Link energy and universality class of a swollen annular knot-free homopolymer chain

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A new method for incorporating topological constraints in polymer systems is proposed. The method is based on energy functionals of links and entanglements. The fractal dimensionality of a swollen, annular, knot-free homopolymer chain is shown to be $\mathscr{D}=4/3$.

A fundamental problem in the analytic theory of polymer cross-links and entanglements is to identify geometric characteristics of the trajectories of chains which correctly reflect the tendency of the polymer chains to knot and become cross-linked and which are convenient for calculations. These characteristics do not necessarily have to be topological invariants. Of particular interest are energy characteristics of links and entanglements.[1-3] The energy is calculated along the trajectory $\gamma(u)$ of a link or entanglement. The minimum of the energy of all realizations of the given type of link or entanglement is a topological invariant. The number of types of links for which there exists a realization with an energy no greater than E increases roughly exponentially with E. A key idea here is to evaluate the decrease in entropy due to topological constraints by means of an energy functional which depends on the parameter λ. It turns out that we have $\lambda=3\mathscr{D}/2$, where $\mathscr{D}$ is the fractal dimensionality of the trajectory of the polymer chain. The closed system of equations which arises can be used to find $\mathscr{D}$.

For a straightened curve $\gamma(u)$ of length L with a parameter λ satisfying $2\leqslant\lambda<3$, we define the following energy functionals:

$$E_\lambda(\gamma)=\left\{\int\int\left(|\gamma(u)-\gamma(v)|^{-\lambda}-D[\gamma(u),\gamma(v)]^{-\lambda}\right)\right.$$
$$\left.\times|\dot\gamma(u)||\dot\gamma(v)|\,dudv\right\}^{1/(\lambda-1)}L^{(\lambda-2)/(\lambda-1)},\qquad(1)$$

$$\tilde E_\lambda(\gamma)=\left\{\frac{1}{4\pi}\int\int\frac{|[\dot\gamma(u),\dot\gamma(v),\gamma(u)-\gamma(v)]|}{|\gamma(u)-\gamma(v)|^{\lambda+1}}\,dudv\right\}^{1/(\lambda-1)}L^{(\lambda-2)/(\lambda-1)},\qquad(2)$$

where $|\gamma(u)-\gamma(v)|$ is the distance, and $D[\gamma(u),\gamma(v)]$ the shortest distance, along the curve between $\gamma(u)$ and $\gamma(v)$. Functionals (1) and (2) can also be used at $\lambda\geqslant3$, if we introduce an appropriate cutoff of the integration. For entanglements we have $D[\gamma(u),\gamma(v)]=\infty$ if $\gamma(u)$ and $\gamma(v)$ belong to different components.

Functionals (1) and (2) have similar physical meanings and are invariant under change of scale. We can point out some properties[2,3] in the $\lambda=2$ case: $\tilde E_2(\gamma)$ is the average number of double intersections in projections of $\gamma(u)$ onto a plane, and

$E_2(\gamma)$ is conformally invariant.[3] We denote by T an arbitrary element of the Möbius group (all conformal transformations). If $\gamma(u)$ and $T[\gamma(u)]$ are contained in R^3, then we have $E_2(\gamma)=E_2[T(\gamma)]$. If $T(\gamma)$ passes through ∞, we have $E_2(\gamma)=E_2[T(\gamma)]+4$.

We assume that, for an isotopic link of γ, the minimum possible number of double intersections in projection onto a plane is $c[\gamma]$; we then have $E_2(\gamma)\geqslant 2\pi c[\gamma]+4$. There is an upper limit on the number $[K_2(E)]$ of different types of links which have representatives with $E_2(\gamma)\leqslant E$ (Ref. 3):

$$K_2(E)\leqslant 2\times 24^{(E-4)/2\pi}. \tag{3}$$

An exponential lower estimate of $K_2(E)$ can be found from the following considerations: The number of types of links with two bridges increases roughly as[4] $2^n/6$, where $c[\gamma]\leqslant n$. A link with two bridges and with $c[\gamma]\leqslant m$ can be put inside a cylinder in such a way that we have $E_2(\gamma)\leqslant l_0+l_1 m$ for constants l_0 and $l_1>0$.

