Long-lived interchain contacts in polymer melts

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We will study time dependence of interchain contacts in entangled and unentangled polymer melts. We find that "clusters" of contacts in entangled melts persist in time up to at least 0.2 of the longest relaxation time. The clusters of contacts in un-entangled melts disappear and reappear on at least two orders of magnitude shorter time scale. We also examine time-dependent correlation functions that try to quantify the properties of contacts. © 1997 American Institute of Physics.

I. INTRODUCTION

It is often stated that the dynamics of concentrated solutions and melts of long linear flexible polymers is dominated by interchain entanglements, or by entanglement phenomenon.1,2 Although this statement satisfies those of us who still have childhood memories of mysteriously self-entangling shoelaces, by itself it does not explain anything. The main objection is that we do not have an agreed upon molecular level definition of either individual entanglements or the entanglement phenomenon.

According to the recent excellent review article summarizing present understanding of the dynamics of polymer liquids2 there are at least two ways to visualize entanglement. In the first approach, one thinks about entanglements as of individual, localized entities originating from some of the interchain contacts. On the other hand, in the second approach one abandons the idea of individualized entanglements and imagines the entanglement phenomenon (understood here as a synonym of the slow dynamics) as brought about by some kind of a mean effective field acting on the polymer chains. Both of these approaches lead to yet unresolved problems.2 However, it is a recurring thought in the literature3–6 that the entanglement phenomenon (irrespective of whether we treat entanglements as individual objects or as an effective field) is in some way associated with long-lived interchain contacts.

The first systematic study of interchain contacts was done by Skolnick et al.3 who investigated the time dependence of the fraction of surviving contacts between "blobs" on different chains. They found that the overwhelming majority of interchain contacts decayed on the time scale much shorter than the terminal relaxation time. The persistent contacts were very rare.

Gao and Wiener3 also studied the time dependence of the fraction of remaining contacts. However, in contrast to Skolnick et al. Gao and Wiener counted only contacts at a given time t that survived during the whole time interval (0,t). Therefore their definition of a remaining contact was much more restricted that that of Skolnick et al. Gao and Wiener found that all the contacts were decaying very quickly, but more importantly, there was no chain length dependence of the characteristic decay time. Indeed, the fraction of the remaining contacts in an atomic liquid (N=0) followed the same time dependence as that in an entangled polymer liquid (N=200)!

The most extensive study of persistent interchain contacts was done by Ben-Naim et al.4 They investigated time dependence of real contacts (contacts between interpenetrating chains) and "phantom" contacts (contacts between distant chains when brought together). To this end they introduced and investigated contact correlation functions and contact maps. They found that real contacts near a given contact lasted longer than the phantom ones. On this basis they tentatively identified these persistent contacts as the individual entanglements.

It should be emphasized that both the interpenetrating chains and the distant chains that were used to identify phantom contacts were entangled. The only difference was that the interpenetrating chains were mutually entangled and the distant ones were entangled in two different environments.

Ben-Naim et al. monitored the time dependence of the contacts for times up to "the Rouse time scale for relaxation of chains along the tube". The times close to the terminal relaxation time were beyond their simulation’s range.

The aim of this paper is twofold. First, we study time dependence of contacts in a model polymeric system in which the entanglement phenomenon can be switched "on" and "off" while keeping the equilibrium (e.g., geometric) properties of the polymer chains intact.7 In this way we can easily correlate time dependence of contacts with chains exhibiting entangled or un-entangled dynamics. In particular, we clarify an apparent disagreement between the results of Gao and Wiener (who did not find any correlation between chains being entangled and the dynamics of their contacts) and Ben-Naim et al. (who found persistent contacts and identified them as entanglements). We show that by a slight modification of the definition of the fraction of remaining contacts one can actually see a correlation between the decay of the initial contacts and the entangled dynamics. Second, we follow contacts for times of the order of 0.2 of the terminal relaxation time. By examining long-time behavior of persistent contacts we can check whether they have this important characteristic mark of phenomenological entanglements: Being active for times up to the longest relaxation time.

We start by briefly describing both the model and the simulation procedure. Next we discuss our definition of a
contact. In the following three sections we present simulation results for the fraction of remaining contacts, contact correlation functions, and contact maps. We end up with discussion and conclusions.

