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# Knot complexity and related observables from path integrals for semiflexible polymers

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**Abstract.** We analyse earlier obtained numerical results for the knot complexity and the topological persistence length (i.e. the minimal number of steps on the lattice needed for the knot to be formed) with help of well known path integrals for semiflexible chains. In addition, we provide an estimate for the number of different knots having knot diagrams with exactly  $n$  crossings. Analytical results obtained are in satisfactory agreement with the available numerical data.

## 1. Introduction

Recently, numerical results have become available for the average writhe and knot complexity [1]. Independently, the minimal number of steps on a three-dimensional [ $\mathbf{R}^3$ ] cubic lattice beyond which the first non-trivial knot can be formed was estimated [2, 3] following earlier crude estimates by Delbrück [4]. Knot complexity (to be determined below) plays an important role because the number of distinct knots is directly related to the knot complexity [5, 6].

The presence of knots is expected to play an important role in the kinetics of the coil–globule transition [7, 8] as well as in the rheological properties of polymer solutions [9–11].

The existing description of knots in terms of knot polynomials [12, 13] does not allow a direct comparison with the available experimental (numerical) data. Recently, an alternative approach to knotted polymers was proposed [14]. It is based on the differential-geometric properties of knotted circular polymers and allows us, in principle, to obtain analytically the observed polymer length ( $N$ ) dependences of the physically interesting quantities. Using this differential-geometric approach the  $N$ -dependence of the average writhe  $\langle |Wr| \rangle$  for circular polymers was obtained and is found to behave as  $\sqrt{N}$  in agreement with the existing numerical and analytical (non-path-integral) results. The ability to obtain meaningful analytical information about knotted polymers is based on two largely independent factors. First, to obtain the analytical results, we need to have the explicit analytic expressions for physically observed quantities. Second, we have to have the polymer path integrals (see e.g. [15] for the traditionally used models) which will enable us to calculate (or to estimate) these observables. These requirements are necessary but may not be sufficient. For example, we may have an analytic expression for the knot complexity (see below) which

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is very difficult to calculate (or even to estimate) analytically. At the same time, we may have formal expressions for the path integrals which we may not be able to use (because of technical and other reasons as will be explained below). For these reasons, some additional information is needed. It is provided by independent mathematical results, e.g. Milnor's inequality [16] for knotted rings, discussed in section 2, and knot energy [17], discussed in section 3. Using Milnor's inequality combined with the existing path integral methods for the semiflexible polymers, we obtain in section 2 an analytic estimate for the topological persistence length  $l_T$  (i.e. the minimal number of steps on the lattice for a non-trivial knot to be formed).

In section 3 we use known connection(s) between the knot complexity  $c[\gamma]$  and the knot energy  $E[\gamma]$  [17] in order to estimate the knot complexity as a function of polymer length  $N$ . As a by-product, we also estimate the number of different knots of given complexity and provide an independent check of Milnor's inequality (section 2) based on the known results for the energy for the unknot. Results obtained for the average complexity  $\langle c[\gamma] \rangle$  provide the upper and lower bounds for this quantity which (within the approximations made) is estimated to behave as  $N < \langle c[\gamma] \rangle < N^{1.5}$  while the numerical data [1] produce  $\langle c[\gamma] \rangle \propto N^{\alpha_c}$  with  $\alpha_c \simeq 1.122 \pm 0.005$ . In section 4 we explain why the exponent 1.5 is too high and why the 'true' upper bound exponent should lie *below* 1.4. To improve the above estimate, more sophisticated path integrals are required. They are also discussed in section 4 where, in addition, some practical applications of the obtained results are proposed.

## 2. Topological persistence length from Milnor's inequality

In our previous work [18] we have introduced a notion of the topological persistence length which we would now like to review briefly. To generate knots on a regular lattice several requirements should be met. First, there should be a routine which generates closed self-avoiding (SAW) loops. Second, there should be another routine which allows us to distinguish between the different topologies. Third, in order to achieve an adequate statistical accuracy the number of closed polymer configurations of each topological type should be large to account for all possibilities of putting a knot of a given type on the lattice. Michels and Wiegel [19] have obeyed the above requirements, except the requirement of self-avoidance. More recently, Windwer [20] has taken the above restriction into account and incorporated the self-avoidance constraint into his computer routine. The results of his simulations are in complete accord with Milnor's theorem [16] as we shall demonstrate shortly. The latest results of Diao [2, 3] differ somewhat from that of Windwer but can also be explained using Milnor's inequality.

