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# The statistical mechanics of entangled polymers

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**Abstract.** A particular model of the entanglement of two polymers is studied in which one is taken to have a solenoidal configuration whilst the other is a random walk. The various classes of configurations are analysed, and the probability distribution of the random flight polymer is calculated in detail when it lies in the same topological class as the axis of the solenoidal polymer.

## 1. Introduction

In studying the statistical mechanics of polymerized material if either the material is cross-linked, or if considering a fairly short time scale, one is led to effective thermodynamic functions which require a knowledge of the statistical mechanics of those components which have invariant properties. Thus if the different classes of entanglement possible are labelled '$\tau$', the effective free energy is

$$F = \sum_{\tau} p_{\tau} F_{\tau} \tag{1}$$

where $p_{\tau}$ is the probability of finding a particular topology when the material is formed, and $F_{\tau}$ the free energy of the system in that configuration under current conditions of $P$, $T$, etc. Examples of this have been given (Edwards 1967a, 1967b, 1968, 1969 and Edwards and Freed 1969), and in particular some simple planar problems can be solved completely. But in three dimensions the problem becomes much more difficult, and later work by one of the present authors (Edwards 1971) essentially uses perturbation theory on the problem, and it is valuable to see if any three dimensional problems are soluble. In this paper we consider one such case, in which two polymers are considered, the first taking up a solenoidal configuration, whilst the other is a random flight polymer. In this case $\tau$ will represent the description of the entanglements of the chain with the solenoid. In particular, there are two situations we are interested in, namely, the probability $P_{\tau 0}$ of the chain not being entangled and secondly, the probability of being entangled

$$\sum_{\tau i} P_{\tau i} \qquad (i = 1, 2 \ldots)$$

such that

$$P_{\tau 0} + \sum_{i=1}^{\infty} P_{\tau i} = \frac{1}{(2\pi l L)^{3/2}} \exp\left(-\frac{3}{2}\frac{(\boldsymbol{R}_1 - \boldsymbol{R}_2)^2}{lL}\right) \tag{2}$$

where $L$ is the total length of the chain, $l$ the length of a monomer and $\boldsymbol{R}_1$ and $\boldsymbol{R}_2$ the positions of the ends of the chain. The change in entropy due to stretching of the chain will be given by

$$\Delta S = P_{\tau 0} \ln \frac{P^*_{\tau 0}}{P_{\tau 0}} + \sum_{i=1}^{\infty} P_{\tau i} \ln \frac{P^*_{\tau i}}{P_{\tau i}}. \tag{3}$$

The first term on the right hand side of equation (3) is the change in entropy due to stretching when the chain is not entangled, and the rest of the right hand side is the change in entropy when the chain is entangled.

In order to calculate the $P_{\tau i}$ we need an invariant which characterizes uniquely the curves in the homotopical class $\tau i$. In the case of a 'phantom chain', that is a chain which can pass through itself, this invariant will be the angle swept by the chain around the solenoid. Hence in this particular case the angle $\alpha$ will play the rôle of $\tau$ and therefore we should calculate the probabilities $P_\alpha$ associated with such an angle. However, when we deal with real chains we will also have to consider selfentanglements; these will bring an infinite number of classes of curves entangled with the solenoid to which the angle invariant is not sensitive; examples of these are given in figure 1. The angle swept

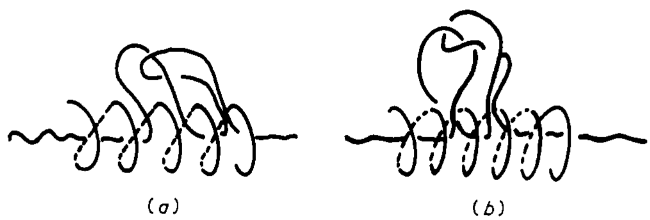

**Figure 1.**

by the curves in figure 1 around the solenoid is the same as in the situation shown in figure 2 which is not entangled with the solenoid. This implies that our invariant (the angle) will only be a lower bound to the degree of entanglement of the chain with the solenoid. That is, let us assume that $\Theta$ is the angle corresponding to the nonentangled situation, then, if the angle swept by the chain around the solenoid is $\Theta + 4\pi n$ ($n$ is an integer), the chain will be *at least* as entangled as the angle indicates.

