Abstract

We consider the force on the end of a polymer chain being pulled through a network at velocity $v$, using computer simulations. We develop algorithms for measuring the force on the end of the chain using lattice models of polymers. Our algorithm attaches a spring to the end being pulled and uses its average extension to calculate the force. General problems associated with the use of lattice models in obtaining forces are discussed. Variants of this method are used to obtain upper and lower bounds to the force. The results obtained are in agreement with recent analytical predictions and experiments.

1 Introduction

Grafted polymer chains have been used to alter physical properties of interfaces. Colloid particles are maintained in suspension by the addition of a dense layer of end-tethered chains. Mixing of incompatible polymeric materials is facilitated by using diblock copolymers which stabilize the interface of microdomains. Reinforcement of junctions by grafting connector chains is yet another example of the numerous applications of grafted polymers.

In this paper we will focus on the force of a chain pulled through a network. This is closely related to the problem of how to reduce slippage of a viscous polymer melt. De Gennes proposed that this could be done by the addition of grafted chains. This was considered further in the case of a chain being pulled though a network by Rubinstein et al., and later generalized to a melt, a network being the limit of a melt with extremely long chains. It
was proposed that the efficiency of slippage reduction by grafted chains is not as great as one
might first expect because of the non-homogeneous deformation of these chains\[4\]. Because
our study will focus on the force of a polymer chain being pulled through a network we will
restrict out discussion to this case.

Rubinstein et al.\[2\] considered the case of a single polymer chain being pulled at one end
at a constant velocity $v$. They pointed out that the mode of relaxation for the chain is similar
to the arm of a star polymer\[5\].

Using scaling arguments, they predicted three separate regimes of behavior of the chain
as a function of the pulling velocity $v$ and the chain length $L$. In the first regime, that of
low speeds, they predicted that the frictional force $f$ is proportional to $v$. The coefficient of
proportionality should scale inversely with the longest relaxation time for the chain $T_{\text{rel}} \propto \exp(\text{const.} \times L)$. Throughout this work we will take the gel spacing to be one.

When the velocity reaches a certain value, the chain can no longer completely equilibrate
before it is pulled further forward. At this point the part of chain closest to the point being
pulled denoted the head, adopts a stick-like conformation while the tail region of the chain
can still adopt a gaussian conformation. Thus one has the picture of the chain being stick-like
at the front and then forming a plume in the back. As the velocity increases, so does the
length of the stick region, and the plume size diminishes. In this regime one expects the force
to be almost independent of velocity as the tension in the chain is almost at its equilibrium
value, but now it is directed opposite the direction of $\vec{v}$. The tension changes little because
these pulling speeds are still very low in comparison with speeds related to the relaxation
time of a Rouse chain, that is $v \sim 1/L^2$.

The third regime, that of high velocity, the plume completely disappears and the frictional
force increases linearly with pulling speed. The sole contribution to the force comes from the
Rouse friction of the constituent monomers.

Some recent experimental data appears to agree with these theoretical predictions\[6, 7\].
In this paper we present further evidence for this behavior using numerical simulations.

Simulation measurement of forces in general, pose interesting questions in computer sim-
ulations. Since the value of the forces in the present situation are quite small, long runs
are necessary to recover a high signal to noise ratio. Because of this fast algorithms such as lattice Monte Carlo models are highly desirable. However it is not obvious how to extract a force out of a lattice simulation. We have devised some new methods for measuring forces which should generalize well to other problems involving polymers.

In the following section, we describe the models used and the simulation procedure. We will explain how and where the methods used to measure forces fail and what regimes one expects the results to be valid. In section 3 we present our numerical results. In section 4 we present our conclusions.

2 The Models

2.1 The Chain

We consider a chain on a two dimensional square lattice of length $L$. The distance between monomers, or beads, is one lattice spacing. The fact that the chain is in a network is represented by entanglement points, or a “cage” that lives between lattice sites at the center of squares formed by adjacent lattice sites, as shown in fig. 1 by the ’s. In our simulation we only considered the case where the cage spacing is one. We neglect the effects of excluded volume and allow the chain to move following two sets of dynamics.