The number  $Q_N^0$  of closed unknotted SAW configurations of walks of  $N$  steps in three dimensions obeys the following equation ( $N \rightarrow \infty$ ) (obtained by Des Cloizeaux, see e.g. [18]):

$$Q_N^0 = \hat{C}_0 (\mu^0)^N N^{-3\nu} \quad (2.1)$$

where  $\hat{C}^0$  and  $\mu^0$  are some non-universal (lattice-dependent) constants, and  $\nu$  is the correlation length exponent (for SAW  $\nu \simeq \frac{3}{5}$  in three dimensions). Windwer [20] had used the analytical form of (2.1) to fit his numerical data. Specifically, if one assumes that for SAW knots

$$\hat{Q}_N = \hat{C}(\hat{\mu})^N N^\omega \quad (2.2)$$

then one can construct the ratio  $\xi_N = Q_N^0 / \hat{Q}_N$  given by

$$\xi_N = \tilde{C} \tilde{\mu}^N N^\alpha \quad (2.3)$$

which is the probability for a closed walk of  $N$  steps to remain unknotted. Windwer found  $\alpha = 0$ ,  $\tilde{\mu} = 0.9949$  and  $\tilde{C} = 1.2325$ . The result (2.3) is in complete agreement with an independent theoretical result by Sumners and Whittington [21]. Equation (2.3) can be conveniently rewritten as ( $\alpha = 0$ )

$$\xi_N = \tilde{C} \left( \frac{1}{\tilde{C}} \right)^{N/l_T} \tag{2.4}$$

where the topological persistence length  $l_T$  is defined to be the least  $N$  for which a knot may occur. Therefore

$$\xi_N = 1 = \tilde{C} \tilde{\mu}^{l_T} \tag{2.5}$$

which follows from (2.3). For  $\tilde{\mu}$  and  $\tilde{C}$  given above one obtains  $l_T \approx 41$ . In our previous work [18] we obtained analytically

$$\tilde{C} = q^{1/2} \exp \left\{ -\frac{\pi}{6} \hat{C} \right\} \tag{2.6}$$

where  $q$  is the number of states of the  $q$ -state two-dimensional Potts model and  $\hat{C}$  is the central charge. We provided arguments which select  $q = 4$  (and, hence,  $\hat{C} = 1$ ) which produce for  $\tilde{C}$  the result  $\tilde{C} = 1.1847696$ , which differs from that obtained by Windwer by about 4%. The lattice-specific topological persistence length  $l_T$  was left undetermined. In this paper, based on Milnor’s theorem [16] we shall demonstrate that  $l_T \simeq 40$ , which is in excellent agreement with Windwer’s results. The above result, if properly interpreted, is also in agreement with the results of Diao [2, 3] as will be explained at the end of this section.

To begin our analytical derivation of  $l_T$ , the following Schwarz inequality [22], valid for any closed curve, is very helpful:

$$(2\pi)^2 \leq \left( \int_0^N d\tau |k(\tau)| \right)^2 \leq N \int_0^N d\tau k^2(\tau) \tag{2.7}$$

where  $k(\tau)$  is the local curvature of the curve of length  $N$ . If we think of the curve as being made of a real physical material, e.g. a polymer, then using polymer terminology we have to perform the statistical average of (2.7) with the help of the path integral for semiflexible chains (see e.g. [15, 23]). The statistical average  $\langle \dots \rangle$  in terms of such a path integral can be defined as

$$\langle \dots \rangle = \mathcal{N} \int_{\mathbf{n}(0)=\mathbf{n}(N)} D[\mathbf{n}(\tau)] \prod_{\tau} \delta(\mathbf{n}^2(\tau) - 1) \dots \exp \left\{ -\frac{\gamma}{2} \int_0^N d\tau k^2(\tau) \right\} \tag{2.8}$$

where the normalization constant  $\mathcal{N}$  is chosen in such a way that  $\langle 1 \rangle = 1$  and the constant  $\gamma$  is related to the rigidity of the polymer’s backbone. In the fully flexible limit,  $\gamma \rightarrow 0$ , the polymer chain behaves as Gaussian [23]. It is known [15, 24] that in this limit the polymer Kuhn’s step length  $l = 2\gamma$ . We can associate in this limit the length  $l$  with the unit step length of the random walk on the regular cubic lattice [23].

Such identification should be done with some caution, however. Indeed, we can make it only if the discrete analogue of the path integral (2.8) is known and is well defined. As the results of [23] indicate, the lattice-dependent factors like  $\sqrt{2}$ , etc are likely to occur when the identifications between the discrete and the continuum formulations are made (see e.g. p 2475 of [23]). These factors are responsible for some differences in the final results for  $l_T$ . From the experimental point of view, the measured combination  $2\gamma N = lN = \langle R^2 \rangle$  does not allow us to separate  $l$  and  $N$ . Some independent measurement of  $l$  is required [25] which

inevitably introduces some errors. Hence, both the discrete and the continuum formulations can provide only the upper and lower bounds for  $l_T$ , as will be further explained below.