II. SIMULATION

We used a version of the bond fluctuation model\(^8\) that was proposed by Shaffer.\(^7\) Briefly, in this model each segment of a polymer chain occupies a single site on a simple cubic lattice. The excluded volume interaction is enforced by forbidding double occupancy. The allowed bond lengths between adjacent segments are 1, \(\sqrt{2}\), and \(\sqrt{3}\).

The virtue of Shaffer’s version of the bond fluctuation model is that the topological interaction that prevents chain crossing and leads to entanglement can be switched ‘on’ and ‘off’. To this end one has to realize that chain crossings in this model proceed through configurations in which two bond midpoints coincide. Therefore by forbidding such configurations one includes the topological interaction while by allowing them one excludes it. The forbidding—allowing can be done efficiently by enforcing the excluded volume condition on the secondary lattice on which bond midpoints are placed.

The simulation itself is a dynamic Monte Carlo (more precisely, a lattice Brownian dynamics) procedure: A single segment is chosen at random and then a trial displacement to one of the nearest-neighbor sites is randomly selected. Next, the bond length condition, the excluded volume condition, and possibly the excluded volume condition for the bond midpoints are checked. If these are satisfied in a new configuration, the trial move is accepted. Otherwise, the move is rejected.

Shaffer’s model was used before to study the effects of topological interaction preventing chain crossing on diffusion and configurational relaxation in polymer melts.\(^7,9\) Briefly, it was found that while the presence of the topological interaction does not influence equilibrium properties (radius of gyration, average end-to-end distance, etc.), it does have a profound effect on the dynamics. In the absence of the topological interaction no transition to entangled dynamics was seen and the center-of-mass self-diffusion coefficient was found to follow Rouse-like scaling \(D_{\text{R}} \sim 0.0131/N\) (hereafter, lattice constant is used as the unit of length and Monte Carlo step per bead is used as the unit of time). On the other hand in the presence of the topological interaction at \(N_e = 40\) a transition to a much stronger chain length dependence was observed. In the long chain regime the center of mass self-diffusion coefficient approximately obeyed entangled scaling \(D \sim 0.2/N^2\) (the prefactor was estimated from Fig. 7 of Ref. 7).

Most of the simulation data presented in this paper pertains to an ensemble of 64 chains, each containing \(N = 500\) monomers. The length of the box is \(L = 40\) and the average density is \(\rho = 0.5\). One should note that according to Shaffer’s estimate of \(N_e\), \(N_e = 20\), the chain length in the present simulation is \(\sim 25N_e\).

Extrapolating data of Ref. 7 for the self-diffusion coefficients and using data of Ref. 9 for the radii of gyration we get for the system of crossing and noncrossing 500mers \(D^{\text{cr}} = 2.6 \times 10^{-5}\) and \(D^{\text{ncr}} = 8 \times 10^{-7}\), respectively, and \(R_g^{\text{cr}} = 211\) and \(R_g^{\text{ncr}} = 220\), respectively. Thus the terminal relaxation times \(\tau^{\text{cr}} \approx R_g^{\text{cr}}/6D\) can be estimated as \(\tau^{\text{cr}} \approx 1.3 \times 10^6\) and \(\tau^{\text{ncr}} \approx 4.6 \times 10^5\), respectively.

To equilibrate the system we run the simulation for \(t_{\text{eq}}^{\text{cr}} = 4 \times 10^5\) and \(t_{\text{eq}}^{\text{ncr}} = 5 \times 10^6\) Monte Carlo steps per monomer for crossing and noncrossing chains, respectively. We note that while this corresponds to several terminal relaxation times for the crossing chains it is an order of magnitude shorter than the terminal relaxation time for the noncrossing chains. One should note at this point that the equilibration times used here are essentially the same as those used in Refs. 7 and 9.

We also present some results pertaining to an ensemble of 200 chains of \(N = 20\) monomers. In this case the average density is \(\rho = 0.5\), and the relaxation times can be estimated to be \(\tau^{\text{cr}} \approx 2 \times 10^3\) and \(\tau^{\text{ncr}} \approx 3 \times 10^3\), respectively. To equilibrate the ensemble of 20mers we run the simulation for \(t_{\text{eq}}^{\text{cr}} = 4 \times 10^4\) and \(t_{\text{eq}}^{\text{ncr}} = 4 \times 10^3\) Monte Carlo steps per monomer.

