the probability that the same entanglement or tube segment exists at time t; if it was present in the system at time 0. In order to compute these probabilities, one has to track individual contacts and detect their appearance and disappearance.

In order to do that, we suggest to perform contact analysis on the mean paths $\hat{r}_i$ rather than on the instantaneous chain coordinates R_i. The mean paths were introduced in ref.[9] as

$$\hat{r}_i(t) = \frac{1}{t_{av}} \int_{t}^{t} R_i(t')dt'$$

i.e. they consists of the average positions of each bead over some averaging time t_{av}. As was shown in ref.[9], the mean path of entangled polymer has a free energy of a semi-flexible chain, i.e. the mean paths should be smooth on small length scales and of course follow the chain random walk on large scales. In this paper we report simulation results of 100 chains made of $N = 150$ beads, which are connected with finitely-extensible nonlinear (FENE) springs and interact with purely repulsive truncated Lennard-Jones potentials. Besides that, we add harmonic bending potential as described in ref.[10] with coefficient $k_b = 3$. This is done to create more entangled system relatively cheaply. The time step of the simulation is $t = 0.012$, and the system was run for much longer than the longest relaxation time to ensure proper equilibration. According to the tube theory, the number of entanglements in our system is in the range of 7-15 depending on the definition, and the relaxation time of the strand between entanglements $_e$ 300 1000. For mean paths, we will use $_{av} = 1200$; or 10^5 timesteps, unless specified otherwise. We have also analyzed chains of different lengths and chains without bending potentials. However, for clarity and in the interest of space, we do not include these results unless they produce something qualitatively different from our $N = 150$ and $k_b = 3$ chains.

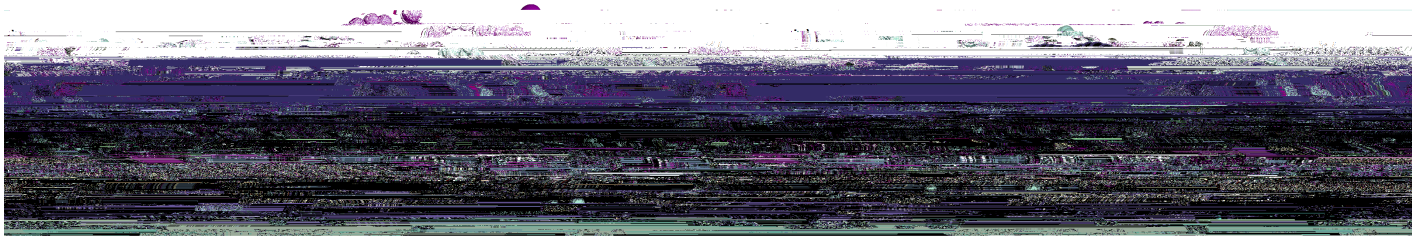

Figure 1: Illustration of mean path and contacts, for $N = 150; k_b = 3$ system. (a) Instantaneous positions of one chain

