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Rollers—a new type of defect in dipoled polymer chains

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Abstract. We present a new defect which can occur in dipoled worm-like polymer chains in the presence of an electric field. These defects, 'rollers', are small loops in the chain and represent solutions of the equations of mechanical equilibrium. They are thus analogous to de Gennes' hairpins in nematic chains. The statics of rollers is studied for a dipoled chain which may also have a nematic component to its potential. The one-dimensional ideal gas model of roller thermodynamics is presented briefly. It is shown that rollers are unstable and that the dynamics of a single roller in the linear regime will be for it to roll diffusively off the end of a chain. Other possible dynamical regimes are briefly discussed as is the dynamics of n rollers on a single chain.

1. Introduction

In this paper we introduce a new type of molecular defect which can occur in a dipoled polymer chain. Such a chain consists of a series of electric dipoles (possibly separated by spacing monomers), all pointing in the same sense along the chain backbone, as in figure 1. Such dipoled chains have been suggested as possible nonlinear optical materials [1, 2], in the case where they also possess nematic liquid crystal monomers in the backbone. The effect of dipoles upon liquid crystalline ordering has also been studied in [3-5].

The statics, dynamics, and thermodynamics of main chain nematic liquid crystalline polymers has been the subject of much recent study [6-11], both because these materials are technologically important and because the understanding of their rheology presents an interesting challenge. A molecule of such a material consists of a series of nematic monomers separated by inactive spacers. Such chains are often modelled as being



Figure 1. A representation of a dipoled chain. The chain can bend but it cannot stretch. It is thus worm-like. Non-dipolar spacers may be put in between the dipoles to allow more flexibility.

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inextensible worms, that is, they conserve length locally and are unable to stretch at all. However, they may bend, although there is an energy penalty for doing so. An energy penalty is also paid for swimming across the nematic field. If we represent the spatial trajectory of a given chain of length L , in two dimensions, by the angle its tangent makes with the nematic director, $\theta(s)$, then its energy is given by:

$$U[\theta(s)] = \frac{1}{2} \int_0^L ds [\varepsilon(\theta(s))^2 + 3aS \sin^2 \theta(s)]. \quad (1)$$

Here S is the order parameter $\langle P_2[\cos \theta(s)] \rangle$ (where the average is taken over all chains for all values of s) and ε and a are the elastic bend and nematic mean field coupling constants respectively. The first term represents the bending energy, and the second the nematic energy. One important fact needs to be noted about the nematic term—it is of the form $P_2(\cos \theta)$ and thus does not distinguish up from down. The nematic field only forces the molecule to lie locally parallel to a particular line.

The obvious configuration for a polymer molecule to have in order to minimize its energy is for it to lie entirely along the nematic direction. As the temperature is increased there will be many small excursions $\theta(s) \neq 0$ away from the director. If the worm is flexible enough de Gennes [12] has suggested it will undergo rapid reversals in direction to form hairpins (see figure 2). The energetic cost of a hairpin is counter-balanced by the entropy of where it can be placed along the chain's length. Such defects drastically affect chain dimensions (the first one halves the dimension of the chain along the director) and are predicted to have a significant influence on the dielectric response [1].

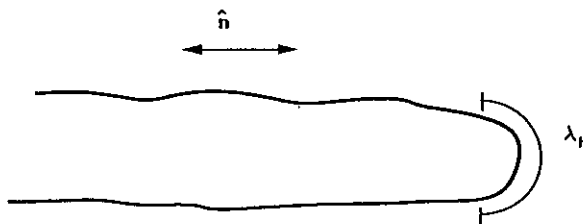


Figure 2. A hairpin in a nematic main-chain polymer liquid crystal. λ_h is the hairpin length, and gives an indication of the size of the bend. The direction of the director is shown by \hat{n} .

In order to obtain the hairpin trajectories de Gennes used as an Euler-Lagrange 'minimization' of the energy given in equation (1). The equation of mechanical equilibrium obtained is

$$\varepsilon \frac{d^2 \theta(s)}{ds^2} = 3aS \sin \theta(s) \cos \theta(s). \quad (2)$$

The free ends of the polymer imply that the appropriate boundary conditions are $d\theta(s)/ds = 0$ at both ends of the worm. This is simply a pendulum type equation and the solutions can thus be expected to be elliptic functions [2]. However for an infinitely long chain, with $s \in (-\infty, \infty)$, the solution is much simpler, being

$$\tan\left(\frac{\theta(s)}{2}\right) = \exp\left(\frac{s}{\lambda}\right) \quad (3)$$

with a minimum energy (the 'hairpin energy') of

$$U_h = 2\sqrt{3}aS\epsilon \quad (4)$$

and a 'hairpin length' of

$$\lambda_h = \sqrt{\frac{\epsilon}{3aS}}. \quad (5)$$

From (3) it is clear that λ_h represents the length scale upon which the chain bends.

One very important fact which arises from (3) is that the influence of the hairpin solution dies away exponentially with distance from the bend. Thus parts of the chain which are more than a few hairpin lengths from the bend are very well aligned along the director and do not sense that there is a hairpin in the chain.

The hairpin solution obtained here represents a balance between the nematic energy which forces the chain to turn as rapidly as possible (thus avoiding swimming against the nematic field for long) and the bending energy which is minimized for a bend which is as slow as possible. This balance is clearly seen in the length and energy scales (5) and (4).

We can now ask what the effect is of putting dipoles along a nematic chain and applying an electric field to the system. This was done in a perturbative way in [1] and [2], where the effect was manifested as a biasing of hairpin arm lengths. Here we are interested in changes to the solutions of the equations of mechanical equilibrium.

