

The statistics of polymers on rough surfaces

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1988 J. Phys. A: Math. Gen. 21 2963

(<http://iopscience.iop.org/0305-4470/21/13/019>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 31/05/2010 at 16:35

Please note that [terms and conditions apply](#).

The statistics of polymers on rough surfaces

S F Edwards and Yang Chen

Cavendish Laboratory, Cambridge University, Madingley Road, Cambridge CB3 0HE, UK

Received 1 February 1988

Abstract. It has been shown by simulation by Baumgartner and Muthukumar, and by a theoretical model by Edwards and Muthukumar, that disorder localises the locus of a random polymer. This work is extended here to include excluded volume effects and we suggest a model of how the statistics of a polymer lying on a surface is affected by the roughness of the surface. It is shown that an appropriate equation for the mean size of the polymer R is derived from an entropy $R^2/L + L/R^2 + w(L/R)^2 - vL \ln R$ corresponding to the three-dimensional form $R^2/L + L/R^2 + wL^2/R^3 - vL/R$ where w is the excluded volume, v is the 'scattering power' of the disorder and L is the length of the polymer. For w small the polymer localises but, however small w is, for large enough L the excluded volume becomes dominant. The localised radius is independent of L and is proportional to $v^{-1/2}$ on a surface and v^{-1} in three dimensions. A remarkable intermediate case arises in which $R = wL/v$ for small w .

1. Introduction

A remarkable simulation by Baumgartner and Muthukumar (1987) has shown that, when a random flight in three dimensions encounters randomly placed obstacles, for example forbidden sites, in a lattice simulation, the walk localises so that, whereas for small number N of steps l one has the Einstein relation $R^2 = Nl^2$, for a large number of steps one eventually reaches $R^2 = v^{-2}$, i.e. an interpolation formula might be

$$R^2 = v^{-2}[1 - \exp(-Nl^2v^2)]$$

where v is a measure of the concentration of the obstacles, and, where it is an appropriate concept, their scattering cross section.

Edwards and Muthukumar (1988) have shown that a simple analytic model can be used to derive these results. In this paper we consider the problem of the walk on a surface with excluded volume interactions. The reason for this is that the three-dimensional problem, although a prime candidate for simulation, is not easily available experimentally. The polymer in a sponge, for example, has other features than just obstacles; it is rather a series of channels, which requires and indeed has received different consideration. A surface, however, is a prime focus of polymer interest and a rough surface is in fact a standard situation. It is therefore worthwhile to study the two-dimensional problem. To be realistic we have included excluded volume. Our calculation in the next section will be at a crude intuitive level, but will result in some very simple formulae which give one a good feeling for the problem. The results are in accord with the intuitive feeling that excluded volume will oppose localisation, and we predict that a sufficiently long polymer will settle into a random-walk statistic with an effective step length of w/v , where w is the excluded volume and v measures the

effect of the ‘scattering’, i.e. the roughness of the surface. A more elaborate analysis is given in § 3 where the problems involved in a complete theory are stated.

2. The extrapolation formula

Suppose the probability of finding the random walk, which starts at the origin, to have its endpoint at r is $P(r, [V])$, where $[V]$ denotes the fact that there is a random background.

Then

$$\langle r^2 \rangle = \left\langle \int d^3 r r^2 P(r, [V]) \right\rangle \tag{1}$$

where $\langle \ \rangle$ means an average over $[V]$. Thus if the number of configurations is $\Omega(r, [V])$ so that

$$P(r, [V]) = \Omega(r, [V]) \left(\int d^3 r' \Omega(r', [V]) \right)^{-1} \tag{2}$$

then

$$\langle r^2 \rangle = \left\langle \int r^2 \Omega \left(\int \Omega \right)^{-1} \right\rangle. \tag{3}$$