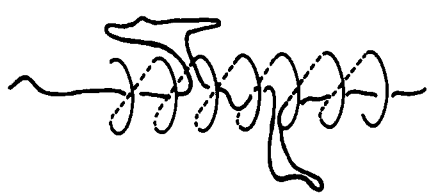

**Figure 2.**

Let $P_\Theta$ be the probability associated with the angle $\Theta$. We will assume that the main contribution to $P_\Theta$ arises from the class of curves not entangled with the solenoid, and not from the class of entangled curves which satisfy the same angle condition. This seems to be a fairly reasonable assumption from the evidence we have in two dimensions

(Edwards 1967a, 1967b). What is not very clear, is whether or not the sum of the probabilities associated with these 'degenerate' classes will be greater or comparable with the probability we are interested in.

If we allow for knots of zero length, the number of such 'degenerate' classes will be infinite. However, because our chain has a finite length, if the knots are not allowed to use less than a minimum length it follows that the number of these 'degenerate' classes becomes finite. Assuming we had included such a condition, the angle invariant will be fairly representative of the degree of entanglement. The condition on the minimum length the knots are allowed to use, could be included as a constraint on the curvature of the curve. This will reduce considerably the contribution coming from tight knots. The weighting on the curvature of the path does not alter the mathematical formulation of this problem except in that instead of a diffusion equation (without curvature) we get a Fokker–Planck type of equation. Here we shall only consider the case without curvature.

Let us denote the intrinsic equation of the solenoid and the chain by $\xi(\eta)$ and $\boldsymbol{r}(s)$ respectively. The angle swept by the chain around the solenoid will be given by

$$\int \frac{\mathrm{d}\boldsymbol{r} \times \mathrm{d}\boldsymbol{\xi}}{|\boldsymbol{r}-\boldsymbol{\xi}|^3} \cdot (\boldsymbol{r}-\boldsymbol{\xi}) = \int \dot{\boldsymbol{r}} \cdot \boldsymbol{B}(\boldsymbol{r})\, \mathrm{d}s \tag{4}$$

where

$$\boldsymbol{B}(\boldsymbol{r}) = \operatorname{curl} \int \frac{\mathrm{d}\boldsymbol{\xi}}{|\boldsymbol{r}-\boldsymbol{\xi}|} \tag{5}$$

which has the form of a magnetic field produced by a constant current going along the curve $\xi(\eta)$. If our solenoid is tight then

$$\boldsymbol{B}(\boldsymbol{r}) = \text{constant} \frac{\text{number of turns}}{\text{unit of length}} (1-\Theta(r))\boldsymbol{n} \tag{6}$$

where $\boldsymbol{n}$ is a unit vector along the axis of the solenoid and

$$\Theta(r) = \begin{cases} 0 & r < a \\ 1 & r > a \end{cases} \tag{7}$$

where $a$ is the radius of the solenoid.

If we take the $z$ axis as the axis of the solenoid, we have

$$\boldsymbol{B}(\boldsymbol{r}) = B_0(1-\Theta(r))\boldsymbol{n} \tag{8}$$

where $B_0$ = constant.

The angle swept by the nonentangled chain will be

$$\int_0^L \boldsymbol{B}(\boldsymbol{r}) \cdot \dot{\boldsymbol{r}}\, \mathrm{d}s = \int_{z_1}^{z_2} B_0\, \mathrm{d}z \tag{9}$$

where $z_1 = z(0)$ and $z_2 = z(L)$ are fixed for all paths. In another path that starts at $(r_1, \phi_1, z_1)$ inside the solenoid and ends at $(r_2, \phi_2, z_2)$ equation (9) is equal to the angle swept by the segment $(z_2 - z_1)$ going through the $z$ axis. If our solenoid is not tight then equation (6) will be only approximately true.