From a symmetry point of view a dipoled chain is clearly different from a nematic chain. The latter has no sense of up and down, whereas the former can sense the direction of the electric field. The dipoles couple the chain to a $P_1(\cos \theta)$ field. In section 2 we shall show that this difference leads to the creation of new kinds of defects in dipoled chains. In keeping with de Gennes' hairdressing terminology we have christened these defects 'rollers'. Like hairpins, rollers represent a balance between the bending energy of the chain and the energy of the chain in the surrounding field. Section 2 looks at the statics of rollers in an infinitely long chain. The effect of the dipoles is treated in full—not as a perturbation (as was done in [1]). The chain considered has both a nematic and a dipole component to the energy and thus one obtains hairpin-like defects as well as rollers. In section 3 the statics for a finite chain are examined. The thermodynamics, which are similar to those for hairpins are briefly discussed in section 4. In section 5 it is shown that a single roller on a finite chain is unstable. If the temperature is low enough that only linear modes of the chain need to be accounted for then the most likely dynamics for the destruction of a single roller is shown to be simple diffusion along the chain, followed by unwinding at the chain end. At higher temperatures the dynamics of roller destruction prove more complicated.

2. Statics for the infinite chain

In order to study the dynamics and thermodynamics of the dipoled PLC it is first necessary to understand the statics. By statics we mean the solutions of the equations of mechanical equilibrium for an isolated chain. The model adopted here for a dipoled chain is as simple as possible. We consider each chain separately, the only interaction with other chains being through the mean field nematic potential. The chains are infinitely thin and have no excluded volume interaction with themselves or with other chains. The electric field seen by each chain is assumed to be spatially constant.

Screening of the field by other chains is allowed provided its only effect is to change the constant E field. Even with this simple model the statics of nematic dipoled chains is complicated and will be seen to contain a rich variety of species.

We represent a polymer chain of length L by the angle it makes with the x axis $\theta(s)$ and the azimuthal angle $\phi(s)$. Here s is the arc length as measured from one end of the chain. This coordinate system guarantees that the chain cannot stretch. If we let ' mean d/ds then the energy functional of a given single chain is made up of three terms:

$$U[\theta(s), \phi(s)] = \frac{1}{2} \int_0^L ds [\varepsilon((\theta(s)')^2 + (\phi(s)')^2 \sin^2 \theta(s)) + 3aS \sin^2 \theta(s) - 2\kappa \cos(\theta(s))]. \quad (6)$$

The first term represents the bending term and ε is the bending constant. The second term is the nematic contribution. This comes from the interactions of a single monomer at position s with monomers on surrounding chains and monomers on the given chain. The final term represents the contribution from the backbone electric dipoles. Here $\kappa = \nu E$ where ν is the dipole moment per unit length along the chain. We have assumed for simplicity that the nematic director points along the x axis, as does the electric field. This is obviously the lowest energy choice. The chain thus pays an energy penalty for bending, for swimming across the nematic direction and for running against the electric field. It is important to note that the nematic field is a P_2 field whereas the electric field is a P_1 field. Thus the latter has a polarity and the former does not. It is this fact which makes hairpins and rollers very different objects. In order to find the mechanical equilibrium configurations one can carry out Euler-Lagrange 'minimization' on (6) or, which amounts to the same thing, one can add small perturbations to $\theta(s)$ and $\phi(s)$ and demand that they vanish to first order. This yields two coupled nonlinear differential equations for $\theta_0(s)$ and $\phi_0(s)$:

$$\varepsilon \theta_0''(s) = \frac{3aS}{2} \sin 2\theta_0(s) + \kappa \sin \theta_0(s) + \frac{\varepsilon}{2} \sin 2\theta_0(s) (\phi_0')^2 \quad (7)$$

and

$$\frac{d}{ds} (\phi_0'(s) \sin^2 \theta_0(s)) = 0. \quad (8)$$

The boundary conditions for a chain with free ends may be written as $\theta_0'(s) = 0$ and $\sin^2 \theta_0(s) \phi_0'(s) = 0$, at both ends of the chain. Applying the second of these to (8) immediately gives the result that $\sin^2 \theta_0(s) \phi_0'(s) = 0$ along the whole length of the chain. This implies that either $\phi_0(s)$ is constant or $\theta_0(s) = 0$ or π . The latter possibility indeed is consistent with (7) and the first boundary condition, but is a very trivial solution because once $\theta_0(s) = 0$ or π the chain is aligned along the nematic director and $\phi_0(s)$ becomes irrelevant and may as well be set equal to a constant. Thus all the geometrically meaningful solutions of (7) and (8) have $\phi_0(s)$ constant. This is a more formal proof of a result which was argued as being physically obvious in [2], namely that (at least for the purposes of statics) hairpins are the only kind of defects that can occur in non-dipoled PLCs. That is, the θ coordinate is the only one which needs to be studied, and the ϕ coordinate introduces no new exotic solutions of the equilibrium equations.

We have thus simplified the solution of the equilibrium problem to solving the equation:

$$\theta''_0(s) = \frac{1}{2\lambda_h^2} [\sin 2\theta_0(s) + 2R^2 \sin \theta_0(s)] \tag{9}$$

which is equation (2) of [2] with a dipole term added to the right-hand side. Here we use two lengths, the hairpin length λ_h , previously defined in the introduction, and the roller length λ_r , given by

$$\lambda_r = \sqrt{\frac{\epsilon}{\kappa}}. \tag{10}$$

It is also useful to define the ratio of the hairpin to the roller length $R = \lambda_h/\lambda_r$. As for the case of a chain with only a nematic field present it is much simpler [12, 2] to first study the statics of a chain of infinite length. Looking at the case $R \ll 1$ the solution of (9) is:

$$\theta(s) = 2 \tan^{-1} \exp\left(\frac{s}{\lambda_h}\right) \quad s \in (-\infty, \infty). \tag{11}$$

This is the infinite hairpin solution of de Gennes. The opposite extreme is when the electric field dominates the nematic field so that $\kappa = \nu E \gg 3aS$ and thus $R \gg 1$. The solution is then superficially very similar to the hairpin case, being:

$$\theta(s) = 4 \tan^{-1} \exp\left(\frac{s}{\lambda_r}\right) \quad s \in (-\infty, \infty). \tag{12}$$

The trajectory in real space is shown in figure (3) and is very different from a hairpin. The fact that the electric field is a P_1 field implies that the chain cannot merely bend but must roll over and eventually follow the same direction it started in. We have called the defect which forms, a 'roller'. Just as the hairpin length gives an estimate of the size of the bend in the hairpin, the roller length provides a rough indication of the 'radius' of the loop in a roller. One fact concerning rollers is immediately obvious—they will not in general reduce the chain dimensions by a significant amount, unless there is a large density of them along the chain or the roller length is very large.

