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LETTER TO THE EDITOR

Polymer entanglement in melts

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Abstract. We propose a new way of characterizing the entanglement complexity of concentrated polymer solutions and polymer melts. This involves considering a randomly chosen cube in the system, and investigating the entanglements between sub-chains in this cube. We present Monte Carlo calculations and scaling arguments for the density dependence of the entanglement complexity, and the way in which this behaviour scales with the size of the chosen cube.

Although the entanglement complexity of isolated rings and linear polymers is now reasonably well understood (see, for instance, Janse van Rensburg *et al* 1996), and linking of two ring polymers has been investigated (Orlandini *et al* 1994), much less is known about entanglements in polymers in dense systems such as concentrated solutions and melts (where the polymer is present at high density but is disordered). Much of our knowledge of entanglement complexity in polymer melts comes from numerical studies in which several polymer chains are modelled in a restricted environment such as a box, and the behaviour is investigated by molecular dynamics or Monte Carlo methods (see, e.g., Dickman and Hall 1988, Smith *et al* 1998). Although such studies give useful information about the behaviour of relatively short polymers in dense systems, current computing facilities make the investigation of very long chains prohibitively difficult. In this letter we propose an alternative approach.

We consider a polymer melt, which we think of as a set of entangled chains which we shall model as a set of self- and mutually avoiding walks, with no other energy terms beyond the repulsions corresponding to mutual exclusion of monomers. We imagine fixing the chain conformations and then drilling out a prism from the system, and investigating the conformations of the parts of the chains which are in the interior of the prism. Typically, chains will enter and leave the prism so that, within the prism, we shall see sub-chains which start and end in the boundary of the prism. In this letter we shall further simplify the problem by imagining cutting the prism into smaller pieces (e.g. cubes). These objects will have one or more sub-chains which start and end in the boundary. By investigating the properties of these chains we can infer properties of the complete melt. In fact, the prisms can be reconstructed from the smaller pieces by properly identifying the boundary faces.

We shall restrict our attention to the simple cubic lattice, Z^3, and consider a cube of side L edges, whose vertices are in Z^3. The cube will contain exactly two self- and mutually avoiding walks which are properly embedded in the cube. By this we mean that the vertices of degree one of the walks are on the boundary of the cube, but no other vertices of the walks are on the boundary. Topologically, the cube and the two walks form a 2-string tangle (see figure 1). Typically, the two walks can be entangled and we shall characterize the entanglement

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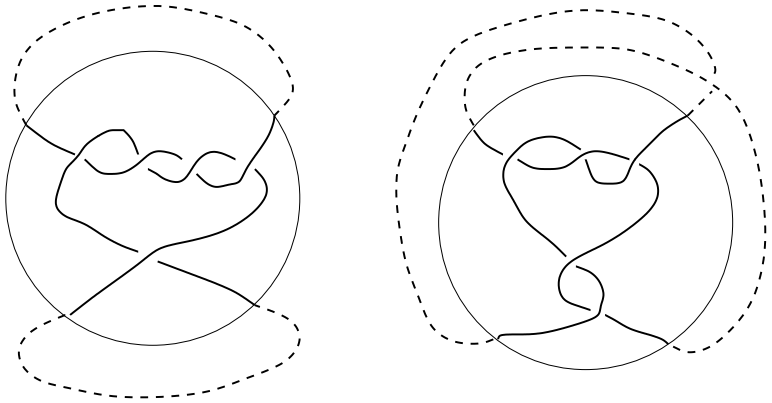

Figure 1. Schematic representation of the projection of two chains properly embedded in a cube, and the completion of the chains to form two polygons by adding edges outside the cube. In the first case no additional crossings are introduced and $|Lk| = 2$, while in the second case one additional crossing is introduced and $|Lk| = 3$.

complexity as follows. First project the cube and its properly embedded walks onto a plane so that all crossings of the walks with themselves or with one another are transverse. It is always possible to join the vertices of degree one by adding edges outside the cube so as to form a two-component link, so that no more than one new crossing is added (see figure 1). To compute the linking number of the two circles first attach an orientation to each circle. At the ith crossing of one circle over the other, attach a signed crossing number ($\sigma_i = \pm 1$) by using a right-hand rule. The linking number is given by

$$Lk = \sum_{i=1}^{k} \sigma_i / 2 \tag{1}$$

where the sum is taken over the k crossings between the two circles. (Crossings of a circle with itself are ignored.) The linking number is always an integer. We take the magnitude of this linking number as a measure of the entanglement complexity of this sub-system. If a new crossing is introduced we choose the sign of this extra crossing at random.