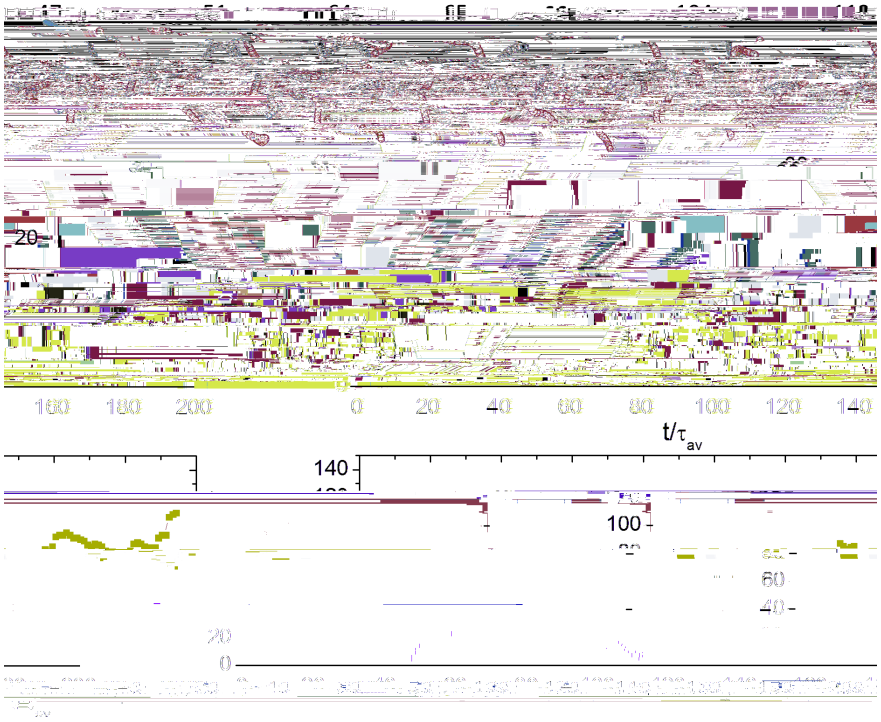

Figure 3: (a) Time evolution of the minimum distance between two chains — a tight contact is clearly ideti…able for time $47 < t = _{av} < 112$

Our contact map algorithm has three parameters: mean path averaging time $_{av}$, the cut-o¤ distance which de…nes a contact d_{cut}, and the coe¢ cient C_l in eq.6. The last parameter has only minor in‡uence on determining the position of entanglements but not on the life time distribution or other important properties. In contrast, the …rst two parameters

Figure 5: Time evolution of the local linking number for the same entanglement as in Fig.3.

With the de…nitions of entanglement slack and local linking number at hand, we can now investigate their probability

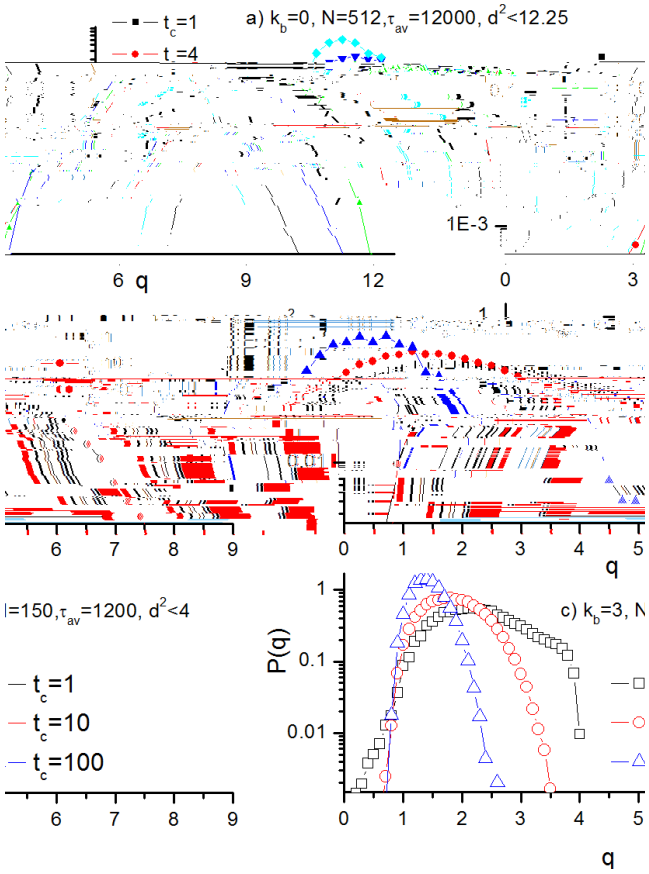

Figure 6: Entanglement slack distribution for contacts with di¤erent cut-o¤ distance and chain sti¤ness and for di¤erent entanglement life times.

Figure 7: Probability density to …nd entanglements with certain slack and local linking number, normalized by the maximum density. Dashed lines show contour plot for all entanglements with lifetime smaller than50 $_{av}$, and solid lines — for entanglements with lifetime longer than50 $_{av}$:

Figure 8: Left: Randomly selected entanglements with $q < 1.5$ and $\ell > 100$ at one moment of time for the mean path analysis. Right: the same from analysis of mean paths with con…gurational averaging over 50 trajectories, for $q < 2$ and $\ell > 50$.

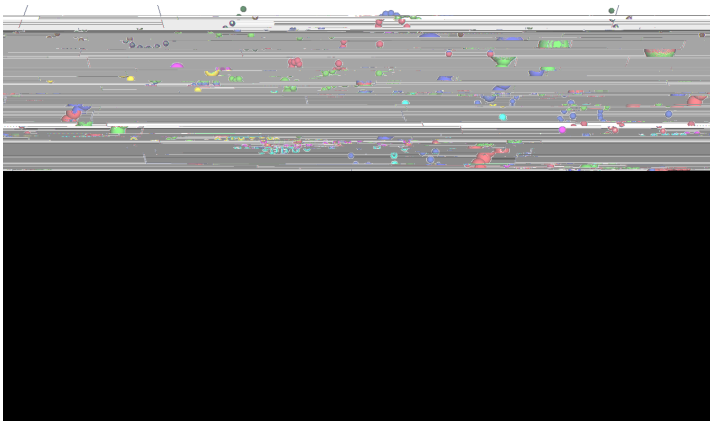

Figure 9: All mean paths entangled with the pink chain with tight longlived entanglements.

