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A topological problem in polymer physics: configurational and mechanical properties of a random walk enclosing a constant area

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Abstract. We show how a random walk in a plane, constrained to enclose a given area, can be used to approximately represent the properties of an entangled polymer molecule. The statistical mechanical properties of the loop are calculated exactly and the distribution function for the enclosed areas is found. For the case of a random walk with free ends joined by a straight line segment, the distribution function is given by the Cauchy distribution. This implies that the area has statistical fractal properties but does not have a mean. For a genuinely closed random walk, a mean exists but the distribution of areas is not fractal. The spatial and mechanical properties of the constrained configurations have also been calculated analytically. If the unrestricted coil can be regarded as an entropic spring of zero natural length, then the area-constrained configurations behave qualitatively like springs with a finite natural length. The deformation behaviour also shows both softening and hardening dependent on the area imposed.

1. Introduction

Entanglements are an ever present feature in the study of long chain-like polymer molecules in the molten or concentrated state (Graessley 1974, 1982). Their description and inclusion into the formalism of statistical mechanics and dynamics presents many interesting and unique features (Prager and Frisch 1967, Edwards 1967, 1968, Brereton and Shah 1980, 1982, Brereton and Williams 1985). The mathematical description of knots and links (Alexander and Briggs 1927, Rolfson 1976, Ball and Mehta 1981) has produced algorithms that enable given topologically entangled configurations to be classified. This approach is suited to the study of entanglements through numerical simulation (Vologodskii *et al* 1974, des Cloizeaux and Mehta 1979, Wiegel and Michels 1986). However the global nature of entanglements necessarily involves large amounts of memory and computer time and the results at present are limited to single self-knotted short chains. This gives virtually no qualitative insight into the effect of entanglements on the configurational and mechanical properties of many polymer chain situations. On the other hand, the use of mechanical models such as a confining tube (Doi and Edwards 1978) or a slip link (Ball *et al* 1981) loses a good deal of the topological content. Whilst these models are quite successful in describing the mechanical properties of entangled systems, such as the observed decrease in the modulus with deformation (Mark 1982), they offer little insight into the topological origins of these effects.

The analytic approach to the description of entanglements is hindered by the relative scarcity of discriminating topological invariants and the results are frequently obscured by associated algebraic complexity. It is, nevertheless, our intention in this paper to persevere with the analytic approach. We will carefully choose a model system, subjected to a genuine topological constraint, for which some exact analytic results for the configurational properties can be obtained. From these results and the relative simplicity of their derivation we hope that reliable qualitative conclusions may be drawn about the effects of entanglements in more general situations.

The simplicity of our model derives from the restriction to configurational properties in two dimensions. In particular we consider a random walk configuration in a plane where the topological constraint is obtained by an application of Cauchy's residue theorem, i.e.

$$\frac{1}{2\pi \mathrm{i}} \sum_n \oint_C \frac{\mathrm{d}z}{z - a_n} = m \tag{1.1}$$

where m is the number of times the contour C winds round the singularities at a_n. The situation where the contour C is taken as a random walk configuration and the singularities randomly distributed in the complex plane is shown in figure 1(a). The application to polymer problems is clear if we let C represent a polymer configuration and the singularities represent other polymers or obstacles perpendicular to the plane. Cauchy's theorem is a topological result since the winding number is independent of the configuration C as long as it does not cross any of the singularities. If we impose this constraint, then for a given distribution of the $\{a_n\}$ the configurational phase space available to the curve C is partitioned up into mutually inaccessible regions labelled by the winding numbers m.

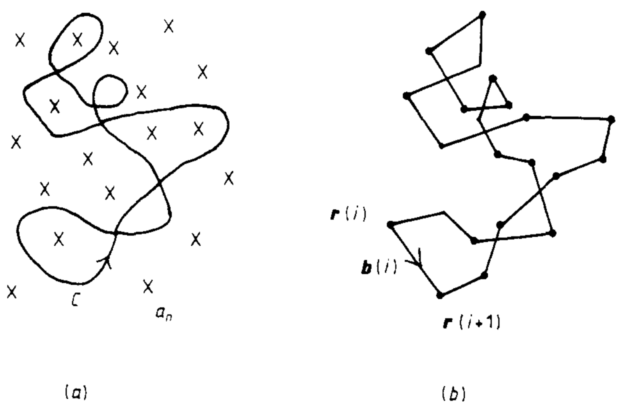

Figure 1. (a) C represents a contour in a complex plane with singularities located at the a_n, denoted by $\times$. (b) A bond vector representation of a polymer configuration.