Combining (2.7) and (2.8) we obtain

$$(2\pi)^2 \leq \left\langle \left( \int_0^N d\tau |k(\tau)| \right)^2 \right\rangle \leq N \left\langle \int_0^N d\tau k^2(\tau) \right\rangle. \quad (2.9)$$

This inequality should be valid for any closed polymer configuration. At the same time, according to Milnor [16], in case the closed curve is a nontrivial knot (of any kind) the following inequality should hold:

$$\int_0^N d\tau |k(\tau)| \geq 4\pi. \quad (2.10)$$

Combining inequalities (2.9) and (2.10) we obtain the following result for the knotted curves:

$$(4\pi)^2 \leq \left\langle \left( \int_0^N d\tau |k(\tau)| \right)^2 \right\rangle \leq N \left\langle \int_0^N d\tau k^2(\tau) \right\rangle. \quad (2.11)$$

The saddle point treatment of the path integral (2.8) was performed by Langer and Singer [26, 27] who considered a three-dimensional variational problem for the functional of the following type:

$$\mathcal{F}_{LS}[\gamma] = \int_0^N ds (k^2(s) + m^2) \quad (2.12)$$

where  $ds$  is the length element along the curve  $\gamma$  and the Lagrange multiplier  $m^2$  accounts for the fact that the length of the curve is fixed. As was shown by Griffiths [28] and later by Bryant and Griffiths [29] (and even more recently in [30]), the variational problem given by (2.12) produces trajectories which are identical to those obtained from the functional

$$\mathcal{F}_{BG}[\gamma] = \frac{1}{2} \int_0^N ds k^2(s) \quad (2.13)$$

where the curves are constrained to lie on some surfaces of constant curvature (the numerical value of the curvature constant is directly related to  $m^2$  [30]). Langer and Singer [27] have shown that for the problem defined by (2.12), 'There exist a countable infinity of (similarity classes of) closed non-planar elastic curves in  $\mathbf{R}^3$ . All such elasticae are embedded and lie on embedded tori of revolution. Infinitely many of these are knotted and the knot types which thus occur are precisely the  $(m, n)$ -tours knots satisfying  $m > 2n$ . The integers  $m, n$  determine the elasticae uniquely (up to similarity)'.

To actually perform the averaging, several steps are required. First, we would like to point out that for the semiflexible polymers it is the dimensionless combination  $N/\gamma$  which actually determines how stiff the polymer chain is. In terms of Kuhn's length  $l$  we have  $\omega = \frac{N}{l} = \frac{N}{2\gamma}$ . In view of this, the action functional in (2.8) can be rewritten as

$$S = \frac{\gamma}{2} \int_0^N d\tau k^2(\tau) = \frac{1}{4\omega} \int_0^1 dt k^2(\tau) \quad (2.14)$$

where in arriving at the last equality we have taken into account that in the case of natural parametrization,  $\mathbf{n}^2 = 1$ , we have  $k^2(\tau) = (\frac{dn}{d\tau})^2$  and  $\mathbf{n} = \frac{dr}{d\tau}$  where  $\mathbf{r}(\tau)$  is the spatial position of the polymer segment at contour position  $\tau$  [15]. Combining (2.8), (2.11) and (2.14) we obtain

$$N \left\langle \int_0^N d\tau k^2(\tau) \right\rangle = \left\langle \int_0^1 dt k^2(\tau) \right\rangle = -4 \frac{\partial}{\partial \omega^{-1}} \ln I(\omega) \quad (2.15)$$

where

$$\begin{aligned} I(\omega) &= \int_{n(N)=n(0)} D[n(\tau)] \prod_{\tau} (n^2(\tau) - 1) \exp \left\{ -\frac{1}{4\omega} \int_0^1 d\tau k^2(\tau) \right\} \\ &= \sum_{n=0}^{\infty} (2n+1) \exp\{-\omega(n+1)n\}. \end{aligned} \quad (2.16)$$

In arriving at the last line we have used the results of our previous work [14]. As in this reference, we would like to replace the summation by integration (which corresponds to the semiclassical level of approximation). This then produces

$$I(\omega) \simeq \int_0^{\infty} dx 2x \exp(-\omega x^2). \quad (2.17)$$

Combining (2.15) and (2.17) produces (within the approximations made)

$$\left\langle \int_0^1 d\tau k^2(\tau) \right\rangle = 4\omega. \quad (2.18)$$

Combining this result with the inequality (2.11) we obtain

$$(4\pi)^2 \leq 4\omega \quad (2.19a)$$

or

$$(2\pi)^2 \leq \omega. \quad (2.19b)$$

Since  $(2\pi)^2 \approx 40$  and since  $\omega$  is the effective number of steps on the lattice we obtain

$$\omega \geq 40 \quad (2.20)$$

which is in excellent agreement with the numerical results of Windwer [20], see e.g. (2.5). At the same time, if we were to choose the rescaled length,  $N \rightarrow N\sqrt{2}$  (or, equivalently the rescaled Kuhn's length,  $l \rightarrow l/\sqrt{2}$ ) we would obtain instead

$$\omega \geq 28 \quad (2.21)$$

which is in good agreement with Diao's rigorous calculation [2, 3] that  $l_T = 24$  for knots on the cubic lattice. Since the factors like  $\sqrt{2}$  reflect the symmetry of the cubic lattice and naturally emerge in the discretized models for the semiflexible polymers [23, 31], the results (2.20) and (2.21) represent the upper and lower bound estimates for  $l_T$  on the cubic lattice. Evidently, if we were to choose a different lattice, the results for  $l_T$  might be somewhat different. If we were to ask a question: 'What is the minimal number of edges (in continuum) required to represent a given knot?' [32], the result would be a topological invariant. Unfortunately, it cannot be used for most real polymers since its existence requires a *fixed* number of bends for the otherwise completely rigid polymer segments (edges) which, in addition, should form a closed polygon in three-dimensional space. The angles between the edges in such a polygon are quite arbitrary. Both the fixed number of bends and the arbitrariness of angles between the segments are not characteristic for real polymers. For polymers the number of bends is a random variable and the angles between the bends are *not* arbitrary. The path integral analysis of the  $l_T$  problem is just a reflection of these facts.