The generation of a sample of chains at high density by Monte Carlo methods is not a trivial problem. We have used a method based on a combination of pivot moves (Madras *et al* 1990) and the BFACF algorithm (Berg and Foester 1981, Aragao de Carvalho *et al* 1983), but with an important addition. Suppose that we have two chains properly embedded in the cube, with coordinates specified for the four vertices of degree one. We define a Markov chain whose states are the set of all pairs of chains within the cube, with specified boundary points. The transition matrix is defined by a combination of two-point pivot moves (Madras *et al* 1990) which do not change the lengths of the two chains, and BFACF moves (Berg and Foester 1981, Aragao de Carvalho *et al* 1983) which vary the lengths of the chains. For a two-point pivot move, choose two points at random on the walk. Disconnect the walk at these two points into three subwalks. Apply a randomly chosen symmetry operation of the lattice to the central subwalk, which leaves its end-points unchanged, and reconnect the three subwalks to form a new walk. If the walk is (a) self-avoiding, (b) avoids the other walk and (c) has no vertices on the boundary of, or outside, the box, then the new pair of walks is accepted as the next state of the Markov chain. Otherwise the current state is the next state. BFACF moves are local moves of two types. In type I two edges incident on a randomly chosen vertex are

permuted (sometimes called 'flipping across a square') while in type II three edges forming a U are replaced by a single edge, or a single edge is replaced by three edges forming a U. If the number of edges remains the same or decreases the move is accepted if it meets conditions (a), (b) and (c) above. If the number of edges increases by two, it is accepted if it meets the same conditions, but with a chosen probability, less than unity. For more details, see the references given above. Note that none of these moves change the locations of the four vertices on the boundary of the cube.

This whole process is implemented using multiple Markov chains (Geyer 1991). To construct initial states of these Markov chains we use an algorithm based on inversely restricted sampling (Hammersley and Morton 1954, Rosenbluth and Rosenbluth 1955). We choose two points, uniformly and independently, on the boundary of the cube. We then generate two self- and mutually avoiding walks by growing walks so that the next vertex occupied is chosen (uniformly) from the set of possible (neighbouring) vertices which are unoccupied, and continue the generation process until both walks reach the boundary of the cube. Pairs of walks generated in this way will not necessarily have the same probability and this bias is accounted for by attaching a weight to the pairs of walks (Rosenbluth and Rosenbluth 1955). If the number of neighbouring lattice sites which are empty as the ith step is to be added is a_i, the Rosenbluth weight of the pair (ω) of walks is

$$W(\omega) = \prod_i a_i. \tag{2}$$

The probability that this pair of walks will be generated is $1/W(\omega)$. These two walks are then the initial state of the Markov chain defined on these four boundary points and we construct many realizations of the Markov chain with different initial states constructed in this way. The initial states are not chosen with uniform probability (because of the inversely restricted sampling algorithm) but if the length of the realization of the Markov chain defined on the boundary points is taken to be proportional to $W(\omega)$, over many realizations we sample uniformly at fixed total length of the two chains. This use of inversely restricted sampling to construct a set of initial states avoids the possible ergodicity problem associated with using a two-point pivot and BFACF moves in a restricted geometry, since in principle any pair of walks could be generated by the walk-growing part of the algorithm.

We have applied this procedure to boxes of side $L = 10, 16, 20, 30$ and 40. We write n for the total number of edges in the two walks and define $\rho = n/L^3$ as the density. In figure 2 we show the average linking number $\langle|Lk|\rangle$ as a function of ρ for various values of L. For each L there is an initial set of values of ρ at which $\langle|Lk|\rangle$ is approximately zero, and the linking number then increases roughly linearly with ρ. As L increases the linear part of the curve becomes steeper and sets in at smaller values of ρ. We expect that, in the regime in which the linking number is close to zero, the two chains will occupy essentially disjoint regions of space, while in the region in which the linking number is linear in ρ the regions occupied by the two chains will have substantial overlap. This corresponds roughly to the distinction between the dilute and semi-dilute regimes in polymer solutions. In figure 3 we show the density dependence of the distance between the centres of mass of the two chains for $L = 30$ and 40. At low density we see that the centres of mass are well separated and become closer as the density increases.