To further simplify our model we will consider a uniform distribution of the singularities $\{a_n\}$ with a surface density σ. This problem is, as we will show, identical to calculating the algebraic area enclosed by such a loop. The statistical mechanical problems posed by this constraint can be solved exactly by the method presented in § 3. In § 4 the probability distribution function for the area enclosed by a closed random coil is given. We show that, if an 'area' is also defined for a chain with free ends by the expediency of joining the ends with a straight line segment, then for long chains this 'area' has fractal properties and is given by a Cauchy distribution. In § 5 the configurational properties and the entropy of random coils subjected to an area constraint are presented. This enables the mechanical properties to be calculated. We find that, if the unrestricted coil can be regarded as an entropic spring of zero natural length, then the effect of an increasing area (entanglement) constraint is qualitatively similar to a spring with a non-zero natural length, i.e. the entangled coil shows a compressive behaviour.

2. Winding numbers and the area of a 2D random coil

The basic topological result (1.1) for the winding number m of a curve C around a distribution of singularities can be written in the form

$$(1/2\pi)\oint_C \boldsymbol{B}(\boldsymbol{r})\cdot \mathrm{d}\boldsymbol{r} = m \tag{2.1}$$

where $\boldsymbol{B}(\boldsymbol{r})$ is a vector field with components

$$\left\{\sum_n y/(\boldsymbol{r}+\boldsymbol{a}_n)^2, \qquad \sum_n x/(\boldsymbol{r}-\boldsymbol{a}_n)^2\right\} \tag{2.2}$$

and x, y are the coordinates of the point $\boldsymbol{r}$ in the plane. Using Stokes' theorem (2.1) becomes

$$(1/2\pi)\int_{S_C} \mathrm{d}\boldsymbol{S}\cdot \operatorname{curl} \boldsymbol{B}(\boldsymbol{r}) = m \tag{2.3}$$

where $\mathrm{d}\boldsymbol{S}$ is an element of the surface S_C enclosed by C. Using (2.2) we also have that

$$\operatorname{curl} \boldsymbol{B}(\boldsymbol{r}) = \sum_n \delta(\boldsymbol{r}-\boldsymbol{a}_n)\boldsymbol{k} \tag{2.4}$$

where $\boldsymbol{k}$ is a unit vector perpendicular to the (x, y) plane. For a uniform distribution of singularities

$$\langle \operatorname{curl} \boldsymbol{B}(\boldsymbol{r})\rangle = \sigma \boldsymbol{k} \tag{2.5}$$

where σ is the surface density of the singularities. If we neglect fluctuations in curl $\boldsymbol{B}(\boldsymbol{r})$ then (2.3) becomes

$$(\sigma/2\pi)\int \mathrm{d}\boldsymbol{S}\cdot \boldsymbol{k} = m \qquad \text{or} \qquad A\{C\} = 2\pi m/\sigma \tag{2.6}$$

where $A\{C\}$ is the algebraic area bounded by $\{C\}$. Therefore in our model the distribution of the enclosed areas is the same as that for the winding numbers. It is well known that, although the winding number is a rigorous topological invariant, it is not a good discriminator between different topological situations, i.e. topologically distinct configurations can have the same winding number. In our present model this is reflected in the algebraic nature of $A\{C\}$ since the sign of $\mathrm{d}\boldsymbol{S}$ depends on the orientation of the contour. Thus a symmetric 'figure of eight' configuration would have an algebraic area of zero and for a random walk configuration there would also be a large amount of cancellation. The importance in physical applications of the imposition of an area constraint is not in the particular value of the area but in its conservation. It is this fact that will prevent a 'figure of eight' configuration unfolding during deformation to, say, a circle. With these remarks we use the area constraint to impose a topology rather than to classify a given topological state.

A vector field with the property

$$\operatorname{curl} \boldsymbol{B}(\boldsymbol{r}) = \text{constant} = \sigma \boldsymbol{k}$$

is given by

$$\boldsymbol{B}(\boldsymbol{r}) = \sigma \boldsymbol{k} \times \boldsymbol{r}/2 \tag{2.7}$$

and so the residue theorem (2.1) becomes

$$(\sigma/4\pi) \oint_C \mathrm{d}\boldsymbol{r} \cdot \boldsymbol{k} \times \boldsymbol{r} = m. \tag{2.8}$$