### 3. Entanglement complexity and knot energy

Recently, we have performed a path integral calculation of the average writhe ( $Wr$ ) for closed SAW [14]. The writhe is an interesting geometric (non-topological) measure of the entanglement complexity of closed SAW [12]. To understand why this is so, we would like to remind the reader that our information about any given knot is mainly based on the analysis of its projection onto some two-dimensional plane. As a result of such projection, we obtain a four-valent graph for which we have to assign information at each vertex (otherwise the same graph will correspond to more than one knot). The rule consists in assigning under- (over-) crossings at each vertex. If, in addition, we select an orientation along the contour path, then for each over-crossing we can assign the sign ‘ $\pm 1$ ’ according to the usual conventions. If we move along the contour, the algebraic sum of these signed crossing numbers defines the writhe of the closed curve [12, 13]. Since the writhe is not a topological invariant, by repeating this procedure for another plane whose normal is oriented in a direction different from the original normal direction, we would obtain a different value for the writhe. Repeating this procedure many times we can thus define the angular averaged writhe of a knot or oriented link.

The above statements can now be made more precise by using the analytical expression for the writhe [14]:

$$Wr[\gamma] = \frac{1}{4\pi} \int_0^N d\tau \int_0^N d\tau' \frac{(\dot{\mathbf{r}}(\tau) \times \dot{\mathbf{r}}(\tau')) \cdot (\mathbf{r}(\tau) - \mathbf{r}(\tau'))}{|\mathbf{r}(\tau) - \mathbf{r}(\tau')|^3} \quad (3.1)$$

where  $\dot{\mathbf{r}}(\tau) = \frac{d\mathbf{r}}{d\tau}$ . Such a defined writhe has a clear geometrical meaning. Let  $\mathbf{r}(\tau)$  be an embedding of a circle  $\gamma$  into  $\mathbf{R}^3$ . We can construct a unit vector

$$\mathbf{n}(\tau, \tau') = \frac{\mathbf{r}(\tau) - \mathbf{r}(\tau')}{|\mathbf{r}(\tau) - \mathbf{r}(\tau')|} \quad (3.2)$$

which provides a Gauss map  $S' \times S'$ -(diagonal)  $\rightarrow S^2$ . The degree of such a defined Gauss map (i.e. the winding number) is writhe [12, 17]. One can consider the absolute value  $|Wr[\gamma]|$  instead, and its angular average  $\langle |Wr[\gamma]| \rangle$  as described above. Calculations of this quantity were performed in [14] with the result

$$\langle |Wr[\gamma]| \rangle \propto \sqrt{N} \quad (3.3)$$

which is in excellent agreement with the existing numerical data [1]. At the same time, the same authors also enumerated the average entanglement complexity  $c[\gamma]$  which differs from the writhe by the rule by which the crossings in the projection plane are calculated. In the case of entanglement complexity, the signs of crossings are disregarded so that  $c[\gamma]$  is a non-negative number by construction [12]. The averaged entanglement complexity is found numerically to scale as

$$\langle c[\gamma] \rangle \propto N^{\alpha_c} \quad (3.4)$$

with  $\alpha_c = 1.122 \pm 0.005$ . The authors of [1] caution the reader that ‘this value is likely to be an underestimate’. They suggest (without proof) that  $1 \leq \alpha_c \leq 2$ . Here we analytically re-examine these results in the light of recent developments in knot theory [17, 33].

As was shown by Arnold [34] and more recently in [17, 33], the entanglement complexity  $c[\gamma]$  also has an analytic expression which is related to the expression for the writhe (3.1). Indeed, following [17], we obtain

$$c[\gamma] = \frac{1}{4\pi} \int_0^N d\tau \int_0^N d\tau' \frac{|(\dot{\mathbf{r}}(\tau) \times \dot{\mathbf{r}}(\tau')) \cdot (\mathbf{r}(\tau) - \mathbf{r}(\tau'))|}{|\mathbf{r}(\tau) - \mathbf{r}(\tau')|^3}. \quad (3.5)$$

In general,

$$|Wr[\gamma]| \neq c[\gamma]. \tag{3.6}$$

According to [35], the relation between  $Wr$  and  $c$  can be formulated in terms of the Bennequin conjecture stated below. If  $\gamma$  is constructed as the closure of a braid on  $\hat{n}$  strings, then

$$\frac{1}{2}(|Wr[\gamma]| - \hat{n} + 1) \leq u[\gamma] \leq \frac{1}{2}(c[\gamma] - \hat{n} + 1) \tag{3.7}$$

where  $u[\gamma]$  is the unknotting number (i.e. the minimal number of self-crossings that will turn the knot into an unknot). Unlike  $Wr[\gamma]$  and  $c[\gamma]$ , the unknotting number  $u[\gamma]$  is a topological invariant [12, 36]. The minimum number of strings in any braid representation for a given knot is defined as the braid index  $\beta[\gamma]$  [37]. For the unknot  $\beta[\gamma] = 1$  and, in general,