Let us write equation (9) as

$$\int_0^L \boldsymbol{B}(\boldsymbol{r}) \cdot \dot{\boldsymbol{r}}\, \mathrm{d}s - \int_{z_1}^{z_2} B_0\, \mathrm{d}z = \alpha \tag{10}$$

where $\alpha = \pm 4\pi n (n = 0, 1, 2 \ldots)$; for $\alpha \mp 0$ we get other homotopical classes rather than the nonentangled class. The probability that the angle swept by the chain is $\int_{z_1}^{z_2} B \, dz + \alpha$ is given by

$$P_\alpha(\boldsymbol{r}\boldsymbol{r}'L) = \mathcal{N} \int \delta\left(\int_0^L \boldsymbol{B}(\boldsymbol{r}) \cdot \dot{\boldsymbol{r}} \, ds - \int_{z_1}^{z_2} B_0 \, dz - \alpha\right) \exp\left\{-\left(\frac{3}{21} \int_0^L \dot{\boldsymbol{r}}^2 \, ds\right)\right\} \delta \boldsymbol{r} \tag{11}$$

where $\mathcal{N}$ is a normalizing factor and the integral with respect to $\delta\boldsymbol{r}(s)$ is a path integral. This Weiner integral is introduced and discussed by Edwards (1967a, 1967b), and equations (11)–(15) are similar to that discussion. Equation (11) can be written as

$$P_\alpha = \mathcal{N} \int_{-\infty}^{\infty} d\lambda \exp(-i\lambda\alpha) P_\lambda \tag{12}$$

where

$$P_\lambda(\boldsymbol{r}\boldsymbol{r}'L) = \int \delta \boldsymbol{r} \exp\left\{-\frac{3}{2l} \int_0^L \left(\dot{\boldsymbol{r}}^2 + \frac{i2\lambda l}{3} B_0 \Theta(r) \boldsymbol{n} \cdot \dot{\boldsymbol{r}}\right) ds\right\} \tag{13}$$

and consequently $P_\lambda$ can be reduced to the following differential equation:

$$\left(\frac{\partial}{\partial L} - \frac{l}{6}(\nabla_z + i\lambda B_0 \Theta(r))^2 - \frac{l}{6}(\nabla_x^2 + \nabla_y^2)\right) P_\lambda(\boldsymbol{r}\boldsymbol{r}'L) = \delta(\boldsymbol{r} - \boldsymbol{r}')\delta(L) \tag{14}$$

which written in cylindrical coordinates reads

$$\left[\frac{\partial}{\partial L} - \frac{l}{6}\left\{\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2} + \left(\frac{\partial}{\partial z} + i\lambda B_0 \Theta(r)\right)^2\right\}\right] P_\lambda(\boldsymbol{r}\boldsymbol{r}'L)$$
$$= \frac{\delta(r - r')}{\sqrt{rr'}} \delta(\phi - \phi') \, \delta(z - z') \, \delta(L). \tag{15}$$

Our problem then is reduced to solving (15) with sufficient accuracy to be able to Fourier transform back as in (12), and this is carried out in the next section.

## 2. Calculation

The basic equation is reduced to Bessel's equation by Fourier transforming equation (15)

$$P_\lambda = \frac{1}{(2\pi)^{3/2}} \sum_m \left(\int g_\lambda(m, k, r, r') \, e^{iEL} \exp\{-ik(z - z')\} \, dk \, dE\right) \exp\{im(\phi - \phi')\} \tag{16}$$

where $g_\lambda(m, E, k, r, r')$ is given by

$$\left\{iE - \frac{l}{6}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} - \frac{m^2}{r^2} - k^2 + (2k\lambda B - \lambda^2 B^2)\Theta(r)\right)\right\} g_\lambda = \frac{\delta(r - r')}{\sqrt{rr'}}. \tag{17}$$