To study the intermediate R regime in an infinite (or indeed a finite) chain we note that the problem may be mapped onto a much more familiar and intuitively clear one of a single Newtonian particle of unit mass moving in a potential in one dimension. If θ is the position of the particle along the x axis and s is time then the potential for the particle is:

$$U_p(\theta) = \frac{1}{4\lambda_h^2} [\cos 2\theta + 4R^2 \cos \theta]. \tag{13}$$

This may be seen from the differential equation (9). The fact that the chain is infinite

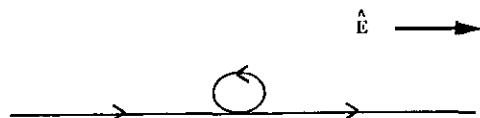


Figure 3. The approximate trajectory of a roller on a long dipoled chain. The direction of the dipoles along the chain is represented by arrows. Apart from the roller section the chain spends most of its length pointing along the field direction.

means that the particle must take an infinite amount of time to complete its trajectory and thus the particle must finish at a maximum in the potential.

For the infinite chain there are three possible cases of interest. These are shown in figures (4) to (6). The first is $R = 0$ (figure 4). In this case the electric field is zero and one is left with only the hairpin solutions. There are two types of hairpin solutions shown in this figure. These are of course equivalent energetically as they have the same lengths against the field and along the direction of the field. A more interesting case is where $0 < R < 1$ (figure 5). Again there are two hairpin-type solutions which are of equal energy. However, these do not have arms of equal length. Because the potential for the particle is much steeper for the region of the trajectory along the direction of the electric field the chain travels most of its length against the field. In fact it spends an infinite amount of time in the $\theta = \pi$ direction. There is also a roller solution in which the chain travels along the electric field direction for most of its length, with a small loop in the middle. As the value of R is increased the size of this loop shrinks because the bump which the particle must travel over at $\theta = \pi$ decreases relative to the original energy of the particle. Eventually the bump disappears entirely and for $R > 1$ only the roller solution exists (figure 6).

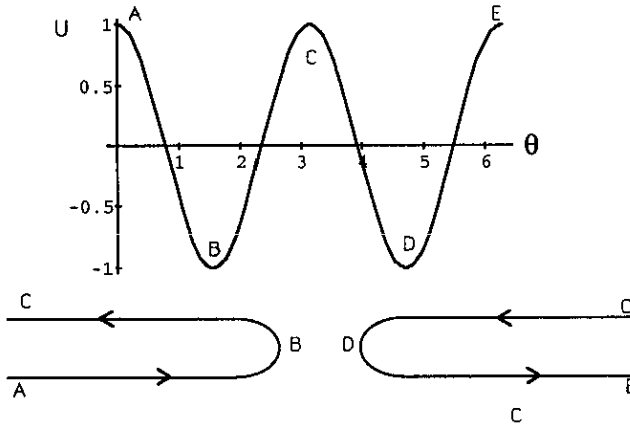


Figure 4. The infinite chain trajectories in the case of zero electric field so that $R = 0$. The graph shows the potential felt by the 'ghost' particle whose trajectory in time is the same as the chain's trajectory in space. Here θ is the coordinate describing the particle's position, which corresponds to the angle made by the chain with the field axis. The two possible hairpin solutions are also shown, as are the corresponding points of the potential and the space curves. Note that the chains extended to infinity in the C and A and the C and E directions respectively.

One can obtain explicit expressions for the solutions just discussed. The hairpin type solutions are:

$$1 + \cos \theta(s) = \frac{4(1 - R^2)}{R^2 \cosh\left(\frac{2s\sqrt{1 - R^2}}{\lambda_h}\right) - R^2 + 2} \quad s \in (0, \infty) \quad R < 1 \quad (14)$$

and the roller solutions are:

$$1 - \cos \theta(s) = \frac{4(1 + R^2)}{R^2 \cosh\left(\frac{2s\sqrt{1 + R^2}}{\lambda_h}\right) + R^2 + 2} \quad s \in (-\infty, \infty) \quad R > 0. \quad (15)$$

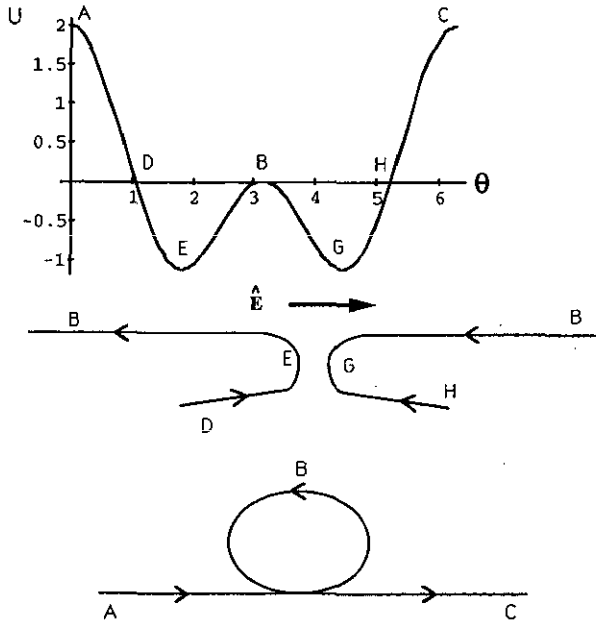


Figure 5. The infinite chain trajectories in the case of $0 < R < 1$. There are two possible hairpin-like solutions D-E-B and B-G-H. Note that these solutions spend most (an infinite amount) of their time pointing against the field, and because near D and H the potential is not flat the chains spend very little time pointing along the field. The roller solution is also shown. This solution has a reasonably low energy because most of the chain points along the field direction.