$$\beta[\gamma] \leq s[\mathcal{D}] - \text{ind}[\mathcal{D}] \tag{3.8}$$

where  $s[\mathcal{D}]$  is the number of Seifert circles obtained from a given planar knot diagram  $\mathcal{D}$  for some knot  $\gamma$ . These circles are obtained by splitting each crossing of  $\mathcal{D}$  in such a way that the resulting knot diagram becomes a set of closed non-intersecting (disconnected) Jordan curves (Seifert circles). The index of the knot diagram,  $\text{ind}[\mathcal{D}]$ , is defined in [37]. In general, its definition is rather complicated. Therefore, we would like to quote the related result which is more familiar to physicists. As a by-product, we shall obtain an inequality similar to (3.7) which provides an additional support to the Bennequin conjecture.

Begin with a two-variable link (knot) polynomial  $P_\gamma(v, z)$  for the oriented link (knot)  $\gamma$ . Following [38] we write

$$\frac{1}{v}P_{\gamma^+} - vP_{\gamma^-} = zP_{\gamma^0} \tag{3.9}$$

where  $\gamma^+$ ,  $\gamma^-$  and  $\gamma^0$  have link (knot) diagrams which differ by one crossing (figure 1).

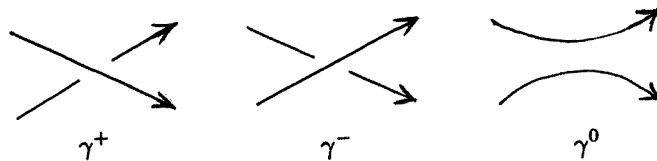


Figure 1.

Using (3.9) and  $P_{\text{unknot}} = 1$ , this ‘HOMFLY’ polynomial of any link (knot) can be written as a polynomial in  $z$  or a Laurent polynomial in  $v$ . In the first case one has  $P_\gamma(v, z) = \sum_{n=3}^{n=E} a_n(z)v^n$  with  $a_e(z) \neq 0 \neq a_E(z)$ , while in the second one has  $P_\gamma(v, z) = \sum_{n=m}^{n=M} b_n(v)z^n$  with  $b_m \neq 0 \neq b_M$ . By definition [37], the  $v$ -span  $(P_\gamma) = E - e$  and  $z$ -span  $(P_\gamma) = M - m$ . Using these definitions, it can be shown [37] that

$$\frac{1}{2}[v\text{-span}(P_\gamma)] \leq \beta[\gamma] - 1 \leq \hat{n} - 1 \tag{3.10}$$

where  $\beta[\gamma]$  has the same meaning as in (3.8). Moreover, according to [38], we also have

$$M \leq c[\gamma] - (s[\mathcal{D}] - 1). \tag{3.11}$$

In view of (3.8), we may write as well

$$(\beta[\gamma] - 1) + \text{ind}[\mathcal{D}] \leq s[\mathcal{D}] - 1. \tag{3.12}$$



By rewriting (3.11) as

$$(s[\mathcal{D}] - 1) + M \leq c[\gamma] \tag{3.13}$$

and using (3.12) we arrive at the inequality

$$[\beta[\gamma] - 1] + \text{ind}[\mathcal{D}] + M \leq (s[\mathcal{D}] - 1) + M \leq c[\gamma]. \tag{3.14}$$

This inequality allows us to write

$$\text{ind}[\mathcal{D}] + M \leq c[\gamma] - (\beta[\gamma] - 1). \tag{3.15}$$

Comparison between this result and (3.7), assuming  $\text{ind}[\mathcal{D}] \leq M$ ,

$$M \leq \frac{1}{2}(c[\gamma] - (\beta[\gamma] - 1)). \tag{3.16}$$

Hence the Bennequin conjecture is related to the assertion

$$M \simeq u[\gamma]. \tag{3.17}$$

In general,  $M \leq u(\gamma)$ , as can be seen by inductive application of (3.9). There are examples in which inequality is strict: it seems that equality holds in ‘most’ cases.

There is yet another number  $K[n]$  which is closely related to  $u[\gamma]$  and  $c[\gamma]$ .  $K(n)$  is defined as the number of *distinct* knots which have plane projections with at most  $n$  crossings. It was shown [5, 6] that for large  $n$

$$2^n \leq K[n] \leq 2 \cdot 24^n. \tag{3.18}$$

Following [17], we shall demonstrate that if  $c[\gamma]$  is known, then  $K[n]$  can be estimated. It is also clear that  $n$ ,  $M$  and  $u[\gamma]$  should (on average) depend on  $N$ . According to the definition of  $c[\gamma]$  which was provided after (3.3), for a given knot with  $c[\gamma] = n$  we can write inequality (3.18) as

$$2^{c[\gamma]} \leq K[n] \leq 2 \cdot 24^{c[\gamma]}. \tag{3.19}$$

Fortunately,  $c[\gamma]$  can be estimated with the help of an auxiliary quantity, knot ‘energy’  $E[\gamma]$ , defined according to [17] as

$$E[\gamma] = \int_{-\frac{N}{2}}^{N/2} d\tau \int_{\tau-\frac{N}{2}}^{\tau+\frac{N}{2}} d\tau' \left\{ \frac{1}{|\mathbf{r}(\tau) - \mathbf{r}(\tau')|^\alpha} - \frac{1}{|\tau - \tau'|^\alpha} \right\} \tag{3.20}$$

where the arc-length parametrization is used (i.e.  $|\frac{d\mathbf{r}}{d\tau}| = 1$ , see e.g. [15]) and  $\alpha$  is some constant,  $1 < \alpha \leq 3$ . It is shown in [17] that (for  $\alpha = 2$  only!)