This is the ‘quenched’ average. The ‘annealed’ average is

$$\langle r^2 \rangle = \left\langle \int r^2 \Omega \right\rangle \left\langle \int \Omega \right\rangle^{-1} \tag{4}$$

and has been studied by Thirumalai (1988). The quenched average has a fixed background and the average corresponds to the fact that, for a macroscopic sample, the various configurations of $[V]$ will all be represented and a physical measurement of many random walks will be represented by equation (3). The annealed average corresponds to the distribution $[V]$ being in equilibrium with the random walks and not being frozen. The problem is now clear: it is very awkward to calculate $\int r^2 \Omega$ and $\int \Omega$, divide them and then average. But we can learn from the annealed case: suppose $[V]$ is a set of potentials centred around points R_a and that $[V]$ is soft, but the R_a numerous. Then a convenient compact notation is the Wiener integral for the locus for the walk $r(s)$:

$$\Omega = \int [\delta r] \exp \left(-(3/2l) \int_0^L ds r'^2 - \int_0^L ds \sum_a V(r(s) - R_a) \right). \tag{5}$$

In the case of many soft potentials, if one takes the mean of V to be zero

$$\begin{aligned} & \left\langle \exp \left(- \int_0^L ds \sum_a V[r(s) - R_a] \right) \right\rangle \\ &= \int \prod_a \frac{d^3 R_a}{(\text{vol})} \exp \left(- \int_0^L ds \sum_a V(r(s) - R_a) \right) \\ &= \int \frac{d^3 R_a}{(\text{vol})} \exp \left(- \int_0^L ds V(r(s) - R) \right)^N \\ &= \left(1 - V + \frac{1}{2} \int \int \int \frac{d^3 R_a}{(\text{vol})} V(r - R) V(R - r) + \dots \right)^N. \end{aligned} \tag{6}$$

Now, as $\int V$ is small and N large, the limit is $\exp(-cV_2)$ provided we take $V_1 = \int V = 0$, where c is the concentration of the \mathbf{R}_a , i.e. $N/(\text{vol})$ and

$$V_2 = N \int_0^L ds_1 \int_0^L ds_2 \int \frac{d^3 \mathbf{R}_a}{(\text{vol})} V(\mathbf{r}(s_1) - \mathbf{R}) V(\mathbf{r}(s_2) - \mathbf{R}) \tag{7}$$

$$\sim v \int_0^L ds_1 \int_0^L ds_2 \delta[\mathbf{r}(s_1) - \mathbf{r}(s_2)] \tag{8}$$

where $v = N(\int d^3 \mathbf{r} V^2(\mathbf{r}))$. Thus in the limit of a large number of soft potentials, which are now taken to be short range compared to the polymer dimension,

$$\langle \Omega \rangle = \exp\left(-\frac{3}{2l} \int_0^L ds \mathbf{r}^2 + v \int_0^L ds_1 \int_0^L ds_2 \delta(\mathbf{r}(s_1) - \mathbf{r}(s_2))\right). \tag{9}$$

Note the positive sign in front of v . Alternatively one could directly postulate that the functional probability of finding $V(\mathbf{r}(s))$ is given by $\exp[-(1/2v) \int d^3 \mathbf{r} V^2(\mathbf{r})]$, which again gives equation (9). Thus the annealed problem amounts to that of a self-attracting walk. The quenched problem can be studied in the same way if one uses the replica method (Edwards and Muthukumar 1988) but we will not develop this here but rather make the hypothesis that one can model both the annealed and quenched situations by working to second order in V , relying on the replica or other arguments to justify the formulae used.

Now

$$\langle \mathbf{r}^2 \rangle = \left\langle \int \mathbf{r}^2 \exp(-A - V) \left(\int \exp(-A - V) \right)^{-1} \right\rangle$$

where $A = (3/2l) \int ds \mathbf{r}^2$ and V stands for $\int ds \sum_a V(\mathbf{r}(s) - \mathbf{R}_a)$.