The first allows only for short range moves and is called the Evans Edwards model[8, 9, 10]. The backbone of the chain is not allowed to cross entanglement points, and therefore the only moves that can take place are that of “kinks”. Kinks are local conformations of two links that are doubled up on top of each other. The dynamics proceed as follows. A monomer is picked at random from the chain. If it is not the tip of a kink, no move is attempted. If it is, then it is flipped randomly with equal probability to any one of four conformations as shown in fig. 1(b). The tail of the polymer is handled in much the same way as a kink.

The head of the polymer, that is the point being pulled, is modeled in a slightly more complicated manner. We consider it being pulled by an anisotropic spring, with a spring constant for vertical motion of $k$. Motion of the end in the horizontal direction is prohibited. Therefore the end of the chain is not pulled directly but by a somewhat stiff spring shown
in fig. 1(c). The other end of the spring represented in the figure by the solid circle is pulled with velocity $v$. We will discuss below the precise way that we move this spring. Motion of the head of the chain then proceeds by the normal Metropolis algorithm. The potential energy of the system is that of the spring which is $k \Delta z^2 / 2$ where $\Delta z$ is the spring length.

The second algorithm we consider is one developed by one of the authors previously to study electrophoresis in strong fields\[11\]. This long range algorithm obeys detailed balance, and it was shown to more correctly model the motion of chains under high tension than short range models, which dramatically fail to describe electrophoresis\[12\]. It adds long range moves in addition to the short range moves described above. In one step, a kink can move anywhere between its two adjacent kinks. The details of the algorithm and its implementation are described in ref. \[11\].

2.2 The Force

The force is measured in three ways. They are all based on relating the length of the spring to the force on the chain. If the system was in equilibrium, for example if the chain was hanging from a spring that was tethered to a fixed point, then it is straightforward to relate the average displacement of the spring $\langle \Delta z \rangle$ to the force at the end of the chain. The energy of the system is $E = k \Delta z^2 / 2 - f \Delta z$. Therefore at fixed temperature, taken to be unity, $\langle \Delta z \rangle$ is a function of $f$

$$\langle \Delta z \rangle = \frac{\sum \Delta z e^{-E}}{\sum \Delta z e^{-E}}$$

There is a measurement time $t_m$ necessary to get a good estimate of the force. Notice that the spring constant should not be chosen to be too large. Otherwise $t_m$ becomes very long $\propto \exp(k/2)$.

The end of the spring jumps discretely between even lattice sites. The reason we cannot simply move the end to adjacent lattice sites is that the square lattice is bipartite and as a consequence of the dynamics described above, the end of the chain can only live on half the sites. The time spent at a given lattice site is $\Delta t = 2/v$, recalling that we have chosen the lattice spacing to be one.

One would expect that when the velocity is small this formula should still apply as the
measurement time $t_m$ will be much less than $\Delta t$. However when the velocity of the chain is sufficiently high one expects that this formula should break down because now the spring is always out of equilibrium and therefore eqn. (1) cannot apply.

We also note that we cannot make $k$ too small or this would allow the end of the chain to move far from the point it is being tethered. We do not want this, as it would alter the physics of the problem considerably.

The method above, by Newton’s third law should certainly be valid in a continuum, when we consider moving the end of the spring continuously at constant velocity $v$. The definition of force on a lattice is an extension of force in a continuum. However there are many possible ways of extending its definition. We are interested in the definition that best mimics this continuum behavior. The fact that on a lattice we are forced to move the chain in a discontinuous manner creates some additional difficulties we must be aware of. These are related to the fact that one needs $t_m \ll \Delta t$. As a consequence, the above method for measuring force should result in an answer that is expected to be an upper bound to the true continuum force.

To understand this, consider the extreme case where the spring coefficient is very large. We expect that the answer for the force $f$ should be almost independent of the value of $k$ chosen, and therefore the average length of the spring $\langle \Delta z \rangle = f/k$ which we are assuming is much less than 1. However when the end of the spring moves forwards by two lattice spacings, this generates an instantaneous spring length of 2 as the chain has not yet had a chance to move. On a continuum this would never happen as the chain is moved in infinitesimal steps so that the spring length never deviates much from its small equilibrium value. Here however this initial transient behavior can dominate the results for large $k$, resulting in too high a measured force. Even if $k$ is not very large, one would expect to notice some effect due to this problem.