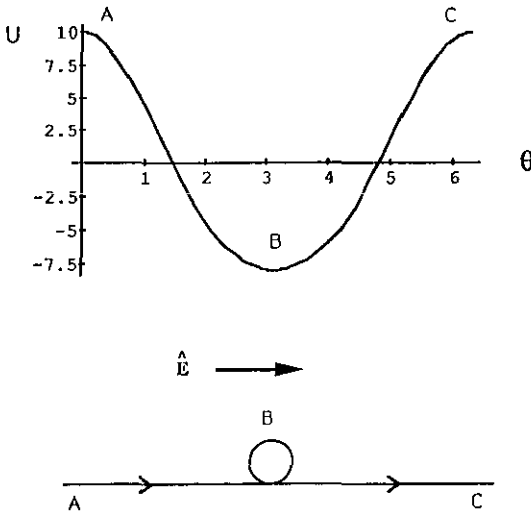


Figure 6. The infinite chain trajectories for the case of $R > 1$. There is no longer a double well in the potential and hence there are no hairpin solutions. The only available solution is the roller shown above.

It is not difficult to show that (15) reduces to the roller solution (12) in the limit $R \gg 1$. To show that (14) reduces to (11) in the limit $R \rightarrow 0$ one first needs to translate coordinates so that the point where $\cos \theta = 0$ lies at the origin.

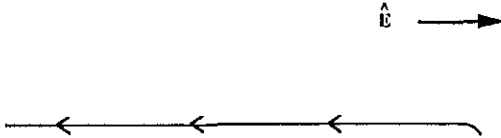


Figure 7. The infinite 'hairpin' trajectory for $1/\sqrt{2} < R < 1$. There is no point where $\theta = \pi/2$ and the chain spends most of its length in the high energy configuration pointing against the field and is hence always on one side of the defect. The shape represents a subtle balance between the various energy terms. To first order the bent part of the chain would like to unbend and hence pay less bending and nematic penalty. However, in doing so it would pay an equal dipolar energy penalty.

Using the solution (14) or the particle potential (13) it is easy to show that for $1/\sqrt{2} < R < 1$ there is no place on the hairpin solution where the chain is actually at right angles to the nematic director. In this range of R the chain thus looks something like figure 7 and it is not clear that the term hairpin is appropriate.

There are also a few trivial solutions to the mechanical equilibrium equations. These are:

$$\theta(s) = 0 \quad R \geq 0 \quad s \in (-\infty, \infty) \tag{16}$$

$$\theta(s) = \pi \quad R \geq 0 \quad s \in (-\infty, \infty) \tag{17}$$

and

$$\cos \theta(s) = -R^2 \quad 0 \leq R \leq 1 \quad s \in (-\infty, \infty).$$

In the zero electric field ($R = 0$) case the first two of these are the 'ground' state solutions whereas the latter is of very high energy per unit length because it maximizes the nematic energy.

3. Statics for the finite chain

The statics for the case of a finite length dipoled chain in the presence of a nematic field is much more complicated than the infinite case. In general there are a large number of exotic solutions. The reason for this can be seen by using the classical particle analogy. For a particle in the given potential (such as figure 8) the only conditions that it must obey in order produce a viable chain trajectory is that it is stationary at both ends of its time trajectory and takes a given amount of time to complete the trajectory. Thus given a certain amount of time or chain length the particle

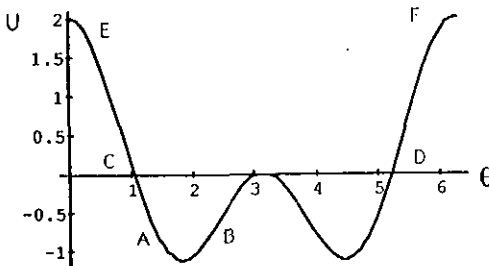


Figure 8. A possible situation for the particle potential. Trajectories $E \rightarrow F$, $A \rightarrow B$ and $C \rightarrow D$ might all take the small amount of time thus allowing for several different kinds of stationary solutions on a given length of chain.

may complete oscillation $A \rightarrow B$ or $C \rightarrow D$ or even $E \rightarrow F$. These trajectories may all take the time to complete and are thus possible chain trajectories. Here we avoid the derivation of the solutions to (9) and merely present them. We divide the solutions into three kinds. To find solution (A) we first need to solve

$$\frac{L}{p\lambda_h} = \frac{kK(k)}{\sqrt{-1 + \frac{2}{k^2} - \sqrt{R^4 + \frac{4}{k^4} - \frac{4}{k^2}}}} \tag{18}$$

for the parameter k used in elliptic function theory [13]. Here p is an integer. We then calculate:

$$x_0 = -1 - R^2 + \frac{2}{k^2} - \sqrt{R^4 + \frac{4}{k^4} - \frac{4}{k^2}} \tag{19}$$

and

$$g = \frac{k}{\sqrt{x_0 + R^2}}. \tag{20}$$

These allow the actual trajectory to be calculated as (for $s \in (0, L)$)

$$\cos \theta(s) = x(s) = 1 - \frac{1 + 2R^2 - x_0(x_0 + 2R^2)}{1 + x_0 + 2R^2 - 2(x_0 + R^2) \operatorname{sn}^2(s/(\lambda_h g), k)}. \tag{21}$$

The first thing that should be noted about this solution is that it never has a point where $\theta = \pi$ and is hence a hairpin-like solution rather than a roller solution. The integer p may be varied to give different solutions as could the hairpin number n in [2]. However, there are a limited number of solutions because the right-hand side of (18) is always $\geq \pi/\sqrt{1 - R^4}$. This solution is also only valid for $R < 1$.

The solution of type (B) may be found by solving:

$$K(k) = \frac{L}{2n\lambda_h h} \tag{22}$$

for k where n is an integer, h is given by

$$h = \frac{1}{\sqrt{R^2 + x_0}} \tag{23}$$

and we use

$$x_0 = -1 - R^2 + 2k^2 + \sqrt{R^4 - 4k^2 + 4k^4}. \tag{24}$$

The trajectory is:

$$\cos \theta(s) = x(s) = -x_0 - 2R^2 + \frac{4R^4 - 2R^2 - 2x_0 + 6R^2x_0 + 2x_0^2}{2R^2 + 2x_0 - (1 + x_0) \operatorname{sn}^2(K(k)((2ns/L) - 1), k)}. \tag{25}$$

These solutions are valid for $R > 0$. If $1 < R < 2$ then for a given n in (22) there are two solutions for k , whereas for $R > 2$ there is only one k solution, and hence one trajectory.