We denote by $K_\lambda(E)$ the number of different types of links which have representatives with an energy $E_\lambda(\gamma)\leqslant E$, by analogy with $\tilde{K}_\lambda(E)$ for (2). In this context it is simpler to deal with functional (2), and we have[4]

$$2^E\leqslant \tilde{K}_2(E)\leqslant 2\times 24^E. \tag{4}$$

Working from an inequality from the theory of convex functions,[5] we see that $\tilde{E}_\lambda(\gamma)$ is a strictly increasing function of λ. On the basis of this result and the right side of (4) we find an exponential upper estimate of $\tilde{K}_\lambda(E)$. An exponential lower estimate of $\tilde{K}_\lambda(E)$ can be proved by the same method as was used above for $K_2(E)$.

We denote by $\gamma(u)$ a typical representative from the ensemble of chains with a monomer unit of length l, with N units, and with a fractal dimensionality $\mathscr{D}$.

Heuristic principle: the parameter $\lambda=3\mathscr{D}/2$. Motivation. In the trajectory of an annular knot-free chain we consider two subchains consisting of n_1 and n_2 units, respectively. Both subchains are inside a sphere of radius r. We wish to evaluate the contribution of the "topological interaction" of the two subchains to the decrease in entropy, drawing on the analogy[6] with the motion of a charged particle in a magnetic field. The average energy density of the field produced by a unit current flowing in the first subchain, inside the sphere and outside a thin tube whose axis is the first subchain, is $\sim n_1^{2/\mathscr{D}} l/r^3$. A logarithmic factor is ignored here. The dimensionality of the length of the second subchain is $\mathscr{D}$; hence we have the dimensionless combination $n_1 n_2/(r/l)^{3\mathscr{D}/2}$ and $\lambda=3\mathscr{D}/2$.

The mathematical expectation of a Gauss invariant of the modulus of the entanglement of two subchains is $\sim[n_1 n_2/(r/l)^{3\mathscr{D}/2}]^{1/2}$. The values of n_1 and n_2 must be large enough to get outside the region of the phantom approximation.

The case $\mathscr{D}=2$ was studied in Ref. 7 in another problem and by another method. The case $\mathscr{D}=3$, the "crumpled globule state," was studied in Refs. 8 and 9 by a different technique.

Let us calculate $E_\lambda(\gamma)$, where $\lambda=3\mathscr{D}/2$, for an annular knot-free chain. We will evaluate the quantity in braces (curly brackets) in expression (1). The standard information being used here is covered in some monographs.[10,11] We denote by r the distance between the first and N_1th units of the chain; we have r, $N_2=N-N_1$ and $x\sim r/l$. The expression for the differential probability is

$$\sim(N_1N_2)^{-(3+g)/\mathscr{D}}\exp\{-(N_1^{-\delta/\mathscr{D}}+N_2^{-\delta/\mathscr{D}})x^\delta\}x^{2+2g}dx, \tag{5}$$

where, according to Ref. 12, it is reasonable to assume $\delta=\mathscr{D}/(\mathscr{D}-1)$. The differential for the quantity in braces is found from (5) by multiplying by $x^{-3\mathscr{D}/2}$. The second contribution, with the factor $\sim\tilde{N}^{-3\mathscr{D}/2}$, where $\tilde{N}=\min\{N_1,N_2\}$, is being ignored. Integrating and dividing, we find

$$\sim\{\Gamma[(6+4g-3\mathscr{D})/2\delta]/\Gamma[(3+2g)/\delta]\}\{N_1^{-\delta/\mathscr{D}}+N_2^{-\delta/\mathscr{D}}\}^{3\mathscr{D}/2\delta}, \tag{6}$$