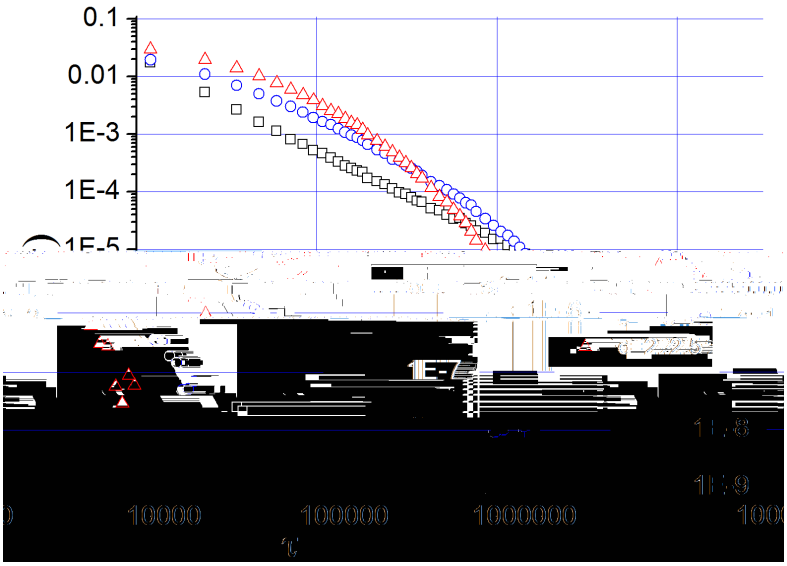

Figure 10: Probability density that a randomly selected entanglement within a certain slack range will have a lifetime .

5 Results and discussion

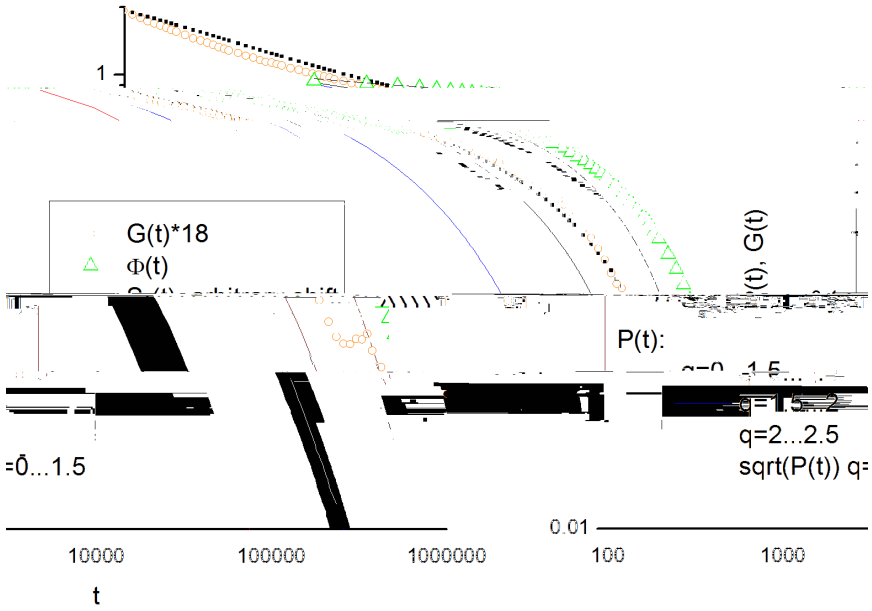

Figure 11: Entanglement survival probability function $P(t)$ compared with stress relaxation (circles), end-to-end relaxation (triangles) and orientation tensor auto-correlation (squares) functions.

faster. Note that according to Fig.6 there are very few entanglements with$q < 1$, so decreasing t5(a)1(re)-394(v)28(e)-12with