Suppose we model the effects by writing an effective exponent B and put $C = A - B$. Then

$$\langle \mathbf{r}^2 \rangle = \int \mathbf{r}^2 \exp[-B - (C + V)] \left(\int \exp[-B - (C + V)] \right)^{-1}.$$

Now studies of the excluded volume effect show that good results are obtained if it is recognised that C is of order V^2 when calculated self-consistently using B , i.e. we can write, using $\langle \rangle_B$ to mean an average,

$$\langle \mathbf{r}^2 \rangle = \langle \mathbf{r}^2 \rangle_B - \langle \mathbf{r}^2 C \rangle_B + \langle \mathbf{r}^2 \rangle_B \langle C \rangle_B + \frac{1}{2} \langle \mathbf{r}^2 VV \rangle_B - \frac{1}{2} \langle \mathbf{r}^2 \rangle_B \langle VV \rangle_B - \langle \mathbf{r}_1^2 V_1 V_2 \rangle_B. \tag{10}$$

At this point we can average over the \mathbf{R}_a to give, for example, $\langle \mathbf{r}^2 VV \rangle_B$ equal to

$$\int [\delta \mathbf{r}] [(\mathbf{r}(L) - \mathbf{r}(0))^2] c \int d^3 \mathbf{R} \int_0^L ds \int_0^L ds' V[\mathbf{r}(s) - \mathbf{R}] V[\mathbf{r}(s') - \mathbf{R}] \exp[-C(\mathbf{r})] \\ \times \left(\int [\delta \mathbf{r}] \exp(-C) \right)^{-1}$$

where c is the concentration of the \mathbf{R}_a , and $\langle \mathbf{r}_1^2 V_1 V_2 \rangle_B$ equal to

$$\int \delta[\mathbf{r}_1] \delta[\mathbf{r}_2] [(\mathbf{r}_1(L) - \mathbf{r}_1(0))^2] c \int d^3 \mathbf{R} \int_0^L ds_1 \int_0^L ds_2 V(\mathbf{r}_1(s_1) - \mathbf{R}) \\ \times V(\mathbf{r}_2(s_2) - \mathbf{R}) \exp[-C(\mathbf{r}_1) - C(\mathbf{r}_2)] \\ \times \left(\int \delta(\mathbf{r}_1) \delta(\mathbf{r}_2) \exp[-C(\mathbf{r}_1) - C(\mathbf{r}_2)] \right)^{-1}.$$

At this point we set $\langle r^2 \rangle = \langle r^2 \rangle_B$ so that our basic equation for B becomes

$$\langle r^2 C \rangle_B - \langle r^2 \rangle \langle C \rangle_B = \frac{1}{2} \langle r_1^2 V_1 V_1 \rangle_B - \frac{1}{2} \langle r_1^2 \rangle \langle V_2 V_2 \rangle_B - \langle r_1^2 V_1 V_2 \rangle_B. \quad (11)$$

Finally we can add an excluded volume $w \int ds \int ds' \delta(\mathbf{r}(s) - \mathbf{r}(s')) = W$ say, giving

$$\langle r^2 C \rangle_B - \langle r^2 \rangle \langle C \rangle_B = \frac{1}{2} \langle r^2 V_1 V_1 \rangle_B - \frac{1}{2} \langle r^2 \rangle \langle V_1 V_1 \rangle_B + \langle r^2 W \rangle_B - \langle r^2 \rangle \langle W \rangle_B - \langle r_1^2 V_1 V_2 \rangle_B. \quad (12)$$

Thus the problem of an annealed system is that of

$$(3/2l) \int ds [\mathbf{r}'(s)]^2 + (w - v) \int ds \int ds' \delta[\mathbf{r}(s) - \mathbf{r}(s')] \quad (13)$$

whereas the quenched system can be regarded as a two-walk system, since a straightforward calculation using

$$\int \mathbf{r}_1'^2 + \int \mathbf{r}_2'^2 - w \iint (\delta_{11} + \delta_{22} - 2\delta_{12}) - v \iint (\delta_{11} + \delta_{22}) \quad (14)$$