Strictly speaking, the winding number or area can only be defined for closed curves. However, it will be both useful and instructive to consider the integral (2.8) even when C is not closed. For finite arc lengths it will be well defined and will change continuously as the contour C changes. In fact, the integral represents the area obtained by joining the two endpoints of a free chain by a straight line and for long configurations it should provide some indication of the degree of entanglement. Our purpose in introducing this quantity is to show that the distribution function for the integral (2.8) defined for an open curve is a stable distribution (Montroll and West 1979). This means that, if $P(m, N)$ is the probability that the integral (2.8) evaluated over an open contour C of N segments has a value m, then $P(m, N)$ satisfies the chain property

$$\int P(m-m', N')P(m', N-N')\,\mathrm{d}m' = P(m, N). \tag{2.9}$$

Such distributions naturally possess fractal properties (Mandelbrot 1977). The corresponding distribution for the closed curve will be shown not to satisfy the chain property (2.9). A similar situation also occurs for the distribution function of the spatial vector between two points on a chain. It is only for the open chain where the distribution is Gaussian that (2.9) is satisfied.

In the next section we formulate the constraint on the contour C to enclose a given area as a path integral taken over all possible configurations.

3. Path integral formulation

We consider the contour to be described, as in figure 1(b), by a set of N bond vectors

$$\boldsymbol{b}(j) = \boldsymbol{r}(j) - \boldsymbol{r}(j-1) \tag{3.1}$$

where the $\boldsymbol{r}(j)$ are the position vectors to a point j on the chain. The Gaussian or random walk model of a polymer is generated by assuming that the $\boldsymbol{b}(j)$ are Gaussian distributed, so that the probability of a given configuration $\{C\} = \{\boldsymbol{b}(1), \boldsymbol{b}(2), \ldots \boldsymbol{b}(N)\}$ is given by

$$p\{C\}d\{C\} = (1/\pi l^2)^N \exp(-\boldsymbol{b}^2(j)/l^2)\,\mathrm{d}\boldsymbol{b}(1) \ldots \mathrm{d}\boldsymbol{b}(N) \tag{3.2}$$

where l^2 is the average length of bond vector $\langle \boldsymbol{b}^2(j)\rangle = l^2$. The restriction of the configurations $\{C\}$ to those which enclose a given area A can be imposed by using a delta function, parametrised by

$$\delta(A\{C\}-A)=(1/2\pi)\int_{-\infty}^{\infty} \mathrm{d}g\,\exp[\mathrm{i}g(A\{C\}-A)] \tag{3.3}$$

where $A\{C\}$ is the area enclosed by the configuration $\{C\}$ and is given from (2.8) as

$$A\{C\}=\tfrac{1}{2}\oint_C \mathrm{d}\boldsymbol{r}\cdot\boldsymbol{k}\times\boldsymbol{r}. \tag{3.4}$$

In terms of the bond vectors (3.1) we consider a discrete version of (3.4) written as

$$\begin{aligned} A\{C\} &= -\tfrac{1}{2}\sum_{j=1}^{N} \boldsymbol{b}(j)\times\boldsymbol{r}(j)\cdot\boldsymbol{k} \\ &= -\tfrac{1}{2}\sum_{j=1}^{N} \boldsymbol{b}(j)\times\boldsymbol{r}(0)+\sum_{i=1}^{j}\boldsymbol{b}(i)\cdot\boldsymbol{k} \end{aligned} \tag{3.5}$$

where $\boldsymbol{r}(0)$ is the position vector to an arbitrary point on the contour or to a chain end on an open contour. This term and our subsequent analysis is simplified by using normal mode coordinates $\boldsymbol{b}_n$, defined by

$$\boldsymbol{b}_n=(1/N)\sum_{j=1}^{N}\boldsymbol{b}(j)\exp(2\pi\mathrm{i}nj/N). \tag{3.6}$$

Then (3.5) for the area enclosed by the curve C becomes

$$A(C)=\tfrac{1}{2}\boldsymbol{r}(0)\times\boldsymbol{b}_N\cdot\boldsymbol{k}+N\sum_{n=1}^{N}\boldsymbol{k}\cdot(\boldsymbol{b}_n\times\boldsymbol{b}_{N-n})\beta_n \tag{3.7}$$

where

$$2\beta_n=1/[1-\exp(-2\pi\mathrm{i}n/N)].$$

For a closed loop we have from the definition (3.6) that

$$\boldsymbol{b}_N=(1/N)\sum_{j=1}^{N}\boldsymbol{b}(j)=(\boldsymbol{r}(N)-\boldsymbol{r}(0))/N=0. \tag{3.8}$$