$$c[\gamma] + \frac{2}{\pi} \leq \frac{1}{2\pi} E[\gamma]. \tag{3.21}$$

For large  $N$  we expect  $c[\gamma]$  also to be large, which allows us to ignore the factor  $\frac{2}{\pi}$  in (3.21) so that, on average, we can write

$$\langle c[\gamma] \rangle \leq \frac{1}{2\pi} \langle E[\gamma] \rangle. \tag{3.22}$$

Although, in principle, it is possible to perform an average with the help of the path integral defined in (2.8), for large  $\omega$  the polymer chain is expected to be very flexible [15, 25] so that *in the limit only (!)* one can replace (2.8) by a simpler, Gaussian-like, path integral defined by

$$\langle \dots \rangle = \mathcal{N}_G \int_{\mathbf{r}(0)=\mathbf{r}(N)} D[\mathbf{r}(\tau)] \dots \exp \left\{ -\frac{3}{2l} \int_0^N d\tau \left( \frac{d\mathbf{r}}{d\tau} \right)^2 \right\}. \tag{3.23}$$

Such replacement is done mainly for technical (computational) reasons. Alternative, more rigorous methods of averaging will be discussed in the next section.

The presence of the second term in the right-hand side of (3.20) removes the unphysical short distance singularities arising from the removal of the cut-off  $l$ . Indeed, for  $\tau \rightarrow \tau'$ , following [23], we can write

$$\mathbf{r}(\tau') = \mathbf{r}(\tau) + \frac{d\mathbf{r}}{d\tau}(\tau - \tau') + \frac{1}{2} \frac{d^2\mathbf{r}}{d\tau^2}(\tau - \tau')^2 + \dots \tag{3.24}$$

Using Serret–Frenet formulae in (3.24), we obtain after some algebra [23]

$$|\mathbf{r}(\tau) - \mathbf{r}(\tau')| \simeq s \left[ 1 - \frac{s^2}{12} k^2(\tau) \right]^{\frac{1}{2}} \tag{3.25}$$

where  $k^2(\tau)$  is the same as in (2.7) and  $s = |\tau - \tau'|$ . For small  $s$  use of expansion (3.25) in (3.20) demonstrates that the expression for  $E[\gamma]$  is manifestly non-singular (for  $1 < \alpha \leq 3$ ). The energy functional  $E[\gamma]$  for  $\alpha = 2$  has an additional useful property, Möbius invariance, which makes the exponent  $\alpha = 2$  somewhat special. To appreciate the significance of this exponent, following [17], let us consider the energy of the unknot  $\gamma_0$ . If we use the arc-length parametrization of the circle of radius  $R$ , then the energy of a circle  $\gamma_0$  can be calculated as

$$E[\gamma_0] = R^2 \int_{-\pi}^{\pi} d\tau \int_{-\tau-\pi}^{\tau+\pi} d\tau' \left\{ \frac{1}{[2R \sin \frac{|\tau-\tau'|}{2}]^\alpha} - \frac{1}{[R|\tau - \tau'|]^\alpha} \right\}. \tag{3.26}$$

For  $\alpha = 2$ ,  $E[\gamma_0]$  becomes independent of the radius  $R$  and, hence, of the length of the curve  $N$ . For any other  $\alpha$  we obtain, evidently,

$$E[\gamma_0] \propto R^{2-\alpha} \propto N^{2-\alpha}. \tag{3.27}$$

If we assume that the above  $N$ -dependence persists also for more complicated (knotted) situations, then using (3.22) we obtain

$$\langle c[\gamma] \rangle \leq N^{2-\alpha} \tag{3.28}$$

which would require  $\alpha$  to be less than or equal to one in order to be in qualitative agreement with the numerical results of [1]. This, however, is *not permissible* according to [17] (since the domain of  $\alpha$  lies between 1 and 3).

The resolution of this contradiction can be found if we analyse the averaged value of  $E[\gamma]$ . The averaged energy is defined by

$$\langle E[\gamma] \rangle = \int_0^N d\tau \int_0^N d\tau' \left\langle \frac{1}{|\mathbf{r}(\tau) - \mathbf{r}(\tau')|^\alpha} \right\rangle \tag{3.29}$$

where equation (3.23) was used and we have disregarded the singular counter-term in (3.20) since the averaged quantity happens to be non-singular (as is well known from similar calculations, see e.g. [39, 40]).