The problem we are considering has two length scales, the natural linear dimension of a chain of m monomers, $L_F \sim m^{\nu}$, and the linear dimension of the cube, L. For $L_F \ll L$ we expect linking to be rare and that linking should start to be important when $L_F \approx L$. Since $m \sim n = \rho L^3$, at fixed L the density ρ^* at which linking starts to be important is determined

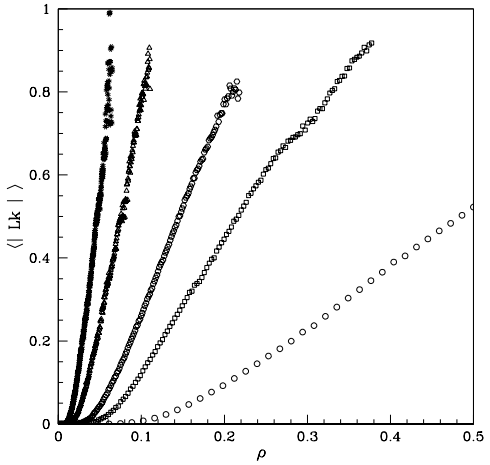

Figure 2. The expectation of the absolute value of the linking number as a function of the density ρ. The five curves correspond to $L = 10$ (bottom), 16, 20, 30, 40 (top).

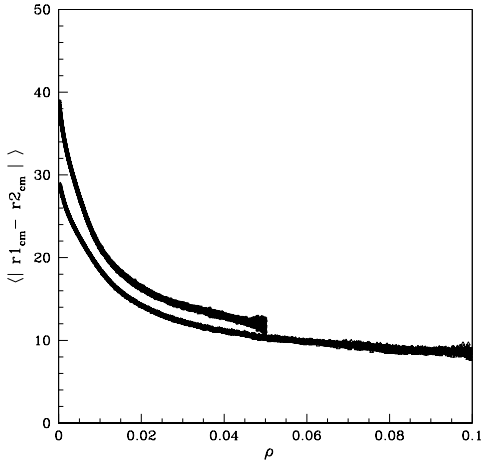

Figure 3. The difference between the centres of mass of the two chains as a function of density for $L = 30$ (bottom curve) and 40 (top curve).

by

$$L \sim m^{\nu} \sim (\rho^* L^3)^{\nu} \tag{3}$$

so that

$$\rho^* \sim L^{(1-3\nu)/\nu}. \tag{4}$$

Using the Flory value for the exponent in the expanded phase, $\nu = \frac{3}{5}$, we have $\rho^* \sim L^{-4/3}$. This implies that at fixed density ρ entanglements become important on length scales greater than $L^* \sim \rho^{-3/4}$.

Because of the competition of length scales one expects that the linking number will depend on the ratio of these two lengths, and we write

$$\langle |Lk| \rangle = f(L/L_F) \tag{5}$$

where $f(\cdots)$ is a function only of the single variable L/L_F. Using the fact that $m \sim n = L^3\rho$ we have

$$L/L_F \sim [\rho L^{(3\nu-1)/\nu}]^{-\nu} \tag{6}$$

and we can define a new function $g(\cdots)$ such that

$$\langle |Lk| \rangle = g(\rho L^{(3\nu-1)/\nu}). \tag{7}$$

Again, note that g only depends on the scaled variable $\rho L^{(3\nu-1)/\nu}$. If we use the Flory value, $\nu = \frac{3}{5}$, this gives

$$\langle |Lk| \rangle = g(L^{4/3}\rho). \tag{8}$$

At higher densities (i.e. $\rho \gg \rho^*$) the competing length scales should be the correlation length, ξ (de Gennes 1977) and L. In this regime one expects that