to calculate $[\mathbf{r}_1(L) - \mathbf{r}_1(0)]^2$ by the above fitting method gives equation (10) for B . To keep comparability with Flory's argument we take three dimensions to begin with. Suppose the size of the polymer is R ; then very crudely the mean-field argument would estimate $w \iint \delta$ by wL^2/R^3 and the $\int ds \mathbf{r}'^2/l$ term by R^2/Ll . Hence an estimate of the free energy is $R^2/L + wL^2/R^3$, having a minimum at $R^2 \sim w^{2/5} L^{6/5}$, first given by Flory. In no sense is this any more than an indication of the way things go, but it is fast and useful. Let us now proceed to consider more generally what can be expected if a localisation were to take place within the radius R . One knows that a localised state will always have an entropy proportional to its length, for example a harmonic diffusion has a basic probability $\exp(-\frac{1}{2} \int q r^2/l)$ an entropy ql where q is R^{-2} . If we model the localisation by $\exp[-(3/2l) \int r'^2 - \int (q^2/l) r^2]$ the basic replacement of R^2/L will be L^2/R . To handle both problems we argue that $\int_{\text{confined}} \exp(-\int r'^2)$ is modelled by $\exp(-R^2/L - L/R^2)$, w is modelled by wL^2/R^3 , leaving $v(\iint \delta_{11} + \iint \delta_{22}) - 2v \iint \delta_{12}$. The difference between these integrals lies in the correlation between \mathbf{r}_1 and \mathbf{r}'_1 in the first integral and its absence in the $\iint \delta[\mathbf{r}_1 - \mathbf{r}_2]$ integral. One can then argue that these terms differ by a term which is the ratio of the correlation length squared to the whole length of the chain, i.e. R^2/Ll . Therefore $v \iint [\delta_{11} + \delta_{22} - \delta_{12}]$ is of the order of $2v(L^2/R^3 - L/R - L^2/R^3)$. Thus gathering up all the terms we have an entropy (numerical factors are ignored at this level of crudity) $R^2/L + L/R^2 + wL^2/R^3 - vL/R$, which is minimised at $R/L - L/R^3 - wL^2/R^4 + vL/R^2 = 0$ or $R^5 + vL^2R = wL^3 + L^2R$. We offer this as a generalisation of the Flory result $R^5 = wL^3$ in three dimensions. On a surface we have an entropy $R^2/L + L/R^2 + w(L/R)^2 - vL \ln R$ and hence $R^4 + vL^2R^2 = wL^3 + L^2$. The solution to this equation has the following range:

$v = 0$	$R^2 = w^{1/2} L^{3/2}$	L large
$w = 0$	$R^2 = v^{-1}$	L large
$v = w$	$R^2 = L$	all L .

For general w, v for large L one has $R^2 = (w/v)L$. The general solution is $R^2 = \frac{1}{2}[-vL^2 + (v^2L^4 + 4wL^3 + 4L^2)^{1/2}]$ which is clearly always well behaved and extrapolates between $w^{1/2}L^{3/2}$ and $(w/v)L$. (We emphasise that numerical constants have no standing whatever.) We now make a more formal attack on the problem.

3. The potential-well model

In this section we follow Edwards and Muthukumar and differ from them only in deriving the next-order term in the free energy and by including the excluded volume. The problem is that when one models equation (14) by a harmonic well one would like to be able to model the swollen polymer as well. However, the q^2 term can only make it smaller. Edwards and Singh (1979) have suggested a very simple way to treat the swollen polymer problem, which is to use the model $\exp[-(3/2l_1) \int r'^2]$ where $l_1 > l$. It turns out that this is unsatisfactory to study entropy, but is quite powerful if the value of $\langle r^2 \rangle$ is studied. Thus if one looks at the simple excluded volume problem

$$\exp\left(-\frac{3}{2l} \int_0^L ds r'^2 - w \int_0^L \int_0^L ds ds' \delta(\mathbf{r}(s) - \mathbf{r}(s'))\right)$$

and model it by

$$\exp\left[-\frac{3}{2l_1} \int_0^L ds r'^2 + \left(\frac{3}{2}(1/l_1 - 1/l) \int_0^L ds r'^2 - w \int_0^L \int_0^L ds ds' \delta(\mathbf{r}(s) - \mathbf{r}(s'))\right)\right] \tag{15}$$

and calculates $\langle r^2 \rangle$ one finds

$$\langle r^2 \rangle = Ll_1 + L[L_1^2(1/l_1 - 1/l) - w(L/l_1)^{1/2}] + O[\]^2 \tag{16}$$