To perform an average in (3.29), let us formally define the Fourier transform of the potential  $|\mathbf{r}|^{-\alpha}$  via

$$v_\alpha(\mathbf{k}) = \int d\mathbf{r} |\mathbf{r}|^{-\alpha} e^{i\mathbf{k}\cdot\mathbf{r}} = \frac{4\pi}{k} \int_0^\infty dr r^{1-\alpha} \sin kr = \frac{4\pi}{k^{3-\alpha}} \text{constant}(\alpha) \tag{3.30}$$

where  $\text{constant}(\alpha) = \int_0^\infty dx x^{1-\alpha} \sin x$ . The  $\text{constant}(\alpha)$  is well defined only for  $1 < \alpha < 3$  and this result is in complete agreement with [17] where the same bounds were obtained using completely different arguments. Using (3.30) we can write as well

$$v_\alpha(\mathbf{r}) = \frac{1}{|\mathbf{r}|^\alpha} = \frac{1}{(2\pi)^3} \int d\mathbf{k} e^{-i\mathbf{k}\mathbf{r}} v_\alpha(\mathbf{k}). \quad (3.31)$$

By combining (3.29) and (3.31) we obtain

$$\langle E[\gamma] \rangle = \frac{1}{(2\pi)^3} \int d\mathbf{k} v_\alpha(\mathbf{k}) S(\mathbf{k}) \quad (3.32)$$

where  $S(\mathbf{k})$  is defined by

$$S(\mathbf{k}) = \int_0^N d\tau \int_0^N d\tau' \langle e^{-i\mathbf{k}\cdot(\mathbf{r}(\tau) - \mathbf{r}(\tau'))} \rangle.$$

This quantity (up to numerical prefactor) is the static scattering form-factor for circular Gaussian-like polymers. This quantity was calculated in [41] and it is for this reason that we have used the averaging procedure specified by (3.23). The action in the exponent of (3.23) is *not* reparametrization-invariant while the energy, (3.26), is (for  $\alpha = 2$ ). The lack of reparametrization invariance for this and related action(s) and its consequences for the calculation of physical observables was recently discussed in [23]. The experience with flexible polymers suggests, nevertheless, that for large  $\omega$ 's the Gaussian approximation, (3.23), is quite adequate (the excluded volume effects can be easily incorporated into (3.23) if necessary (see section 4)). For large  $\omega$  the difference between the circular and the linear polymers becomes unimportant when computing  $S(\mathbf{k})$ , see e.g. [40]. This fact allows us to write at once the result for  $S(\mathbf{k})$ :

$$S(\mathbf{k}) = N^2 \int_0^1 dy \int_0^1 dy' e^{-\frac{iN}{6}|y-y'|}. \quad (3.33)$$

Combining this result with (3.32) we obtain

$$\begin{aligned} \langle E[\gamma] \rangle &= \frac{N^2}{(2\pi)^3} (4\pi)^2 \text{constant}(\alpha) \int_0^\infty dk k^{\alpha-1} \int_0^1 dy \int_0^1 dy' e^{-\frac{iN}{6}|y-y'|k^2} \\ &= \text{constant}'(\alpha) N^{2-\frac{\alpha}{2}} \end{aligned} \quad (3.34)$$

where  $\text{constant}'(\alpha)$  is defined by the first line of (3.34) (with appropriately rescaled  $k$ ). The result (3.34) should be compared against (3.27) and against the numerical results of [1]. For  $\alpha \simeq 1$  we have  $\langle E[\gamma] \rangle \propto N^{3/2}$  while for  $\alpha \simeq 3$  we obtain  $\langle E[\gamma] \rangle \propto N^{1/2}$ . While the first value lies within the domain of expected values of  $\alpha_c$  (see e.g. (3.4)) in view of (3.22), the second value is considerably lower. To sharpen our estimates, let us now take a closer look at the value of  $\text{constant}'(\alpha)$  in (3.34). We have (upon proper rescaling)

$$\begin{aligned} \text{constant}'(\alpha) &\propto 2 \int_0^\infty dk k^{\alpha-1} \int_0^1 dy \int_0^1 dy' e^{-k^2|y-y'|} \\ &\propto \int_0^1 dy \int_0^1 dy' \frac{1}{|y-y'|^{\alpha/2}} \int_0^\infty dk k^{\alpha-1} e^{-k^2}. \end{aligned} \quad (3.35)$$

The last integral is manifestly non-singular for  $1 < \alpha < 2$  which produces at once

$$C_\alpha N \leq \langle E[\gamma] \rangle \leq C'_\alpha N^{3/2} \quad (3.36)$$

in view of (3.34) where  $C_\alpha, C'_\alpha$  are constants depending on  $\alpha$ . Using (3.22) we conclude as well that the observed value of  $\alpha_c$  (defined by equation (3.4)) lies within the range of the above estimate. Moreover, because  $\alpha$  is strictly larger than one we can finally write for  $\alpha_c$

$$1 + \delta < \alpha_c < 1.5 - \delta \quad (3.37)$$

with  $\delta \rightarrow 0^+$ . The lower bound for  $\alpha_c$  is also in complete accord with an earlier independent theoretical estimate presented in [36].