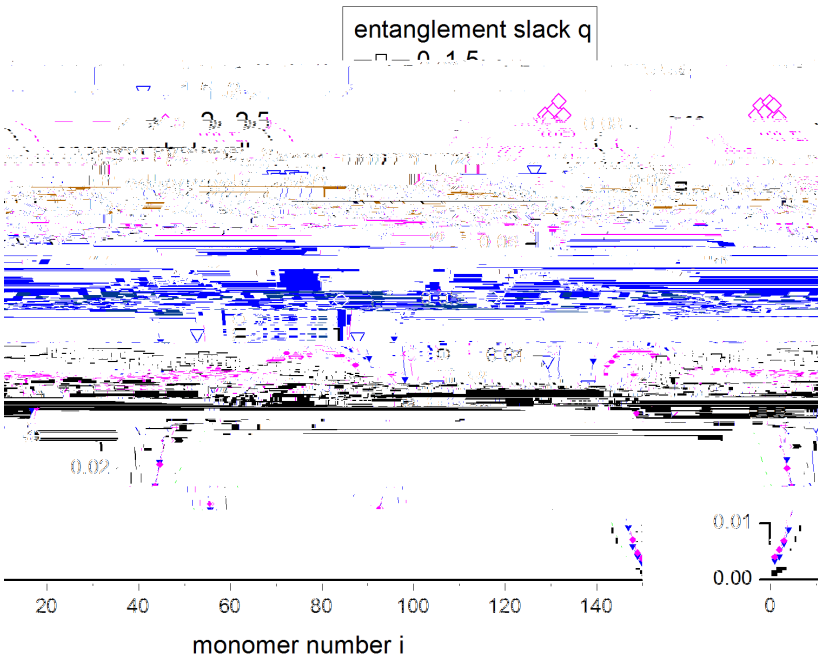

Figure 12: Entanglement density along the chain for di¤erent entanglement slack. Open symbols show all entnglements, whereas …lled symbols - only entanglements with life time > 50.

where the disentanglement time $_d$ is the characteristic time of the longest mode, L is the tube length and D_c is center-of-mass di¤usion coe¢ cient along the tube (one-dimensional di¤usion). Including CLF has two e¤ects of $(s;t)$ function. First, it will decrease signi…cantly faster close to the ends of the tube. Second, the relaxation of the middle segments of the chain will still be described by eq.7, but with an e¤ective tube length L_{eff} , which is reduced by CLF as compared to the original L.

We would like to compare and contrast entanglement survival probability with the tube survival probability. An entanglement in our de…nition is made by two chains, and therefore is characterized by two participating monomer

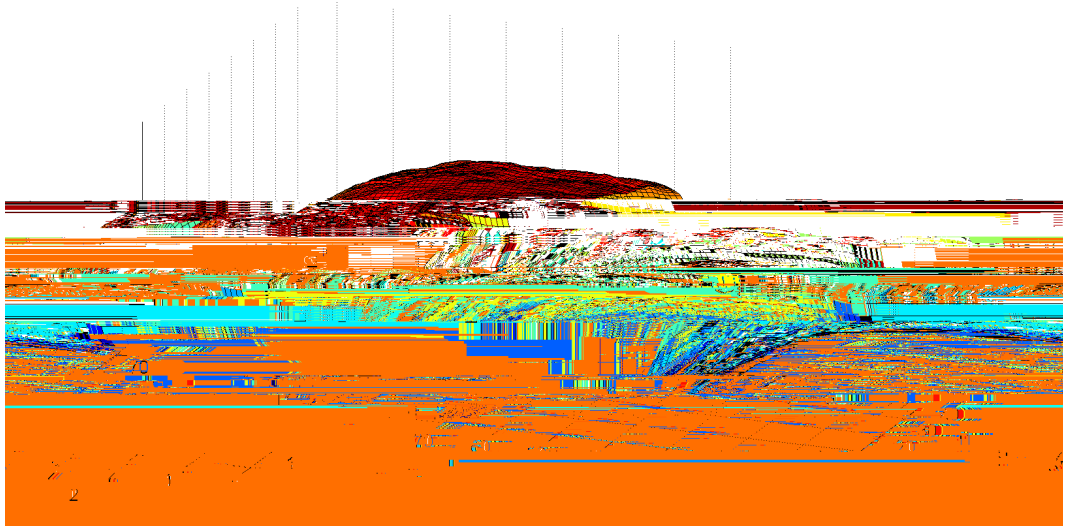

Figure 13: Entanglement survival probability for $t = 64; 128; 256; 512$ in units of $_{av} = 1200$. The chain is $N = 150$ with bending energy $k_b = 3$:

is then simply given by

$$(t) = \sqrt{P(t)}$$

which is what we used in Fig.11 (dashed line).