A way to avoid this problem is to neglect the initial transient behavior. That is after moving the end of the spring, one only starts to measure $\Delta z$ after the first time $\Delta z$ becomes zero. This cuts off the initial transient behavior and should get rid of the above problem. However it also neglects the average of $\Delta z$ in this time interval. This is not as serious a
problem at low speeds, as first it might seem. The average time it takes $\Delta z$ to become zero is short. It scales as the time it takes the nearest kink to diffuse to the head of the chain. Because in most situations we consider, the kink density remains of order unity, this time is of order the time for motion of individual kinks. On the other hand, the relaxation time for the tension of the chain scales as a power of chain length. Therefore for long chains and kink densities of order unity, we can safely cut off this initial transient behavior. Because this initial transient is neglected the result should give a lower bound to the continuum force.

An intermediate strategy for obtaining the force that does not cut off the initial transient behavior nor give too large a value for $\langle \Delta z \rangle$ is as follows. We still keep fixed time intervals with duration $\Delta t$ in this method, but now the beginning of an interval does not signify the spring end moving forward. Instead, at the start of a new interval the spring end is moved only when the head of the chain is above it by two lattice spacings. This insures that when the spring end moves forward, its $\Delta z$ is zero. We calculate the force by time averaging $\Delta z$ as in the first method. If $v$ is sufficiently small, the chances of the head never moving above the spring end is negligibly small, however at high velocities this will break down, and in some time intervals it will not move forwards. In this case the velocity is not constant but will fluctuate. We will only consider velocities that are sufficiently low so that this is not a problem. A further problem with this method is that we have introduced a “Maxwell’s demon” by choosing exactly when to move the head of the polymer forwards. Of order $k_B T$ of free energy is expended in making this decision. This is expected to reduce the force somewhat over a short time-scale, which again should be the microscopic kink-jump time. As argued in the previous paragraph, this initial transient can be neglected for long chains and kink densities of order unity.

In summary, we consider three different definitions for the force obtained by measuring the length of a spring that is pulling the head of a chain and then relating it to the force through eqn. (1). First we use the time averaged spring length which should lead to an upper bound to the continuum force. Second we do not time average the spring length when the end of the spring is first moved, but wait until the first time where the spring length is zero. Third we average over all times but only move the spring end when the head of the chain is
above it, to insure that the length of the spring is initially zero.

## 3 Results

We now present the results of our simulations. Measurements for each data point were done over a period where the chain went 20 times its total length. We chose a spring constant $k = 1$. Smaller values were also tested and we found that our results differed only slightly. The force as a function of velocity is shown in fig. 2 for a chain of length 20 for the case of short range moves. The different symbols show the three different methods for measuring the force. The first method is shown with the crosses, the circles represent the second method and the triangles represent the third method. Note that for low speeds, all three methods give the same results within statistical error, but at high speeds they deviate somewhat. We expect that the crosses represent an upper bound and the circles a lower bound to the continuum force.

In fig. 3 we plot the ratio of the radius of gyrations in the horizontal and vertical directions. It decreases to about half of its equilibrium value. This shows that even at the highest speeds we were able to consider, there are still large fluctuations in the shape of the molecule. The stick-like region of the molecule on average is still not the entire chain length. This is confirmed further in fig. 4. Here we plot the distance between the head of the chain and its center of mass, in the vertical direction. At the highest speeds this distance is about 4.

The force versus velocity for the long range move case is shown in fig. 5. Because the algorithm allows for faster diffusion of kinks, one can go out to higher velocities. The results however look quite similar.