Therefore in the second term of (3.7) the loop constraint (3.8) removes the $n=N$ term in the sum over modes. For $n=N$ the term β_n is singular, but it can be shown that

$$2N\lim_{n\to N}(\boldsymbol{b}_n\times\boldsymbol{b}_{N-n})\beta_n \Rightarrow \boldsymbol{r}(0)\times\boldsymbol{b}_N-\boldsymbol{R}_{\mathrm{CM}}\times\boldsymbol{b}_N \tag{3.9}$$

where $\boldsymbol{R}_{\mathrm{CM}}$ is the centre of mass of the chain. If we consider an open chain and locate the centre of mass at $\boldsymbol{R}_{\mathrm{CM}}=0$, then we can define an associated quantity

$$A^*\{C\}=(N/2)\sum_{n=1}^{N}\boldsymbol{k}\cdot(\boldsymbol{b}_n\times\boldsymbol{b}_{N-n})\beta_n \tag{3.10}$$

where $A^*\{C\}$ would be roughly interpreted as the algebraic area spanned by an open chain. We will discuss the distribution of both A^* and A.

Finally in order to be able to calculate configurational properties we consider a generating term of the form

$$\exp[\boldsymbol{\lambda}\cdot(\boldsymbol{r}(s)-\boldsymbol{r}(0)]=\exp\left(\boldsymbol{\lambda}\cdot\sum_{j=1}^{s}\boldsymbol{b}(j)\right) \tag{3.11}$$

where $\boldsymbol{r}(s)-\boldsymbol{r}(0)$ is the spatial distance between s points along the chain. In normal mode coordinates this is given as

$$\exp\left(\boldsymbol{\lambda}\cdot\sum_{n=1}^{N}b_n\theta_n(s)\right) \tag{3.12}$$

where

$$\theta_n(s)=[1-\exp(2\pi is/N)]/[\exp(-2\pi in/N)-1].$$

The partition function of interest is given by

$$Z(\lambda, A, N)=\int d\{C\}p\{C\}\delta(A\{C\}-A)\exp[\boldsymbol{\lambda}\cdot(\boldsymbol{r}(s)-\boldsymbol{r}(0)] \tag{3.13}$$

from which the distribution function $P(A, N)$ for the area A enclosed by the random walk of N steps is given by

$$P(A, N)=Z(0, A, N) \tag{3.14}$$

and the spatial distance between two points s on a chain constrained to enclose an area A or to possess a winding number $m=A/2\pi\sigma$ with regard to the background 'obstacles' is given by

$$\langle(\boldsymbol{r}(s)-\boldsymbol{r}(0))^2\rangle_A=\frac{\mathrm{d}^2}{\mathrm{d}\lambda^2}\ln Z(\lambda, A, N)|_{\lambda=0}. \tag{3.15}$$

Using (3.2) for $p\{C\}$ and (3.3) and (3.7) for the constraint term, the partition function $Z(\lambda, A, N)$ can be written as

$$Z(\lambda, A, N)=(1/2\pi)\int \mathrm{d}g\exp(\mathrm{i}gA)Z(\lambda, g, N) \tag{3.16}$$

where

$$Z(\lambda, g, N)=\int\prod_n \mathrm{d}\boldsymbol{b}_n\exp\left(-\sum_{n=1}^{N-1}\boldsymbol{b}_n^2/l^2+\mathrm{i}g\sum_n\boldsymbol{k}\cdot(\boldsymbol{b}_n\times\boldsymbol{b}_{N-n})\beta_n+\lambda\sum_n\boldsymbol{b}_n\theta_{N-n}(s)\right). \tag{3.17}$$

Since $b_{N-n}=b_n^*$ the integral can be reduced to a product of standard Gaussian integrals. The vector product requires some attention but some straightforward algebra leads to the result

$$Z(\lambda, g, N)=\prod_{n=1}^{N-1}\left(\frac{1}{1+g^2l^4\beta_n''^2}\right)\exp\left(\sum_{n=1}^{N-1}\frac{\lambda^2|\theta_n(s)|^2l^2}{4N(1+g^2l^4\beta_n''^2)}\right) \tag{3.18}$$

where

$$\beta_n''=\mathrm{Im}(\beta_n)=\tfrac{1}{4}\cot(\pi n/N)$$

and

$$|\theta_N(s)|^2=(\sin^2\pi ns/N)/(\sin^2\pi n/N). \tag{3.19}$$

By defining

$$P(g, N) = \prod_{n=1}^{N-1} 1/(1+g^2 l^4 b_n''^2) \tag{3.20}$$

and

$$R^2(g, N, s) = (l^2/N) \sum_{n=1}^{N-1} |\theta_n(s)|^2/(1+g^2 l^4 \beta_n''^2). \tag{3.21}$$

(For the open loop there is an additional term $n = N$.) Then (3.18) can be written as

$$Z(\lambda, g, N) = P(g, N) \exp(-\lambda^2 R^2(g, N, s))/4. \tag{3.22}$$

This completes the statistical mechanics calculation. We now consider the various configurational properties that can be derived from (3.18) starting with the distribution function for the area enclosed by C.