III. DEFINITION OF A CONTACT

There is a considerable arbitrariness with regards to which beads we consider to be in contact. This is especially true for the continuous space models like those used by Gao and Wiener,\(^5\) and Ben-Naim \(\text{et al.}\).\(^4\) Both of these studies used a truncated Lennard-Jones potential for the repulsive interaction between the nonbonded beads. According to this potential, the repulsion vanishes at the distance of \(2^{1/6}\sigma\), where \(\sigma\) is the length parameter of the Lennard-Jones interaction.

In Gao and Wiener’s study two cutoff distances for contacts were used: Two beads were defined to be in contact when the distance between them was smaller than \(1.5\sigma\) or smaller than \(2\sigma\). As one would expect, the larger cutoff distance led to a slower decay of the initial contacts. However, in both cases there were no exceptionally long lived contacts. In the work of Ben-Naim \(\text{et al.}\) \(1.5\sigma\) was used as the cutoff distance for contacts.

In our study a lattice model is used and therefore the choice of possible cutoff distance is more limited. Most of the results were obtained using the smallest possible cutoff distance: Two beads are defined to be in contact when the distance between them is equal to one lattice constant of the simple cubic lattice. We also present some results pertaining to the cutoff distance of \(\sqrt{3}\).

IV. FRACTION OF REMAINING CONTACTS

To investigate the time dependence of interchain contacts Gao and Wiener\(^4\) monitored fraction of contacts present at \(t = 0\) that survived during the time interval \((0, t)\). They found that the contacts decayed very quickly and there was essentially no chain length dependence of the characteristic decay time.
We have calculated the fraction of remaining contacts defined as in Ref. 5 for noncrossing 500mers and 20mers, and for crossing 500mers and 20mers. It should be recalled here that noncrossing 500mers exhibit entangled dynamics whereas both noncrossing and crossing 20mers and crossing 500mers exhibit Rouse-like dynamics.

It is clear from Fig. 1 that the fraction of remaining contacts defined as in Ref. 5 does not qualitatively differentiate between entangled and un-entangled dynamics. The characteristic decay times seem to correlate with fractions of accepted moves calculated by Shaffer\(^7\) that quantify the amount of the local motions of the monomers.

The same fraction of remaining contacts was recalculated using the cutoff distance of \(v/3\). As can be seen from Fig. 2, apart from an overall slower decay, the results are qualitatively the same.

Next we have modified the definition of the fraction of the remaining contacts. In the spirit of Skolnick \textit{et al.}\(^3\) we have monitored the fraction of the original contacts (present at \(t=0\)) that were present at time \(t\). These contacts do not necessarily survive during the whole time interval \((0,t)\).

From Fig. 3 one can see that the fraction of contacts present at a later time differentiate between entangled and un-entangled dynamics: Contacts present at \(t=0\) are much more probable to be present at a later time for noncrossing 500mers than for any of the other chains.

The above statement should be taken with a grain of salt: On the time scale relevant for Gao and Wiener’s function the fraction of contacts present at a later time also does not differentiate between entangled and un-entangled dynamics. The differences show up after several thousands time steps when Gao and Wiener’s function is essentially zero.

Two additional observations can be made. First, curiously, for quite some time contacts between noncrossing 20mers decay slower than these between crossing 500mers although the overall motion (self-diffusion) of 20mers (both noncrossing and crossing) is much faster than that of crossing 500mers. Second, one should note that Fig. 3 suggest that for intermediate times (before the original contacts decay completely) the decays of the fractions of contacts present at a later time seem to follow different power laws for entangled and un-entangled dynamics (note that for 20mers we are apparently able to go beyond this intermediate time regime whereas this is not possible for 500mers).

V. CONTACT CORRELATION FUNCTIONS

Contact correlation function was introduced by Ben-Naim \textit{et al.}\(^4\) in order to quantify the difference between the time dependence of the real contacts and the phantom ones. For a pair of chains, say chain 1 & 2, that have many contacts at the initial configuration, the contact correlation function, \(g(x,y;t)\), is defined as
various values of $d$. distant chains. chains and the phantom ones were artificial contacts between that the real contact originated from mutually entangled cally for the phantom ones. This was attributed to the fact.