We followed this procedure and computed $(s; t)$ for di¤erent times, and …tted them with Doi-Edwards expression eq.7, as shown in Fig.14. We have used two …tting parameters and successfully …tted all times simultaneously, excluding points with $js \quad 1=2j > 0:35$, which are a¤ected by CLF and other end-e¤ects. The …tting parameters were the terminal time $_d$ and an e¤ective tube length

Figure 14: Tube survival probability extracted from the entanglement survival probability for 5 di¤erent times (symbols) compared to Doi-Edwards predictions with e¤ective tube length.

Figure 15: Entanglement survival probability along $s_1 = s_2$ and $s_2 = 1=2$ lines (symbols) compared with predictions obtained from $(s;t)$ function (linecomp

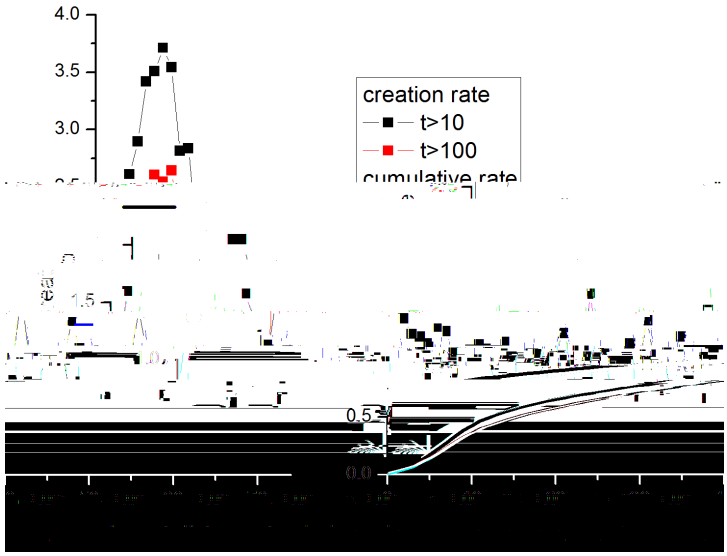

Figure 16: Closest distance to the chain end at the moment of entanglement creation.

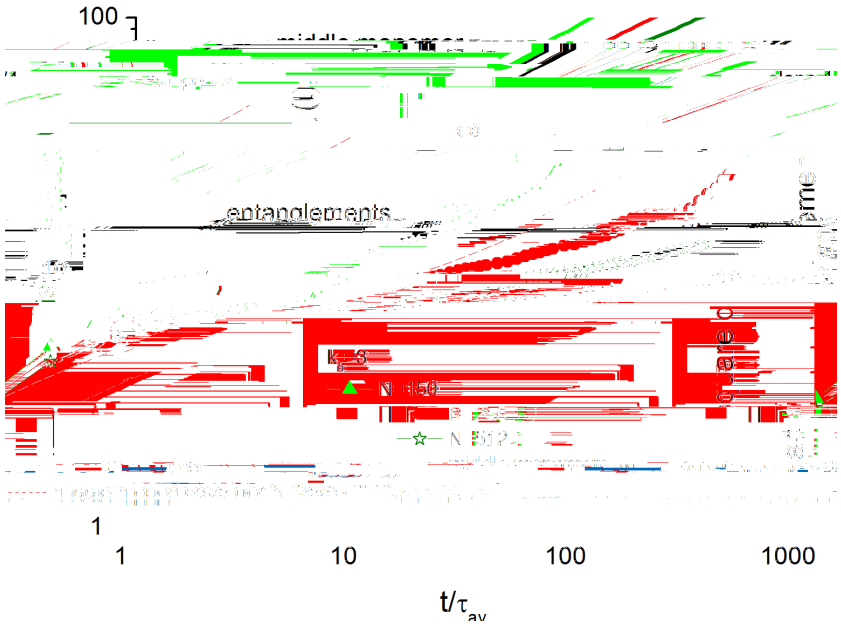

Figure 17: Mean square displacement of entanglement position in real space for chains with bending k_b (= 3) and different lengths. For comparison, the usual mean square displacement of the middle monomer is also shown.

a better name would be the tube Kuhns step. Indeed, the Kuhn step is de…ned in exactly the way is de…ned. In turn, Z is then a number of tube Kuhn steps. The physical meaning of a and Z are the following: if we construct a freely jointed chain with the same contour length and the same average square end-to-end distance, this equivalent chain must have Z steps of length a. Note that this de…nition does not assume that the tube is a freely-jointed chain. Interpreting tube theory equations in this precise manner shows that the number of entanglements, however we choose

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