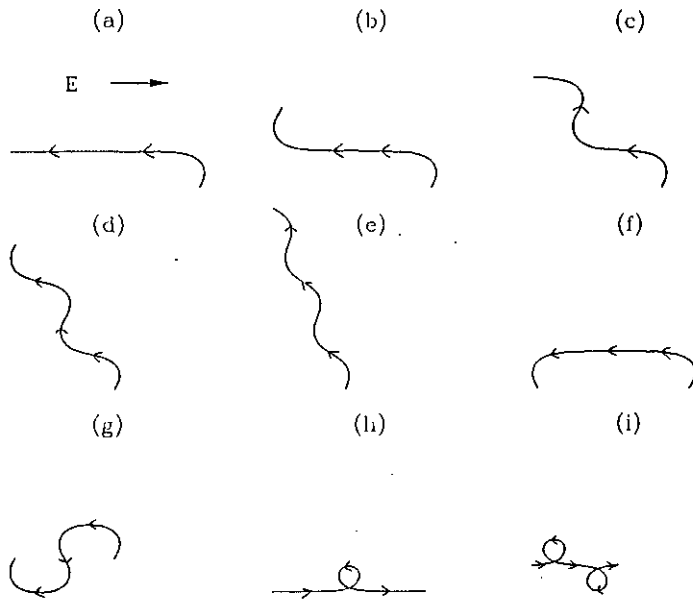


Figure 9. All the possible equilibrium solutions on a chain of length 25 with $\lambda_h = 1.3$ and $\lambda_r = 2.6$ and hence $R = \lambda_h/\lambda_r < 1$. Note that the hairpins spend most of their length against the field whereas the rollers follow the field. The solutions (f) and (g) are interesting in that they represent an intermediate stage between a hairpin and a roller. They are the chain representatives of particles which just make it over the bump (B) in figure 5.

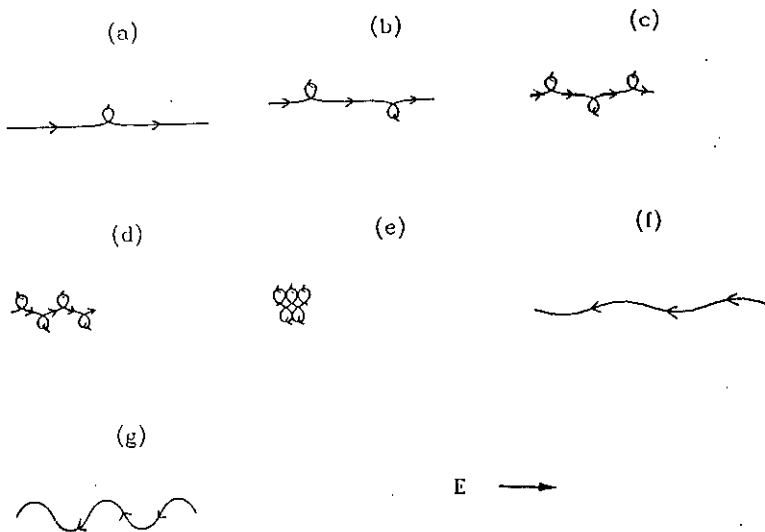


Figure 10. All the possible equilibrium solutions on a chain of length 25 with $\lambda_h = 1.3$ and $\lambda_r = 1.1$ and hence $1 < R = \lambda_h/\lambda_r < 2$. The non-roller solutions (f) and (g) which have high dipolar energy are the chain representatives of the particle wallowing in the bottom of the well in figure 6.

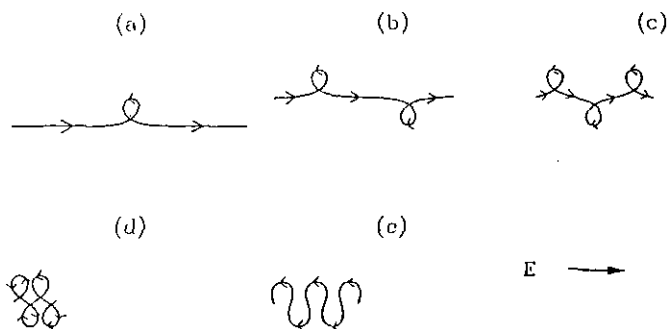


Figure 11. All the possible equilibrium solutions on a chain of length 12 with $\lambda_n = 0.6$ and $\lambda_r = 1.1$ and hence $R = \lambda_n/\lambda_r > 2$. Only the roller solutions remain. Solution (e) is a very degenerate form of roller which has not turned in on itself. It spends much of its length either perpendicular or against the electric field.

To obtain the final type of solution (type (C)) one proceeds as in type (B) but with (24) replaced by

$$x_0 = -1 - R^2 + 2k^2 - \sqrt{R^4 - 4k^2 + 4k^4} \tag{26}$$

This solution is only valid for $R < 1$. For every value of n here there is only one solution. Plots of the various solutions for the cases $R < 1$, $1 < R < 2$ and $R < 2$ are shown in figures 9, 10 and 11 respectively.

In passing we should note that for more than one roller on a chain the exact equilibrium solutions require the rollers to be placed on opposite sides of the chain in a zig-zag style (as in figure 11(c)). However, it is clear that there are many energetically close arrangements possible (which are quasi-equilibrium solutions) in which the rollers make arbitrary angles with the x axis. These arrangements can transform into each other rapidly because of the very small size of rollers and the small energy differences between the configurations.