!\[g(x,y;t) = \frac{1}{N_{\text{tot}}} \sum_{\tau} \sum_{i,j} n(i,j;\tau)n(i+x,j+y;t+\tau).\] (1)

Here $n(i,j;\tau)$ ‘monitors’ the contacts: $n(i,j;\tau)$ is equal to 1 if the bead $i$ on chain 1 is in contact with the bead $j$ of chain 2 at time $\tau$. Finally, $N_{\text{tot}} = \sum_{\tau} n(i,j;\tau)$ is the total number of contacts.

One should note here that the fraction of contacts present at a later time discussed in the previous section is essentially the same as the contact correlation function calculated at $x = 0 = y$ and averaged over all the pairs of chains in the system. As will be seen in the following, the long time decay of the fraction of contacts present at a later time is similar to that of $g(0,0;t)$.

Ben-Naim \textit{et al.} argued that the contact correlation function should exhibit a scaling behavior $g(x,x;\tau) \sim t^{-3/2}$, where $\alpha$ is the exponent describing the time dependence of ‘‘typical curvilinear displacement’’ in the melt, $x(t) \sim t^{1/\alpha}$. In particular, for the Rouse-like dynamics $\alpha = 2$ and $g(x,x;\tau) \sim t^{-3/4}$ for the entangled dynamics $\alpha = 4$ and $g(x,x;\tau) \sim t^{-3/8}$. Ben-Naim \textit{et al.} actually observed $g(x,x;\tau) \sim t^{-1/2}$ scaling that would correspond to $\alpha = 3$ and argued that this might be a crossover effect. The same long-time decay was observed for both real and phantom contacts.

The major finding of Ben-Naim \textit{et al.} was that the contact correlation function $g(x,x;\tau)$ for $x > 0$ had a peak at $t > 0$ for the real contacts whereas it was decaying monotonically for the phantom ones. This was attributed to the fact that the real contact originated from mutually entangled chains and the phantom ones were artificial contacts between distant chains.

We have calculated the contact correlation function for the system of noncrossing 500mers that exhibit entangled dynamics, and for the system of crossing 500mers that exhibit Rouse-like dynamics. Figures 4 and 5 show time dependence of the normalized contact correlation functions for various values of $x = y$ for chains 1 and 18 (noncrossing simulation) and 1 and 30 (crossing simulation).

It is clear that entangled dynamics leads to a maximum in the contact correlation function at $t = 0$ for $x > 0$ and $y > 0$. On the other hand the Rouse-like dynamics leads to a pronounced shoulder or a very small maximum in the correlation function. Thus the difference found in Ref. 4 (see their Fig. 5) should not be interpreted as originating from entanglements. It may however be attributed to the chains being mutually entangled or distant.

On the other hand, in agreement with the scaling analysis of Ref. 4 we observed a different long-time decay of the contact correlation function for entangled and Rouse-like dynamics. In the first case the decay was compatible with the one found in Ref. 4: $g(x,x;\tau) \sim t^{-1/2}$ corresponding to the exponent $\alpha = 3$. For crossing chains the result was compatible with $g(x,x;\tau) \sim t^{-3/4}$ corresponding to the Rouse-like exponent $\alpha = 2$.

Finally, we have also investigated two more noncrossing and crossing pairs that had many initial contacts and we always saw time dependence of the contact correlation function that was similar to that described above.

VI. CONTACT MAPS

The time dependence of the fraction of contacts present at a later time (Sec. IV) and the contact correlation function (Sec. V) suggest that the interchain contacts in systems exhibiting entangled dynamics ‘‘last’’ much longer than those in systems exhibiting Rouse-like dynamics. More precisely, the monomers that were initially in contact tend to remain closer and have higher probability of contacting again in the former systems than in the latter ones. Motivated by the analysis of Ref. 4 we have investigated this difference further by studying three-dimensional contact maps.

The three-dimensional contact maps are constructed as follows. For a given pair of chains at a given time step $t$ we make a two-dimensional map of contacts by putting dots at points with coordinates equal to the indices of monomers being in contact. In other words, if monomer $i$ on the first...
chain is in contact with the monomer $j$ on the second chain we put a dot at the point $(i,j)$. Next, we stacked the two-dimensional maps (recorded in time intervals of $1000$ Monte Carlo steps per bead) on top of each other creating a space-time picture.