where $\Gamma[\ ]$ is the gamma function. Integrating (6) from N_0 to $N-N_0$, and then multiplying by N, we find

$$\sim N^{1/2}\int_\epsilon^{1-\epsilon}[x^{-m}+(1-x)^{-m}]^{3/2m}dx=4N^{1/2}\epsilon^{-1/2}[1-\epsilon^{1/2}a(\mathscr{D})], \tag{7}$$

$$E_\lambda(\gamma)\sim N[1-(N_0/N)^{1/2}(3\mathscr{D}/2-1)^{-1}a(\mathscr{D})], \tag{8}$$

$$\frac{da}{d\mathscr{D}}=\frac{3(\mathscr{D}-1)^4}{4}\int_\epsilon^{1-\epsilon}x^{-m}[x^{-m}+(1-x)^{-m}]^{3/2m-1}\ln\left(\frac{x^{-m}}{x^{-m}+(1-x)^{-m}}\right)dx, \tag{9}$$

where $\epsilon=N_0/N\ll 1$ and $m=(\mathscr{D}-1)^{-1}$. For $\mathscr{D}<3$, the integral in (9) can be evaluated between limits of 0 and 1. The decrease in entropy results from the absence of knots: $A_0N-A(\mathscr{D})N^{1/2}$, where $A(\mathscr{D})\sim(3\mathscr{D}/2-1)^{-1}a(\mathscr{D})$. We note that we have $dA/d\mathscr{D}<0$, since we have $a(\mathscr{D})>0$ and $da/d\mathscr{D}<0$. This approach does not allow us to calculate A_0, but it is sometimes possible to prove that we have $dA_0/d\mathscr{D}=0$.

As a concrete example we consider a swollen annular homopolymer chain which forms a trivial link. We will show that the fractal dimensionality is $\mathscr{D}=4/3$.

1. Derivation from considerations associated with a fixed point of the renormalization group. The discussion is like that for a charged chain,[10] but the "topological repulsion" is specified by the exponent $\lambda=3\mathscr{D}/2$. Two blobs of size L, separated by distance R, contribute $\sim(L/l)^2/(R/l)^\lambda$ to the decrease in entropy. If we take two subchains of n blobs, and if n blobs form one superblob, then L/l becomes $n^{1/\mathscr{D}}(L/l)$, and R/l correspondingly becomes $n^{1/\mathscr{D}}(R/l)$. At the fixed point we must have $n^{(2-\lambda)/\mathscr{D}}=1$; hence we have $\lambda=2$ and $\mathscr{D}=4/3$.

2. Flory's method.[10,11]. We denote by R the size of the swollen ball, by F the free energy, by T the absolute temperature, and by B the second virial coefficient. The virial coefficient changes because of the topological repulsion. In the swelling regime we have $B\to B_*>0$ as $N\to\infty$. The decrease in entropy due to the absence of knots is $A_0N-A(\mathscr{D})N^{1/2}$. It is reasonable to suggest that we have $dA_0/d(R/l)=0$, since

only long-wave changes in the conformal chain are important. As $N \to \infty$, we find the following equation from $d(F/T)/d(R/l) = 0$ and $\mathscr{D} = \ln N/\ln(R/l)$:

$$(R/l)^2 = (\mathscr{D}^2/6)(-dA/d\mathscr{D})N^{3/2}/\ln N + (B_*/2)N^3/(R/l)^3. \quad (10)$$

As $N \to \infty$, we have, correspondingly, $R/l \sim N^{3/4}(\ln N)^{-1/2}$.

For a self-avoiding chain on a plane we also have $\mathscr{D} = 4/3$ (see, for example, the review in Ref. 13). The conformal invariance of the function $E_2(\gamma)$ suggests that in the limit $N \to \infty$ the trajectory of a swollen, annular, knot-free homopolymer chain is also conformally invariant. If this is indeed the case, then we see the reason for the intriguing agreement of the values of $\mathscr{D}$. We also obtain some additional information on the correlation functions.[14]

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