Choosing our unit of length such that $l = 6$ and taking $m = 0$ owing to the cylindrical symmetry of the system we finally obtain

$$\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \epsilon + V_0(r)\right) g_\lambda(E, k, r, r') = \frac{\delta(r - r')}{\sqrt{rr'}} \tag{18}$$

where

$$\begin{aligned} \epsilon &= -(\mathrm{i}E+k^2) \\ V_0(r) &= (2k\lambda B-\lambda^2B^2)\Theta(r) \end{aligned} \tag{19}$$

with the following boundary conditions:

$$\begin{aligned} &g_\lambda(E,k,r,r') \to 0 \qquad \text{as } r \to \infty \\ &g_\lambda(E,k,r,r') \to 0 \qquad \text{as } r' \to \infty \end{aligned} \tag{20}$$

$$g_\lambda(E,k,0,r') \text{ and } g_\lambda(E,k,r,0) \text{ are finite} \tag{21}$$

and finally:

(i) at $r=a$, $g_\lambda(E,k,r,r')$ and $\dfrac{\partial}{\partial r}g_\lambda(E,k,r,r')$ are continuous

(ii) at $r'=a$, $g_\lambda(E,k,r,r')$ and $\dfrac{\partial}{\partial r'}g_\lambda(E,k,r,r')$ are continuous.

There are more conditions than variables to be determined. In fact there are 16 conditions and 9 constants to be determined. However from these conditions only 9 are not redundant and therefore the rest provide a check on the considerable algebra involved. The results are

$$g_\lambda(E,k,r,r')\left[\begin{array}{lll} g_{\lambda\mathrm{I}}\begin{cases} \dfrac{\pi}{2}Y_0(p_1r')\mathrm{J}_0(p_1r)+\dfrac{\pi}{2}\dfrac{Q}{T}\mathrm{J}_0(p_1r)\mathrm{J}_0(p_1r') & 0\leqslant r<r'\leqslant a \\ \dfrac{\pi}{2}\mathrm{J}_0(p_1r')Y_0(p_1r)+\dfrac{\pi}{2}\dfrac{Q}{T}\mathrm{J}_0(p_1r')\mathrm{J}_0(p_1r) & r'<r\leqslant a \end{cases} & & \\ g_{\lambda\mathrm{II}}\left\{-\dfrac{1}{aT}K_0(p_2r')\mathrm{J}_0(p_1r)\right. & 0\leqslant r\leqslant a & r'>a \\ g_{\lambda\mathrm{III}}\left\{-\dfrac{1}{aT}\mathrm{J}_0(p_1r')K_0(p_2r)\right. & 0\leqslant r'\leqslant a & r>a \\ g_{\lambda\mathrm{IV}}\begin{cases} -I_0(p_2r')K_0(p_2r)-\dfrac{P}{T}K_0(p_2r') & r>r'>a \\ -I_0(p_2r')-\dfrac{P}{T}K_0(p_2r')K_0(p_2r) & r'>r>a \end{cases} & & \end{array}\right. \tag{22}$$

where

$$\begin{aligned} p_1 &= (-\mathrm{i}E-k^2)^{1/2} \\ p_2 &= \{(\lambda B-k)^2+\mathrm{i}E\}^{1/2} \end{aligned} \tag{23}$$

and

$$\begin{aligned} T &= p_2\mathrm{J}_0(p_1a)K_1(p_2a)-p_1\mathrm{J}_1(p_1a)K_0(p_2a) \\ P &= p_2\mathrm{J}_0(p_1a)I_1(p_2a)+p_1\mathrm{J}_1(p_1a)I_0(p_2a) \\ Q &= p_1K_0(p_2a)Y_1(p_1a)-p_2K_1(p_2a)Y_0(p_1a). \end{aligned} \tag{24}$$