4. Distribution function for the area

The distribution function $P(A, N)$ for the area of a closed loop of N segments is given from (3.14) and (3.18) by

$$\begin{aligned} P(A, N) &= Z(0, A, N) \\ &= (1/2\pi) \int \mathrm{d}g \exp(\mathrm{i}gAP(g, N)). \end{aligned} \tag{4.1}$$

In view of the Fourier transform relation (4.1), $P(g, N)$ is the characteristic function and is given from (3.20) as

$$P(g, N) = \prod_{n=1} 1/(1+g^2 l^4 \beta_n''^2). \tag{4.2}$$

Using (3.19) for $\beta_n''^2$ this can be written as

$$P(g, N) = \exp\left(-\sum_n \ln(\tan^2(\pi n/N) + g^2 l^4/16)\right) + \text{constant} \tag{4.3}$$

where the term 'constant' is independent of g. To evaluate the sum in (4.3) we consider the large N limit so that it can be replaced by an integral according to

$$\sum_n \rightarrow (N/\pi) \int \mathrm{d}\theta \qquad \theta = \pi n/N.$$

We consider the case of a chain with two free ends so that the $n = N$ term is present. In this case the integral is from 0 to π and is given by

$$\int_0^\pi \mathrm{d}\theta \ln(\tan^2\theta + g^2 l^4/16) = 2\pi \ln(1+gl^2/4) \tag{4.4}$$

so that

$$\begin{aligned} P(g, N) &= 1/(1+gl^2/4)^{2N} \\ &\rightarrow \exp(-Ngl^2/2) \qquad \text{as } N \rightarrow \infty. \end{aligned} \tag{4.5}$$

The Fourier transform of (4.5) is the Cauchy distribution

$$P(A, N) = P(A/Nl^2)$$
$$= 2/\pi Nl^2[(2A/Nl^2)^2+1]. \tag{4.6}$$

We see that the area is scaled by the term Nl^2. The Cauchy distribution is a special case of a Levy or stable distribution (Fuller 1966) which satisfy the chain property

$$P(A, N) = \int P(A-A', N')P(A', N-N')\,\mathrm{d}A' \tag{4.7}$$

and have a Fourier transform of the form

$$\exp(-a|g|^b N) \tag{4.8}$$

where a and b are constants (the Gaussian distribution corresponds to $b=2$).

The Cauchy distribution (4.6) does not have a mean, which we interpret as a reflection of the fact that we are dealing with a chain with open ends. Mandelbrot (1977) has investigated the generation of random flights for the Cauchy distribution and the patterns so obtained show a hierarchy of clusters, i.e. a cluster of values of A occur and then a large displacement is experienced in the value of A around which a new cluster of values develops, then another large shift occurs which starts a new cluster and so on.

The situation for a closed curve, where the integral is correctly identified with the area is quite different. In this case the $n=N$ (or equivalently $n=0$) term is absent in the sum in (4.3). The integral does not cover the entire range 0 to π and cannot be expressed in a closed form. However it does have the following limiting forms:

$$\ln P(g, N) \sim -(gNl^2)^2 \qquad gNl^2 \ll 1$$

and

$$\ln P(g, N) \sim -(gNl^2) \qquad gNl^2 \gg 1. \tag{4.9}$$

A numerical evaluation of $P(g, N)$ from (4.2) is shown in figure 2. We have confirmed that for large N ($N > 100$), $P(N, g)$ is only a function of Ng and can be accurately

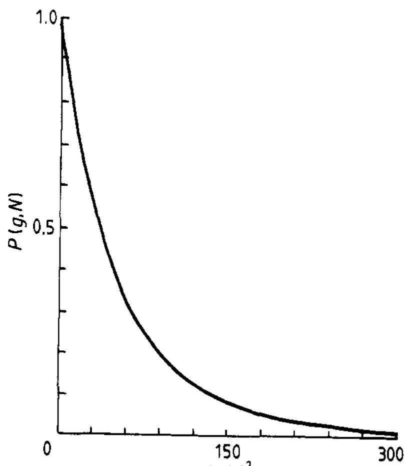

Figure 2. The characteristic function of the area distribution function for a closed curve. The graph was obtained by a numerical evaluation of (4.2) for $N=500$ and is accurately fitted by (4.10).