The tension along the backbone of the chain was measured for the short range algorithm. It was defined as follows. We consider two adjacent bonds at some position along the chain, of which there are $4 \times 4 = 16$ possible conformations. The tension is viewed as the force along the primitive path of the chain that stops it from collapsing. We consider the length of the primitive path for this two bond segment. When the two bonds have formed a kink, the primitive path $s$ for this conformation is zero. When the two bonds are straight, or form a right angle, the primitive path is 2. Therefore the average length of the primitive path
\langle s \rangle is related to the tension \( T \) by summing over all conformations have the same primitive path. For example if the primitive path is in the shape of a right angle, the chain can either be in four kink configurations or be a right angle. There are five conformations altogether associated with a single primitive path that are summed over according to the formula

\[
\langle s \rangle = \sum e^{-Ts} \sum e^{-Ts} \tag{2}
\]

where again we have set the temperature to one. This simply relates \( \langle s \rangle \) to the local kink density. The lower the density, the higher the tension. Note also that with no applied force there is still a finite tension. This is to be expected and it is the entropic ghost force that stops the chain from collapsing in its tube[13]. By measuring \( \langle s \rangle \) one can find the tension through eqn. (2). The tension as a function of arclength is plotted in fig. 6 for different velocities. One sees a linear decrease in the tension as a function of arclength, and an overall increase in its magnitude as \( v \) increases. This is in accord with theoretical predictions[2] and is due to the local Rouse friction of the chain in the tube. The data for the long range moves shows a much smaller slope and therefore a much lower friction coefficient. This is reasonable as the long range moves increase kink mobility.

Finally in fig. 7 we present pictures of a chain of length 50 moving at three different velocities. For chains of this length, it is clear that the description of the system in terms of a plume and and stick-like region is correct.

4 Conclusion

The measurement of forces in polymer simulations is difficult because fluctuations are large compared to the size of the mean. In the cases considered here, we are trying to obtain forces that are the same or smaller than \( k_B T \) divided by a bond length. Because of this, efficient simulation algorithms are necessary. Models that are continuous in space and time, such as molecular dynamics, give the force directly. However they are very slow in comparison with the ones considered here. They are not viable techniques with present computers. Using the lattice algorithms described in section 2 we were able to devise a method that gives an estimate for the force on the end of the chain. Variants of this method give upper and lower
bounds for this force. The methods break down for sufficiently high pulling speeds, as the head of the chain cannot keep up with the end of the spring. Still results were obtained for a wide range of velocities giving useful information for the force, tension, and chain conformation.

The results confirm the picture [2] that there is a plateau region of the force as a function of velocity and the value of the force is close to $k_B T$ over the entanglement spacing. Because the length of chain we were able to consider was not very large, but still respectably long by experimental standards, there are non-negligible fluctuations in configurations. The length of the plume and the stick-like regions of the chain varied considerably between different configurations as a consequence of breathing modes of the chain in the tube. Furthermore, the plateau region of force versus velocity is not very large for length 20 chains. At pulling speeds in the plateau region, the friction term contributes giving a finite linear slope that can be discerned from fig. 3. The long range move case shows this effect to a lesser extent. These problems could certainly be improved by investing more computer time and running longer chains.

However it is probably more interesting to exploit the methods we have developed to consider forces in other problems. One such problem would be to consider forces of tethered chains at interfaces instead of the rather artificial problem of a single chain being pulled in steady state through a gel [14, 15, 16, 17]. In the former case there is the added ingredient that chains are interacting with a surface that is likely to lead to interesting physics.

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Figure 1: Illustration of the lattice model that was used in the simulations. (a) The links of the chain are represented by the thick black lines and the monomers by the filled circles. The +’s represent entanglements that cannot be crossed. (b) The elementary moves allowed in this simulation. The kink on the upper left hand corner can move to one of the four conformations shown with equal probability. (c) The force is measured by attaching a spring to the head of the chain and pulling the other end of the spring, denoted by the filled circle, at velocity $v$. 
Figure 2: The force versus velocity for chains of length 20 using the short range moves. The crosses show the first the method of measuring the force, the circles represent the second, and the triangles represent the third.
Figure 3: The ratio of the horizontal to vertical radius of gyration, plotted as a function of $v$
Figure 4: The distance between the head of the chain and its center of mass as a function of $v$. 
Figure 5: The same as fig. 2 but using long range moves.
Figure 6: The tension of the chain as a function of arclength for different speeds. Different symbols represent speeds as follows. Open squares: $v = 0.001$, filled triangles: $v = 0.000667$, stars: $v = 0.0004$, filled diamonds $v = 0.000133$, open circles: $v = 0.00002$.
Figure 7: Three conformations are shown for chains of length 50 at different speeds.

(a) $v=0.005$  (b) $v=0.0002$  (c) $v=0.00001$