4. Thermodynamics of rollers

It should be clear from the previous section that the equilibrium shapes of rollers on a finite sized chain can be very complicated. In this section we shall restrict our attention to a chain where $R \gg 1$ so the nematic component is unimportant. We also only examine the case $L \gg \lambda_r$, so that the shape of the rollers can be approximated by the infinite roller solution (12). To study the thermodynamics of a system of such rollers we first examine a single roller on an infinite chain. When computing the energy of this system there is an immediate minor problem. Upon substitution of (12) into (6) we find

$$U = \int_{-\infty}^{\infty} ds \left[\frac{4E}{\lambda_r^2} \operatorname{sech}^2\left(\frac{s}{\lambda_r}\right) - \kappa \right] = -\kappa\infty. \tag{27}$$

The quantity we are really interested in is the difference between the ground state of $\theta = 0$ and a single roller. This is just the first term above and is equal to the roller energy:

$$U_r = 8\sqrt{E\kappa}. \tag{28}$$

It is clear from (12) and by analogy with the case of hairpins that rollers on a single chain interact with each other via a potential which decreases exponentially with

distance on a length scale λ_r . Thus, as was done in [1] we may model a chain with n rollers as a one-dimensional ideal gas and carry many of the results across directly. Thus, in particular, the probability of finding n rollers on a chain of length L is given by

$$P_{\text{eq}}(n) = \exp(-\Gamma_r) \frac{\Gamma_r^n}{n!} \quad (29)$$

where

$$\Gamma_r = \exp(-U_r/k_B T) \frac{L}{l_r} \quad (30)$$

and l_r will be given by

$$l_r = \frac{k_B T}{\alpha \kappa} \quad (31)$$

Here α is a constant numerical factor which needs to be calculated using the approach of [7]. The average number of rollers is

$$\langle n_r \rangle = \Gamma_r \quad (32)$$

As noted previously the presence of rollers is unlikely to have any large effect upon the dimensions of a chain. They do however have one slight advantage over hairpins in reducing chain dimensions for every one of them produces a proportional reduction in chain length, whereas for the hairpin case the hairpins perform a random walk and do not cooperatively reduce the chain length. For a chain of arc length L_0 which is stretched out along the electric field direction the presence of rollers reduces its length by:

$$\frac{\beta}{\alpha} \frac{\lambda_r L_0 \kappa}{k_B T} \exp(-U_r/k_B T) = \frac{\beta}{6\alpha} \frac{U_r}{k_B T} L_0 \quad (33)$$

where $\beta \approx 1$. Thus unless $U_r \approx k_B T$ the chain length is not greatly affected. If we chose $U_r = k_B T$ then the chain length could be reduced dramatically but in such a regime the rollers would be tightly packed and would interact strongly. The assumption of treating them as an ideal gas would then be invalid.

5. Roller stability and dynamics

We finish our study of rollers with a brief discussion of their dynamics. In fact to study the dynamics properly we would like to know whether rollers are stable and what the eigenmodes look like if they are unstable. This question can be answered for a single roller on a finite chain by carefully taking the $R \rightarrow \infty$ limit in (22), (24) and (25). Then one finds that the trajectory in the presence of no nematic field is

$$\cos \theta(s)_0 = -1 + 2k^2 \operatorname{sn}^2\left(\frac{s}{\lambda_r} - \frac{L}{2n\lambda_r}, k\right) \quad \phi_0(s) = \text{constant} \quad s \in (0, L) \quad (34)$$

where

$$K(k) = \frac{L}{2n\lambda_r} \quad (35)$$

To look at the stability of this solution we take the approach of [2] and examine the second order perturbations to the energy (6). If we perturb a solution to the equilibrium equations (7) and (8) so that $\theta_0(s) \rightarrow \theta_0(s) + \alpha(s)$ and $\phi_0(s) \rightarrow \phi_0(s) + \beta(s)$ then the second order term in the energy is:

$$\delta U_2 = \frac{1}{2} \int_0^L ds \varepsilon \left\{ \left(\frac{d\alpha}{ds} \right)^2 + \left(\frac{d\beta}{ds} \right)^2 \sin^2 \theta_0 + \left(\frac{d\phi_0}{ds} \right)^2 \cos 2\theta_0 \alpha^2 + 2 \left(\frac{d\phi_0}{ds} \right) \left(\frac{d\beta}{ds} \right) \alpha \sin 2\theta_0 \right\} + \frac{1}{2} \int_0^L ds 3aS \cos 2\theta_0 + \kappa \alpha^2 \cos \theta_0. \tag{36}$$

All the equilibrium solutions have $\phi_0(s) = \text{constant}$ which considerably simplifies the problem. The ϕ and θ perturbations decouple and the ϕ perturbation is:

$$\delta U_{\phi 2} = \frac{\varepsilon}{2} \int_0^L ds \left(\frac{d\beta}{ds} \right)^2 \sin^2 \theta_0 \tag{37}$$

which is always positive. Thus the mechanical equilibrium solutions are stable against any small perturbations in the ϕ variable. The question of stability with respect to θ perturbations is more interesting. We take the eigen approach of [2]. The eigenequation which needs to be solved (with free end boundary conditions) is:

$$\varepsilon \frac{d^2 \psi^\psi(s)}{ds^2} = \psi(\kappa \cos \theta(s) - \sigma). \tag{38}$$

If any of the eigenfunctions ψ have $\sigma < 0$ then the solution (34) will be unstable. Using (34) in (38) and specializing to the case of a single roller ($n = 1$) it is possible to guess the lowest two eigenfunctions and hence obtain their eigenvalues as:

$$\sigma^{(1)} = -\kappa(1 - k^2) \quad \psi^{(1)} = \text{dn} \left(\frac{s}{\lambda_r} - K(k), k \right) \tag{39}$$

and

$$\sigma^{(2)} = \kappa k^2 \quad \psi^{(2)} = \text{sn} \left(\frac{s}{\lambda_r} - K(k), k \right). \tag{40}$$

These are basically the same eigenfunctions as were found for a hairpin. From the fact that $k^2 < 1$ it is clear that $\sigma^{(1)} < 0$ and thus rollers are unstable. The second eigenvalue and all higher eigenvalues are positive and there is thus only one mode of motion which is unstable. This unstable mode is however quasi-stable, for as $L/\lambda_r \rightarrow 1$, $k \rightarrow 1$ exponentially rapidly.