fitted by the form

$$P(gN)\exp\{a-[a^2+b^2(gNl^2)^2]^{1/2}\} \tag{4.10}$$

where

$$a=4.9523 \qquad b=0.4542. \tag{4.11}$$

Accuracy is maintained in $\ln P(Nl^2g)$ to at least two decimal places in the range $0<gNl^2<6$. The approximate form (4.10) has the advantage that it can be Fourier transformed to give

$$\begin{aligned} P(A, N) &= P(A/Nl^2) \\ &= (e^a/\pi)a[b^2+(A/Nl^2)^2]^{-1/2}K_1\{(a/b)[b^2+(A/Nl^2)^2]^{1/2}\} \end{aligned} \tag{4.12}$$

where K_1 is a modified Bessel function. The accuracy of this result can be checked by using the exact expression for $P(A, N)$ obtained from (4.1) and using (4.2) and (3.19)

$$P(A, N)=\int \mathrm{d}g\cos(gA)\prod_{n=1}^{N-1}\frac{\tan^2(n/N)}{\tan^2(n/N)+g^2l^4/16}. \tag{4.13}$$

The g integral is done by contour integration in the complex g plane. The integrand has double poles at

$$g=(\pm 4/l^2)\tan(\pi n/N) \qquad n=1,2,\ldots,N-1$$

and the residue theorem gives

$$P(A, N)=(1/l^2)\sum_{p=1}^{(N-1)/2} t_p\exp(-4At_p/Nl^2)(1+4At_p/Nl^2+4D_p)B_p \tag{4.14}$$

where

$$t_0=\tan(\pi p/N)$$

$$D_p=\sum_{\substack{n=1\\ n\neq p}}^{(N-1)/2} t_p^2/(t_p^2-t_n^2)$$

$$B_p=\prod_{\substack{n=1\\ n\neq p}}^{(N-1)/2} t_n^2/(t_p^2-t_n^2).$$

Figure 3 shows the exact result computed using (4.14) for $N=1000$. There is agreement between the approximate functional form (4.12) and (4.14) to at least two decimal places over the entire A/Nl^2 range. Unlike the result for the open chain, the distribution function (4.12) does have a finite mean, so that $\langle A\rangle \sim Nl^2$. However the distribution function does not satisfy the chain property (4.7). This property is characteristic of statistical fractal quantities and so we conclude that in this sense the closed loop is not a fractal object.

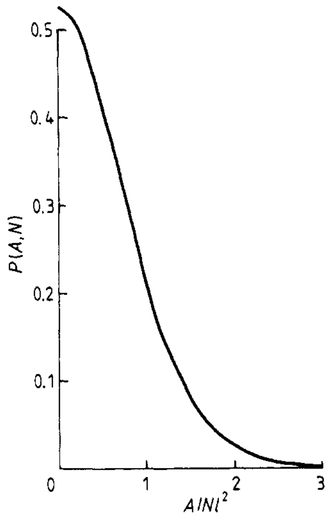

Figure 3. The area distribution function for a closed chain of N segments. This was numerically evaluated from (4.14) and is accurately fitted by (4.12).

5. Configurational properties

5.1. The end-to-end distance

The average distance between two points $(0, s)$ on the chain constrained to enclose an area A is obtained from the generating function (3.18) by the application of (3.15). This gives

$$\langle(\boldsymbol{r}(s)-\boldsymbol{r}(0))^2\rangle = \frac{\int \mathrm{d}g \cos(gA)P(g, N)R^2(g, N, S)}{\int \mathrm{d}g \cos(gA)P(g, N)} \tag{5.1}$$

where $R^2(g, N, s)$ is given by (3.21) and can be written as

$$R^2(g, N, s) = \frac{l^2}{N}\sum_{n=1}^{N} \frac{\sin^2(\pi ns/N)}{\sin^2(\pi n/N)} \frac{\tan^2(\pi n/N)}{\tan^2(\pi n/N) + g^2 l^4/16} \tag{5.2}$$

and

$$P(g, N) = \exp(-gNl^2/2).$$

For the open chain we can find an analytic expression for $\langle(\boldsymbol{r}(s)-\boldsymbol{r}(0))^2\rangle$ and so we have included the $n = N$ term in (5.2). In the $N \to \infty$ limit the sum is converted to an integral and we also replace

$$\tan(\pi n/N) \to \pi n/N \qquad \sin(\pi n/N) \to \pi n/N.$$

Then the term $R^2(g, N, s)$ is given by

$$R^2(g, N, s) = (2l^2/\pi)\int_0^{\pi/2} \mathrm{d}x \sin^2(xs)/(x^2 + g^2 l^4/16). \tag{5.3}$$

If we can extend the range of this integral from $\pi/2$ to ∞ then it can be evaluated in a closed form to give

$$R^2(g, N, s) = 2[1 - \exp(-sl^2 g/2)]/g. \tag{5.4}$$

Using this result the remaining integral over g in (5.1) can be evaluated to give

$$\langle(\boldsymbol{r}(s)-\boldsymbol{r}(0))^2\rangle_A=\frac{Nl^2}{2}(1+a^2)\ln\left(\frac{a^2+(1+s/N)^2}{(a^2+1)}\right) \tag{5.5}$$

where a is the scaled variable $2A/Nl^2$.