where the term in the large round bracket in equation (15) gives rise to the term in the square bracket in equation (16). Thus, if l_1 is the effective Kuhn length, $\langle r^2 \rangle = Ll_1$ and $L_1^2(1/l - 1/l_1) = w(L/l_1)^{1/2}$, leading to $l_1 = w^{2/5}L^{1/5}$ as $L \rightarrow \infty$, the Flory limit and exponent. Note also that, for $l_1 = l$ to be a solution, $w = 0$. We can study $\langle r^2 \rangle$ also in the confined case, and can match the two solutions at the analogue of $w = 0$. Thus we model equation (14) by

$$\exp\left(-\frac{3}{2l} \int r_1'^2 - \frac{3}{2l} \int r_2'^2 - \left(\frac{1}{2}q^2\right) \int (\mathbf{r}_1^2 + \mathbf{r}_2^2)\right) \tag{17}$$

for contraction, and

$$\exp\left(-\frac{3}{2l_1} \int (\mathbf{r}_1'^2 + \mathbf{r}_2'^2)\right) \tag{18}$$

for swelling and evaluate l_1, q from fitting $\langle r^2 \rangle$, as in the Edwards and Singh method. The detailed integrals are placed in the appendix; they involve non-standard functions. In the case of swelling, one has the following form:

$$l_1^2(1/l - 1/l_1) = \frac{\Omega_d}{(2\pi)^d} 2^{1+d/2} \Gamma(1 + \frac{1}{2}d) l_1 (d/l_1)^{-d/2} (2 - \frac{1}{2}d)^{-1} d^{-1} (3 - \frac{1}{2}d)^{-1} \times \{w - v[1 + d(2 - \frac{1}{2}d)(3 - \frac{1}{2}d)]\} \tag{19}$$

valid for $2 < d < 4$.

In the case of contraction one has the following form:

$$q^{-1}[1 - (1 + qL) \exp(-qL)] = f(q, L, w, v).$$

Although f is expressed in terms of non-standard integrals and the analytic form of f is not known, one still has the following small and large q behaviour valid for $d = 3$ and which can be easily calculated:

$$\begin{aligned} f \sim vL^{3/2} - wL^{3/2} & \quad (qL \ll 1) \\ f \sim vq^{-3/2} - wLq^{-1/2} & \quad (qL \gg 1). \end{aligned} \tag{20}$$

We offer here a simple interpolation formula between the small and large q behaviour, i.e.

$$f = vq^{-3/2}[1 - \exp(-qL)]^{3/2} - wLq^{-1/2}[1 - \exp(-qL)]^{1/2}. \quad (21)$$

Let us first consider $d = 3$. Equation (19) is, up to an irrelevant prefactor,

$$l_1^2(1/l - 1/l_1) = (w - \varepsilon v)(L/l_1) \quad (22)$$

where $\varepsilon = \frac{9}{4}$ in three dimensions. One sees from equations (21) and (22) that $l_1 = l$ and $q = 0$ when $w = \frac{9}{4}v$. Both estimates, i.e. using the modified Kuhn length or the harmonic oscillator, provide the same results for the mean-squared end-to-end distance $\langle R^2 \rangle = Ll$. When $w < \frac{9}{4}v$, the chain contracts, and one must use equation (21). Some limiting cases are: for a very long chain

$$q^{-1} = vq^{-3/2} - wLq^{-1/2}$$

or

$$q^{1/2} = (2wL)^{-1}[-1 + (1 + 4wvL)^{1/2}].$$

This gives $q = v^2$ if $wvL \ll 1$, whereas in the opposite limit $wvL \gg 1$ gives $q = v/wL$, but one must still have q large, i.e. $v > wL$. Therefore $\langle R^2 \rangle = v^{-2}$ and $\langle R^2 \rangle = wL/v$, respectively, in these limits, and one must also have $w \ll v$ for these limits to be valid. If we regard $q = '1/R^2'$ and $l_1 = 'R^2/L'$ we can recover the crude extrapolation of the first section by noting that the form given there gives all the limits discovered from the precise mathematics above. In two dimensions, the left-hand side of equation (20) remains the same, but the right-hand side differs from the previous case. We have here the estimates for both large and small q :

$$\begin{aligned} f \sim vL^2 - wL^2 & \quad (qL \ll 1) \\ f \sim vq^{-2} - w(L/q) & \quad (qL \gg 1). \end{aligned}$$