To discover exactly what the unstable mode of motion entails we compare $\psi^{(1)}$ to $d\theta/ds$ in the limit of large L/λ_r ($k \rightarrow 1$). We have

$$\psi^{(1)} \propto \text{dn} \left(\frac{s}{\lambda_r} - K(k), k \right) \rightarrow \text{sech} \left(\frac{s}{\lambda_r} - K(k) \right) \quad \text{as } k \rightarrow 1 \tag{41}$$

and

$$\frac{d\theta}{ds} \rightarrow \text{sech} \left(\frac{s}{\lambda_r} - K(k) \right) \quad \text{as } k \rightarrow 1. \tag{42}$$

Thus by the arguments of [2] the roller must move along its own length. This implies that rollers effectively 'roll' along a chain as shown in figure 12. In the absence of random forces a single roller on a chain will be driven by the exponentially weak

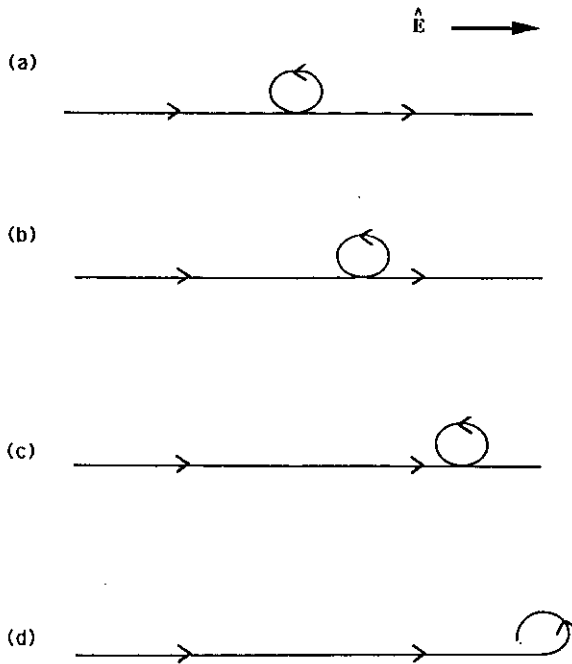


Figure 12. The dynamics of a single roller. The roller merely rolls along the chain ((a) to (c)), either by diffusion (in which case it is just a 1D random walker) or in the low temperature limit by potential effects. Eventually it will reach the end of the chain and unwind because of strong potential effects.

potential towards the ends of the chain. In the presence of temperature effects a single roller will be able to diffuse freely along a chain. The diffusion of such a roller will however be different from the diffusion of a hairpin. The major difference is in the mobility. For a roller to diffuse along a chain the only part of the chain that needs to move is the curved roller part. Thus we expect that the friction 'matrix' for a roller will be given by $\zeta\mu\lambda_r$ where $\zeta \approx 1$ and μ is the friction constant per unit length. To show this more clearly we shall adopt a model for roller motion which is similar to the diffusing pulley model for hairpin motion. This is shown in figure 13. We neglect the extent of the roller perpendicular to the chain and work in the regime $\lambda_r \ll L$ so that the effect of the roller position upon the centre of the mass is minimal. There are two coordinates in this model—the centre of mass \bar{x} and the position of the top of the roller s_1 . The x position of a monomer at arc length position s along the chain is modelled as:

$$x(s) = \begin{cases} \bar{x} - \frac{L}{2} + s & s \in (0, s_1 - \lambda_r) \\ \bar{x} - \frac{L}{2} + s_1 - \lambda_r - \frac{\gamma}{\gamma_r^2} (s - s_1 + \lambda_r)(s - s_1)(s - s_1 - \lambda_r) & s \in (s_1 - \lambda_r, s_1 + \lambda_r) \\ \bar{x} - \frac{L}{2} + s - 2\lambda_r & s \in (s_1 + \lambda_r, L). \end{cases} \quad (43)$$

Here γ is a geometrical factor and we have approximated the shape of the roller by the cubic in s . Upon calculating the Rayleighian for this system, neglecting terms small

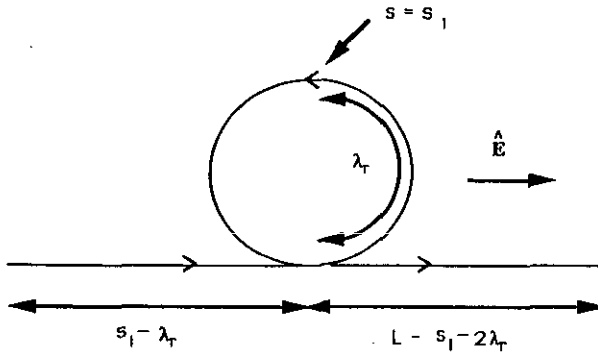


Figure 13. The simple model of roller dynamics. The roller behaves like a bead on a string. The only coordinates needed to describe it are the arc-length position s_1 and the centre-of-mass of the chain \bar{x} . The roller is shown greatly enlarged here for clarity. For the model to be valid we require $\lambda_r < L$.

in λ_r/L and cross terms between \dot{s}_1 and $\dot{\bar{x}}$ (which arise as a result of not including the roller in the centre-of-mass calculation) we obtain the friction for the centre-of-mass motion as μL and that for the s_1 motion as $\approx \mu \lambda_r$. Thus the roller motion only involves a frictional coefficient proportional to λ_r and not to the size of the chain. This has two implications. Firstly the roller may be treated as a freely diffusing particle with a simple diffusion constant which is independent of the position of the roller. Secondly, the timescale for a roller to be destroyed is of the order of $\mu L^2 \lambda_r / k_B T$. There is an L^2 from the fact that it has to do a random walk of length L , and a λ_r factor from the friction. Thus for large chain lengths roller motion should be much faster than hairpin motion, the timescales for which are expected to increase as L^3 .

The foregoing analysis of roller stability and dynamics was limited to an approach based on linearization of the energy. The only way in which a single roller could be destroyed (in the presence of no other rollers) was to roll off the end of the chain. It is clear, however, that a single roller may be destroyed by rotating the defect π radians about an axis perpendicular to the main chain and in the plain of the loop as shown in figure 14. This produces a bump in the chain which can soon be destroyed. The importance of this method of roller destruction is that it involves only the motion of a small section of the chain of size $\approx \lambda_r$. The 'equivalent' motion in hairpins would

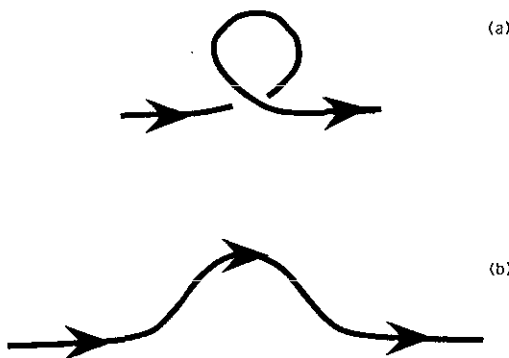


Figure 14. A possible destruction mode for a single roller. The roller in (a) flips out of the page to create a bump (b). This bump then flattens rapidly.

require moving a piece of chain of length $\approx L/2$ and would hence involve a large energy penalty. The energy barrier which needs to be overcome for a roller to rotate into a bump is of the order of the roller energy and hence this method of roller destruction may be important, particularly at higher temperatures. By the principle of detailed balance the rotation of a bump into a roller provides a method of roller creation.