Figure 4 shows the dependence of $\langle(\boldsymbol{r}(s)-\boldsymbol{r}(0))^2\rangle$ on the area constraint A and the distance between the two points. Some limiting values are of interest: for short arc lengths $s \ll N$ the unperturbed random walk result is obtained:

$$\langle(\boldsymbol{r}(s)-\boldsymbol{r}(0))^2\rangle_A \simeq ls. \tag{5.6}$$

This is a reflection of the fact that the area or winding number constraint is a global rather than a local constraint, i.e. at short scales the curve does not perceive the constraint. For an imposed area $A \gg Nl^2$ the molecule is greatly perturbed and

$$\langle(\boldsymbol{r}(s)-\boldsymbol{r}(0))^2\rangle_A \simeq l^2 s(1+s/N)^2/2. \tag{5.7}$$

For $s \sim N$ this shows rod-like properties. Finally the accuracy and internal consistency of these results can be explicitly checked by evaluating the quantity

$$\langle R^2\rangle=\int P(A,N)\langle(\boldsymbol{r}(s)-\boldsymbol{r}(0))^2\rangle_A\,\mathrm{d}A.$$

The integrals are also available in closed form and the expected result

$$\langle R^2\rangle = l^2 s$$

is obtained.

5.2. *Free energy and mechanical properties*

The number of degrees of freedom $\Omega(R, A, N)$ available to a chain of N bond vectors subject to the constraints:

$$\boldsymbol{r}(s)-\boldsymbol{r}(0)=\boldsymbol{R}$$

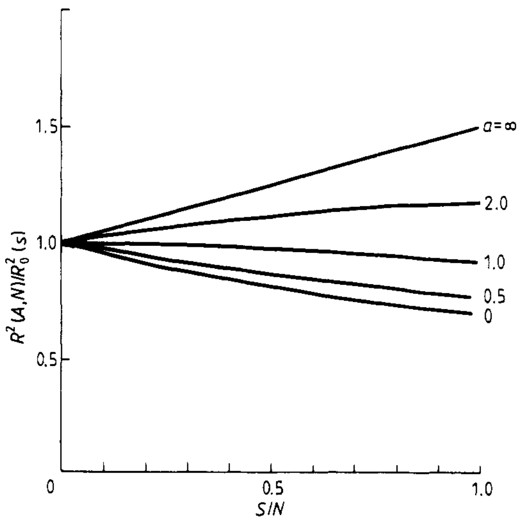

Figure 4. The distance between two points, an arc length sl apart, on an open chain subject to an area constraint A as a function of s for various values of $a=2A/Nl^2$. The curves are based on (5.5), $R_0^2(s)=l^2s$ and represents the unperturbed result.

and

$$A\{C\} = A$$

is proportional to

$$\langle \delta(\boldsymbol{r}(s) - \boldsymbol{r}(0) - \boldsymbol{R})\delta(A\{C\} - A)\rangle_{\{C\}}$$

and hence given in terms of the generating function $Z(\lambda, A, N)$ as

$$\Omega(R, A, N) \propto \int d^2\lambda \exp(i\lambda R) Z(\lambda, A, N). \tag{5.8}$$

$Z(\lambda, A, N)$ can be written from (3.22) in the form

$$Z(\lambda, A, N) = \int_{-\infty}^{\infty} dg \cos(gA) P(g, N) \exp(-\lambda^2 R^2(g, N, s))/4. \tag{5.9}$$

Using this form the integration over λ in (5.8) can be done exactly to give

$$\Omega(R, A, N) = \int_{-\infty}^{\infty} dg \cos(gA) P(g, N) \exp(-R^2/R^2(g, N, s)). \tag{5.10}$$