$$\langle |Lk| \rangle = F(L/\xi). \tag{9}$$

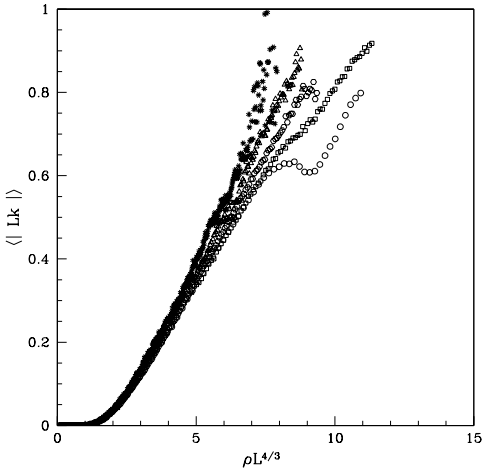

Figure 4. The expectation of the absolute value of the linking number as a function of the rescaled variable $L^{4/3}\rho$. Different symbols correspond to different values of L.

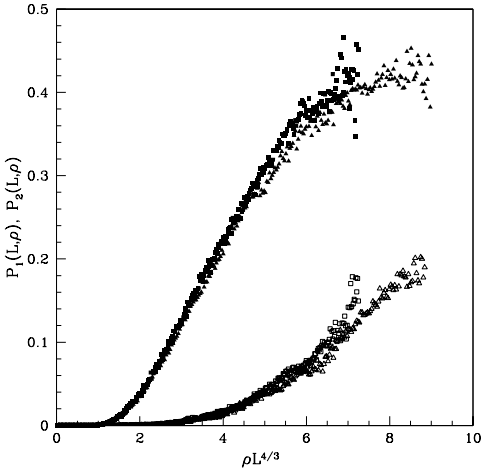

Figure 5. The probability that the linking number is equal to unity $P_1(L, \rho)$ (full symbols) and greater than unity $P_2(L, \rho)$ (open symbols), as a function of the scaled density, for $L = 30$ (△) and 40 (□).

Since, in three dimensions (de Gennes 1977)

$$\xi \sim \rho^{-3/4} \tag{10}$$

this gives

$$\langle |Lk| \rangle \sim F(L\rho^{3/4}) = G(\rho L^{4/3}) \tag{11}$$

so that the scaling variable is still $\rho L^{4/3}$ even at these higher densities.

In figure 4 we plot $\langle |Lk| \rangle$ against $\rho L^{4/3}$ and we see that the data, for modest values of ρ, approximately collapse onto a single curve. It is clear that the scaling deteriorates as $\rho L^{4/3}$ increases. The simple argument given above does not take account of the amount by which one chain must wind around the other, and this might become important when the linking number is typically larger than unity, i.e. at larger values of $\rho L^{4/3}$.

Let $P(L, \rho)$ be the probability that the polygons derived from the two chains have a non-zero linking number, i.e. the probability that they are homologically linked. If most pairs of polygons have a linking number of one, $P(L, \rho) \approx \langle |Lk| \rangle$. Indeed, these quantities would be equal if all linked pairs had a linking number of one. As ρ increases $P(L, \rho)$ is bounded above by unity, and must follow an S-shaped curve. $P(L, \rho)$ will be noticeably different from $\langle |Lk| \rangle$ when links with a linking number greater than unity start to be important. To investigate where more complex linking starts to play a role we can look at the probability, $P_1(L, \rho)$, that the linking number is one, and the probability, $P_2(L, \rho)$, that it is greater than one. In figure 5 we show the probability of the linking number being equal to one and greater than one, as a function of $L^{4/3}\rho$, for $L = 30$ and 40. Both probabilities steadily increase as the scaled density increases, and P_2 is noticeably higher than zero for $L^{4/3}\rho \approx 3$, so that linking numbers greater than one are significant even at quite low density. The scaling for both P_1 and P_2 starts to deteriorate at around $L^{4/3}\rho = 5$ or 6, which is where we start to see a breakdown of the scaling in figure 4.

In this letter we have proposed a new way of describing the entanglement complexity in concentrated polymer solutions and melts, and we have investigated the behaviour of the

entanglement complexity as a function of monomer density. We have suggested how the behaviour scales with the size of the representative cube and have confirmed this behaviour numerically. Finally, we have shown that one can see the region in which higher linking numbers become important.

Many questions remain open. In particular, we are interested in the behaviour at higher density, and the behaviour when the representative cube can contain more than two chains (corresponding to a many-string tangle). We shall address these problems in a subsequent publication.

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