We now discuss briefly the dynamics of more than one roller on a chain. Whilst the rollers are far apart their dynamics are just those for a single roller. To determine whether rollers attract or repel we can examine the energy of a system of rollers on a finite sized chain. Substituting (34) into (6) yields for the energy of the chain:

$$U_r(n) = U_r \left\{ nE(k) + \frac{L}{4\lambda_r} (k^2 - 1) \right\} - \kappa L. \quad (44)$$

Apart from the constant ground state energy this is of the same form as the energy for n hairpins on a nematic chain, and hence the energy of n rollers increase less rapidly than linearly in n . Thus rollers attract each other—although as in the hairpin case this attraction is exponentially weak at distances greater than λ_r . However when two rollers approach each other it is not always clear what happens. At small distances between rollers the fact the chain cannot cross itself needs to be taken into account. Two rollers with the correct original topology can annihilate each other by forming a double hairpin configuration which then rapidly flattens (see figure 15). However two rollers in a different configuration can form a single twisted roller (figure 16) which cannot be destroyed unless it reaches the end of a chain or moves out of the plane. It is clear that in this case the ϕ variable will be important.

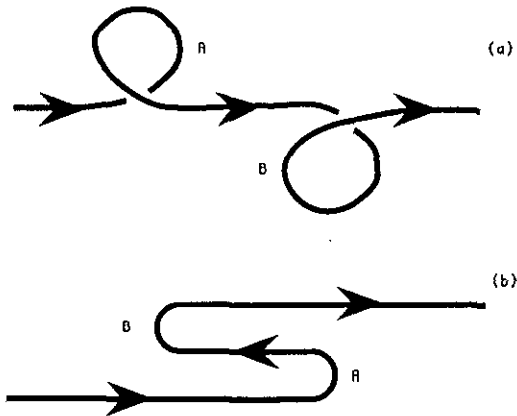


Figure 15. A possible annihilation process for two rollers. If the rollers have the topology shown in (a), then without flipping out of the plane of the paper they can attract each other to form the double hairpin configuration (b), which then decays to a straight line. The roughly equivalent points in the two configurations are marked by (A) and (B).

Here we have considered rollers formed by chains of permanent dipoles. It is also possible that rollers could form in a strong flow field [3-5]. In such a case the dynamics of rollers might well be different. In particular, in strong enough flows one expects the roller to be convected with the flow and in this case the diffusive motion considered here would be unimportant.

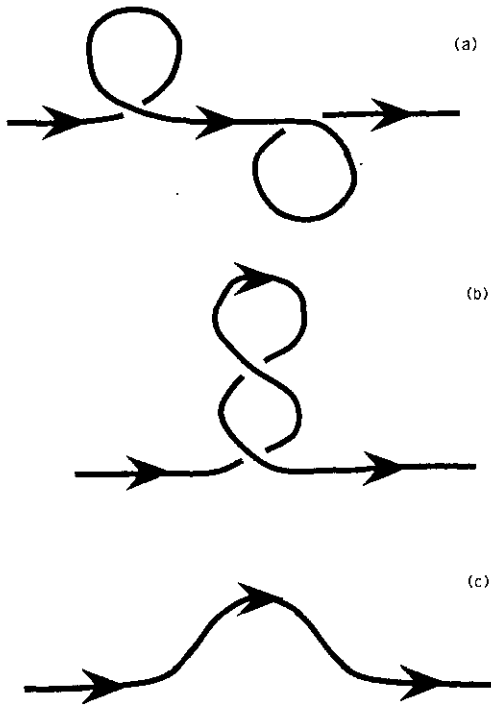


Figure 16. An alternative two roller topology to figure 15. Here the two rollers can annihilate by two single roller processes as in figure 14. Alternatively, if one attempts a similar process to that of figure 15, a tight figure of eight configuration is formed (*b*), which can only be destroyed by flipping out of the plane of the paper and forming a bump, (*c*).

6. Conclusion

In this paper we have presented a study of the types of defects which can occur in dipoled polymer chains, both with and without a nematic component. The main result is that there exists a new type of defect, a 'roller', which is a small thermal loop in the chain. On a finite sized dipoled chain there are also many other defects which are between hairpins and rollers. The number of mechanical equilibrium solutions for a dipoled nematic chain is thus very large.

In the limit of zero nematic field and for the roller length much less than the chain length rollers exhibit properties which are very similar to hairpins. Indeed mathematically the two solutions look very much alike. n rollers have the same energy form as n hairpins and any number of rollers on a chain are unstable as are hairpins. Rollers also attract each other. Dynamically rollers are very different from hairpins. It is true that they move by keeping their shape preserved, but in moving they diffuse very rapidly because only a piece of chain of length $\sim \lambda_r$ needs to be moved. They thus have a destruction time for rolling of the end of the chain proportional to L^2 , unlike the L^3 time for hairpin destruction.

Many questions about rollers still need to be answered. One would like to know the relative thermodynamic importance of the various solutions discussed in section 3. Although all of them are mechanical equilibrium solutions some are of high energy and are unlikely to be numerous in a thermal system. The various internal destruction modes of single and multiple rollers also need to be investigated. The model here is

also over simplified in that excluded volume effects are neglected. These are likely to be of some importance for small rollers. In general however, the fact that the chain cannot cross itself and does not lie exactly in a plane should not be important because the roller resists out of plane motions. In passing we also note that it is possible to envisage chains coupled to a $P_n(\cos \theta)$ field. A whole range of exotic solutions to the equilibrium equations would then be produced. These could be easily analysed using the ghost particle analogy presented here. However, the creation of a $P_n(\cos \theta)$ chain may be difficult experimentally for $n > 2$.

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