As anticipated from the previous sections, we see a completely different behavior of contacts in an entangled system and in an un-entangled one. It should be noticed however, that the time scale of Figs. 6–8 is several order of magnitude larger than that of Figs. 4 and 5.

The first observation that should be made is that the contacts tend to cluster in both noncrossing and crossing chains. This fact is a consequence of the chain connectivity. It is reminiscent of the clustering of the low mobility monomers investigated by Gao and Wiener. It is also consistent with the existence of the maxima in the contact correlation functions. It should be emphasized that the clustering is observed for both noncrossing and crossing chains. However, the clusters in the former system are less diffuse than those in the latter one.

The most important finding of this work is that clusters of contacts in the system of noncrossing $500$mers persisted for the whole duration of the longest simulation run, i.e., for about $0.2$ of the longest relaxation time. As seen in Figs. 6 and 7 the individual contacts were disappearing and appearing but the clusters themselves preserved their identities.

On the other hand clusters of contacts in the system of crossing $500$mers persisted for about few tens of thousands to a few hundreds of thousands of time steps at the most. Then they seemed to disappear (evaporate) and reappear without any distinguishable regularity. That means that the average lifetime of these clusters is at least two orders of magnitude shorter than that of clusters of contacts in the noncrossing system.

It should be noted here that the three-dimensional contact maps for crossing $500$mers are qualitatively different from the contact maps for phantom contacts. This again follows from the fact that distant chains forming phantom contacts are not mutually entangled, but each of them is entangled in its own environment.

We have investigated seven other pairs of noncrossing chains and five other pairs of crossing chains and we always found results qualitatively similar to those presented here.

VII. CONCLUSIONS

We found that the time dependence of interchain contacts in an entangled polymer melt is qualitatively different from that in an un-entangled melt. It should be emphasized that this difference cannot be attributed to different static (equilibrium) properties since these were essentially the same in both systems studied.

The difference in the time dependence was seen in the fraction of contacts present at a later time and in the contact correlation function.

In the contact maps clusters of contacts were observed in both the entangled and the un-entangled system. However, in the entangled system the clusters preserved their identities.
for the whole duration of the longest simulation run (10^7 Monte Carlo steps per monomer), i.e., for about 0.2 of the longest relaxation time. In contrast, the clusters in an un-entangled system were disappearing and reappearing on the time scale of a few tens of thousands to a few hundreds of thousands of time steps, i.e., on the time scale at least two orders of magnitude shorter. The behavior of cluster of contacts in an un-entangled system of long chains was different from the behavior of phantom contacts between distant chains when brought together.

It should be noted here that the differences in the fraction of contacts present at a later time, the contact correlation function, and the contact maps showed up clearly only after a few thousands of time steps. We have tried and failed to identify a property that would differentiate between entangled and un-entangled system on a shorter time scale.

It would be tempting to identify the persistent clusters of interchain contacts as the individual phenomenological entanglements. This is especially appealing since it seems likely that these clusters will preserve their identities up to the longest relaxation time. To check this idea further one should try to estimate the diffusion constant of the clusters of contacts along the contacting chains. Such a calculation seems to require simulation runs that are much longer than the ones reported here.

Instead of arguing for or against individual entanglements, we would like to comment on the significance of the present findings for statistical mechanical theories of polymer melt dynamics. The results presented here cannot differentiate between a snakelike motion of individual chains that is assumed in the reptation theory1,2 and an isotropic motion that is implicitly assumed in the polymer mode coupling theory.10 However, contact maps suggest that the constraints that slow down the dynamics in entangled melts are due to slowly disappearing topological (preventing crossings) inter-chain interactions between pairs of chains. Thus it seems plausible that a theory of entangled polymer dynamics should start from a two-chain level,11 perhaps combining the spirit of the double-reptation approach of des Cloizeaux12 and the statistical mechanical flavor of the mode coupling theory.10 Exactly how to achieve this goal is, at present, unclear.

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6 See also M. Muller, J. P. Wittmer, and M. E. Cates, Phys. Rev. A 53, 5063 (1996). They, among other things, studied the average number of ring polymers touching a given ring.