In particular we are interested in the probability associated with the different classes, when the two ends of the chain lie inside the solenoid, that is, $r < a$ and $r' < a$. We will denote by $P_{\alpha|}$ the probability $P_\alpha$ when $r < a$ and $r' < a$. Substituting equation (22) into equation (12) we get

$$P_{\alpha|} = \mathcal{N}\frac{\pi}{2}\int e^{iLE}\,dE\int \exp\{-ik(z-z')\}\,dk\int_{-\infty}^{\infty} e^{-i\lambda\alpha}\,d\lambda\frac{Q(E,k,\lambda)}{T(E,k,\lambda)}J_0(p_1r')J_0(p_1r)$$

$$+\frac{\pi}{2}\delta(\alpha)\begin{cases}\displaystyle\int e^{iLE}\,dE\int \exp\{-ik(z-z')\}\,dk\,Y_0(p_1r')J_0(p_1r) & 0 \leqslant r < r' \leqslant a\\ \displaystyle\int e^{iLE}\,dE\int \exp\{-ik(z-z')\}\,dk\,J_0(p_1r')Y_0(p_1r) & 0 \leqslant r' < r \leqslant a.\end{cases} \tag{25}$$

If $\alpha \neq 0$ then the second term in equation (25) is zero and we are left with

$$P_{\alpha|} = \mathcal{N}\frac{\pi}{2}\int_{-\infty}^{\infty} e^{iLE}\,dE\int_{-\infty}^{a} \exp\{-ik(z-z')\}\,dk\int_{-\infty}^{\infty} e^{-i\lambda\alpha}\,d\lambda\frac{Q(E,k,\lambda)}{T(E,k,\lambda)}$$
$$\times J_0(p_1r')J_0(p_1r) \qquad \alpha \neq 0 \tag{26}$$

where $\mathcal{N}$ is the corresponding normalization such that

$$\int_{-\infty}^{\infty} P_{\alpha|}(rr'zz'L)\,d\alpha = \frac{1}{(\pi lL)^{3/2}}\exp\left(-\frac{3}{2}\frac{(\boldsymbol{r}-\boldsymbol{r}')^2}{Ll}\right). \tag{27}$$

However if $\alpha = 0$ the second term of equation (25) diverges. Hence we run into difficulties when we try to calculate the $P_{0|}$. This singularity arises from the fact that the Fourier transform of the Green function under consideration contains a term independent of $\lambda B$ and therefore when we Fourier transform back we get the $\delta(\alpha)$. Yet we can avoid this difficulty in the following way: let us calculate the Fourier transform of the Green function of a polymer confined in a cylinder of radius $a$. This is the same as evaluating the Fourier transform of the Green function of a brownian particle confined in a cylinder with *perfect absorbing walls* the result for this case is

$$g(E,k,r,r') = \begin{cases}\dfrac{\pi}{2}Y_0(p_1r')J_0(p_1r) - \dfrac{\pi}{2}\dfrac{Y_0(p_1a)}{J_0(p_1a)}J_0(p_1r')J_0(p_1r) & r < r' \leqslant a\\[2ex] \dfrac{\pi}{2}J_0(p_1r')Y_0(p_1r) - \dfrac{\pi}{2}\dfrac{Y_0(p_1a)}{J_0(p_1a)}J_0(p_1r')J_0(p_1r) & r' < r \leqslant a.\end{cases} \tag{28}$$

In our formalism this result is the limit case when $B \to \infty$ that is

$$\frac{Q}{T} \to -\frac{Y_0(p_1a)}{J_0(p_1a)} \qquad \text{as } B \to \infty \tag{29}$$

and therefore

$$g_{\lambda|}(E,k,r,r') \to g(E,k,r,r') \qquad \text{as } B \to \infty. \tag{30}$$

From equation (28), we realize that, the term that is giving us trouble arises from the contribution of *some* paths going strictly by the inside of the solenoid. This means that the term $\frac{1}{2}\pi(Q/T)J_0(p_1r')J_0(p_1r)$ of $g_{\lambda|}$ contains the contribution coming from: (i) *some* paths going strictly by the inside of the solenoid, and (ii) all other paths which *do not* lie strictly inside the solenoid.