Therefore, for a very long chain, we have $q^{-1} = vq^{-2} - w(L/q)$, which is solved by $q = v$ ($wL \ll 1$) and $q = v/wL$ ($wL \gg 1$). However, equation (22) now has $\varepsilon = 5$:

$$l_1^2(1/l - 1/l_1) = (w - 5v)Ll \quad (23)$$

up to a prefactor. Again equations (21) and (23) give the same $\langle R^2 \rangle$ at $q = 0$ and $l = l_1$ when $w = 5v$. The analysis of limiting cases in three dimensions carries over here, i.e. for a very long chain one has

$$\langle R^2 \rangle = \begin{cases} v^{-1} & wL \ll 1 \\ wL/v & wL \gg 1 \end{cases} \quad \text{with } w \ll 5v. \quad (24)$$

Note that w and v in two dimensions have dimension of inverse contour length. The picture one gains from this analysis is that $w = \varepsilon v$ is some sort of theta point where disorder, which tends to contract the polymer, and excluded volume, which tends to swell the polymer, cancel each other exactly; at this point the polymer chain is a free random walk. In the region where $w > \varepsilon v$, excluded volume repulsion dominates and the chain swells in this region; one finds the Flory exponents that describe a self-excluded walk. When $w \ll \varepsilon v$, the chain tends to contract and is localised in one limit ($wvL \ll 1$, $d = 3$ and $wL \ll 1$, $d = 2$), i.e. $\langle R^2 \rangle$ is independent of the molecular weight and behaves like v^{-2} ($d = 3$) and v^{-1} ($d = 2$), while in the other ($wvL \gg 1$, $d = 3$ and $wL \gg 1$, $d = 2$) $\langle R^2 \rangle = wL/v$, i.e. like a true random walk in behaviour but much smaller than a free random walk since $w \ll v$.

Acknowledgment

We thank Professor M Muthukumar for interesting discussions and for bringing these remarkable problems to our attention.

Appendix. Calculation of ε

The self-consistency equation at the desired order is

$$Ll_1(1/l - 1/l_1) = (w - v)I - 2vJ \quad (\text{A1})$$

where

$$I = \int_0^L ds_1 \int_0^L ds_2 \int d^d k / (2\pi)^d \exp(-k^2 l_1 |s_1 - s_2| / 2d) (l_1 k |s_1 - s_2|)^2 / 2d \quad (\text{A2})$$

and

$$J = \int_0^L ds_1 \int_0^L ds_2 \int d^d k / (2\pi)^d \exp(-k^2 L l_1 / 2d) (L - 2s_1)^2 (l_1 k)^2 / 2d. \quad (\text{A3})$$

A simple calculation for $2 < d < 4$ shows that

$$I = \frac{\Omega_d}{(2\pi)^d} 2^{1+d/2} \Gamma(1 + \frac{1}{2}d) \frac{l_1 (d/l_1)^{d/2} L^{3-d/2}}{d(2 - \frac{1}{2}d)(3 - \frac{1}{2}d)} \quad (\text{A4})$$

$$J = \frac{1}{12} \frac{\Omega_d}{(2\pi)^d} \Gamma(1 + \frac{1}{2}d) 2^{1+d/2} l_1 (d/l_1)^{d/2} L^{3-d/2} \quad (\text{A5})$$

where $\Omega_3 = 4\pi$ and $\Omega_2 = 2\pi$. Substituting I and J into (A1), one finds

$$Ll_1^2 \left(\frac{1}{l} - \frac{1}{l_1} \right) = \frac{\Omega_d}{(2\pi)^d} \Gamma(1 + \frac{1}{2}d) 2^{1+d/2} l_1 (d/l_1)^{d/2} L^{3-d/2} \{ w - v [1 + d(2 - \frac{1}{2}d)(3 - \frac{1}{2}d)] \}.$$

References

- Baumgartner A and Muthukumar M 1987 *J. Chem. Phys.* **87** 3082
 Edwards S F and Muthukumar M 1988 *J. Chem. Phys.* to be published
 Edwards S F and Singh P 1979 *J. Chem. Soc. Faraday Trans. II* **75** 1001
 Thirumalai D 1988 *Phys. Rev. A* **37** 269