Unfortunately the form (5.4) for $R^2(g, N, s)$ does not readily lend itself to an analytic evaluation of the g integration. In order to complete this integral we use an approximate expression, which agrees with (5.4) in the limits $g \to 0$ and $g \to \infty$

$$1/R^2(g, N, s) = 1/sl^2 + g/2 \tag{5.11}$$

so that the g integrals can be done in a closed form. The result for the number of degrees of freedom can be written as

$$\begin{aligned}\Omega(R, A, N) &= \text{constant} \times \exp(-R^2/l^2 s) \\ &\quad \times \int dg \cos(gA) \exp[-g(NL^2 + R^2)/2](1/sl^2 + g/2) \\ &= \text{constant} \times [r^2/(r^4 + a^4) + (r^4 - a^2)/(r^4 + a^2)^2] \exp(-r^2)\end{aligned} \tag{5.12}$$

where r and a are the scaled variables

$$r^2 = (R^2/l^2 s + N/s) \qquad a = 2A/l^2 s. \tag{5.13}$$

The free energy is obtained in the usual way as

$$F = kT \ln \Omega \tag{5.14}$$

and the entropic force acting between the points 0 and s on the chain is defined by

$$\begin{aligned}\boldsymbol{f} &= -\partial F/\partial \boldsymbol{R} \\ &= (2/l^2 s)(\partial F/\partial r^2)\boldsymbol{R} \\ &= K(a, r)\boldsymbol{R}\end{aligned} \tag{5.15}$$

where $K(a, r)$ is the 'spring constant' associated with an arc length s of chain held at a distance $\boldsymbol{R}$ apart. Using (5.14) and (5.12) for the free energy

$$K(a, r) = K_0\left(1 + \frac{r^8 + 2r^6 - 6a^2r^2 - a^4}{(r^6 + r^4 + a^2r^2 - a^2)(a^2 + r^4)}\right) \tag{5.16}$$

where K_0 is the spring constant of the unrestricted chain and is given by

$$K_0 = 2kT/l^2 s \tag{5.17}$$

and is independent of the deformation $\boldsymbol{R}$.

The full range of behaviour contained in this result is shown in figure 5. We have taken an arc length $s = N$ and written the end-to-end distance as

$$R^2 = \langle R^2 \rangle_A E(\lambda) \tag{5.18}$$

where $\langle R^2 \rangle_A$ is the equilibrium end-to-end distance in the presence of the area constraint $A\{C\} = A$. $E(\lambda)$ is a function of the deformation λ with $E(1) = 1$ representing the undeformed state. Using (5.5) for $\langle R^2 \rangle_A$, the reduced variable r^2 can be written as

$$\begin{aligned} r^2 &= 1 + \langle R^2 \rangle_A / Nl^2 \\ &= 1 + (1 + a^2) \ln[(4 + a^2)/(1 + a^2)] E(\lambda). \end{aligned} \tag{5.19}$$

Figure 5 shows $K(a, r)/K_0$ plotted as a function of $E(\lambda)$ for $0 < E < 7$ and for various values of $a = 2A/Nl^2$. When $E(\lambda) > 1$ a range of behaviour is observed with K decreasing (softening) with deformation for $A \leq Nl^2$ $(a < 1)$ and increasing (hardening) for $a > 1$. We also observe that the sign of the entropic force f changes as $E \to 0$ $(\boldsymbol{r} \to 0)$. This is qualitatively similar to a spring with a natural length r_0, i.e. if we write

$$f = K_0(\boldsymbol{r} - \boldsymbol{r}_0)$$

and take $\boldsymbol{r}_0 = r_0 \hat{\boldsymbol{r}}$, then

$$\begin{aligned} f &= K_0(1 - r_0/r)\boldsymbol{r} \\ &= K(r)\boldsymbol{r}. \end{aligned} \tag{5.20}$$

Then $K(r)$ shows a qualitative dependence on r similar to that shown in figure 5 with $r_0 < 0$ for $a < 1$ and $r_0 > 0$ for $a > 1$.

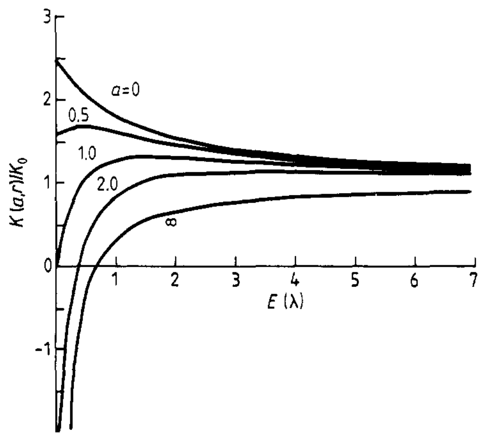

Figure 5. The tensile force f needed to maintain a given end-to-end distance $\boldsymbol{R}$ of a chain subject to an area constraint. If we write $f = K(a, r)\boldsymbol{R}$, then we have plotted $K(a, r)/K_0$, where K_0 is the unperturbed spring constant. E is the deformation from equilibrium and a is the scaled variable $2A/Nl^2$.

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