Yet if $L$ is large such that

$$a < z - z' \ll L$$

then the contribution to the total probability coming from the paths going strictly by the inside is much smaller than the contribution from the ones which at some point go out and in again. To illustrate our point we show in figure 3 (*a* and *b*) the type of paths that contribute to the first and second term of $g_{\lambda|}$ respectively.

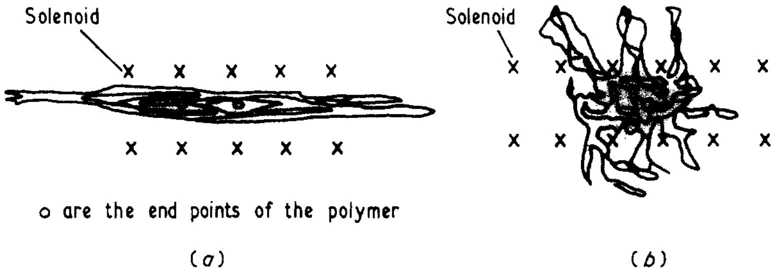


**Figure 3.**

In other words, if we wait long enough it is highly improbable that a brownian particle will remain in the same region of space without ever crossing out of that region.

From the above argument we conclude that we can cancel the first term of $g_{\lambda|}$, before we Fourier transform back without affecting our results significantly. Hence we write for $P_{0|}$ the following:

$$P_{0|} = \mathcal{N}\frac{\pi}{2}\int_{-\infty}^{\infty} e^{iLE}\,dE \int_{-\infty}^{\infty} dk \exp\{-ik(z-z')\} \int_{-\infty}^{\infty} d\lambda \frac{Q(E,k,\lambda)}{T(E,k,\lambda)}$$
$$\times J_0(p_1 r')J_0(p_1 r). \tag{26'}$$

An interesting question is if the absorbing boundary conditions are sufficiently realistic to describe a confined polymer chain? It seems from the previous discussion that apart from the absorbing boundary conditions we should neglect the term which is not sensitive to the 'porosity' of the boundary walls.

The only problem now left is to integrate the expressions given by equations (26), (26′), (27) and substitute these into equation (1). However these integrals are not easy to evaluate and even if approximations are introduced nevertheless the poles of these integrals should be obtained by numerical methods. It is interesting to note that the poles of these integrals are exactly the eigenvalues of equation (18). To be more precise the poles are at the points which satisfy the condition from which the eigenvalues, of the corresponding homogeneous equation to equation (18), are extracted. One could think of an extreme case where $\alpha \to \infty$ $L \to \infty$ and $z - z' \gg 1$, and under these circumstances the entropy of a chain highly entangled† can be calculated analytically. We leave this calculation and the integration of the exact $p_{\alpha|}$ for a future paper.

We must remark that strictly speaking the only reliable result which can be drawn out of the present analysis is in fact $P_{\infty|}(r, r', z, z', \infty)$. Before use in applications we must construct a new parameter which is more representative than the angle in describing

† We are assuming that *we know* the chain is in that topological state, in other words we are proposing a microcanonical point of view.

'the degree of entanglement'. This can be achieved by introducing curvature (and possibly torsion) together with the angle. In this way we would cut the contribution coming from 'degenerate classes' (ie those to which the angle is not sensitive).

## 3. Conclusions

Although we have only considered an idealized situation, this problem already introduces several of the features to be expected in realistic cases. The analysis presented here has ignored, so far, the nonphantom character of the chain with itself. This introduces an infinite number of degenerate classes entangled with the solenoid and therefore makes of the angle a lower bound to the degree of entanglement. To cut the contribution of such classes curvature (and possibly torsion) or at any event a more realistic treatment of short distances has to be introduced.

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