The above bounds are obtained without taking account of the excluded volume effects. The experience with similar types of calculations [39] suggests that the upper bound in (3.36) can be noticeably lowered, thus bringing our estimate (3.36) much closer to the experimentally observed results [1]. We shall consider this subject in more detail in the discussion section of our paper where we shall argue that both the upper bound 1.5 and the lower bound 1 for  $\alpha_c$  have an additional physical meaning associated with packing capacity for knots.

Being able to provide an estimate for  $\langle c[\gamma] \rangle$  we can now make an estimate for  $K(n)$  defined by (3.19). For  $\alpha = 2$  we obtain, using inequalities (3.19) and (3.21), corollary 3.5 of [17] and the results for  $\langle E[\gamma] \rangle$ , the following estimate for  $K(n)$ :

$$K(n) \leq (0.264)(1.648)^{\langle E[\gamma] \rangle} \tag{3.38}$$

with  $\langle E[\gamma] \rangle$  given in (3.36). The average  $\langle E[\gamma] \rangle$  is taken over all closed walks of length  $N$ , while  $n = n(N)$  is the average crossing number  $\langle c[\gamma] \rangle$ .

In [17] the energy of an unknot was calculated. Using equation (3.26) (for  $\alpha = 2$ ) and the inequality (3.21), the authors of [17] obtained for the unknot:  $E[\gamma_0] = 6\pi + 4 = 22.84954$ . In section 2 we made an estimate of the topological persistence length. The following question arises: how is the above estimate (which involves explicitly the length of the curve) related to the above energy estimate which is explicitly length-independent? To reconcile these two seemingly conflicting results, let us use again the result (3.25) in (3.20). We can formally write

$$E[\gamma_0] = \int_0^N d\tau f(\tau)$$

where

$$f(\tau) = \int_0^N d\tau' \left\{ \frac{1}{|\mathbf{r}(\tau) - \mathbf{r}(\tau')|^\alpha} - \frac{1}{|\tau - \tau'|^\alpha} \right\}. \tag{3.39}$$

As in [23], let us consider the conformations which are close to the rigid rod limit (i.e.  $k(\tau) \rightarrow 0$ ). Then, using (3.25) for  $|s| \ll \sqrt{12}/|k(\tau)|$  we obtain

$$\frac{1}{|\mathbf{r}(\tau) - \mathbf{r}(\tau')|^\alpha} \simeq \frac{1}{s^\alpha} \left( 1 + \frac{s^2}{12} k^2(\tau) \right)^{\alpha/2} \simeq \frac{1}{s^\alpha} + \frac{\alpha}{24} s^{2-\alpha} k^2(\tau) + \dots \tag{3.40}$$

The first term in this expansion cancels with the second term in (3.39) while the second term for  $\alpha = 2$  becomes  $s$ -independent. In this limit we can safely write

$$E[\gamma_0] \simeq \frac{N}{12} \int_0^N d\tau k^2(\tau) \approx 22.84954. \tag{3.41}$$

Using the results of section 2, see e.g. equation (2.14), we can rewrite (3.41) as

$$E[\gamma_0] = \frac{1}{12} \int_0^1 d\tau k^2(\tau) \tag{3.42}$$

which indicates that for  $\alpha = 2$  the energy is  $N$ -independent (as required). When this result is combined with the inequality (2.7) we obtain

$$(6\pi + 4) = E[\gamma_0] \geq \frac{1}{12} \left( \int d\tau |k(\tau)|^2 \right) \geq \frac{\pi^2}{3}. \tag{3.43}$$

Hence the energy value for the unknot is in complete agreement with earlier calculations based on total curvature.

#### 4. Discussion

Although the existing knot polynomials [12, 13] provide us with valuable information about knots, it seems to us that Milnor's differential geometric approach [16, 42] (for more recent results, see e.g. [43, 44]) is more convenient for polymer-related problems since it allows us to think of knots (links) as being made of some material with elastic characteristics which are physically measurable. This fact is especially important in biological applications where these characteristics can be readily regulated [23, 45] e.g. by changing the ionic strength of solution, etc.

It is our hope that the methods developed in this paper will help to stimulate more detailed calculations in the future. Among the problems which require further study we would like to mention the following. First, in section 2 we observed that the actual numerical value of  $l_T$  sensitively depends upon the connection between the discrete and the continuum formulations of the corresponding path integrals. Second, in section 3 we used the path integrals which are *different* from that used in section 2. This was motivated by the known difficulties in calculating  $S(\mathbf{k})$  for Kratky–Porod (e.g. (2.8)) chains as discussed in [25]. For long flexible chains the results for  $S(\mathbf{k})$  obtained with the use of simpler (Gaussian) path integral measures (e.g. (3.23)) produce for  $S(\mathbf{k})$  physically acceptable results [25]. Both Kratky–Porod, (2.8) and Gaussian (Wiener), (3.28), path integrals are *not* reparametrization-invariant R-I as was discussed in [23]. At the same time, the expression for the knot energy *is* R-I, see e.g. (3.27) for  $\alpha = 2$ . The averaging of the R-I quantity (such as  $E[\gamma]$  for  $\alpha = 2$ ) with the help of path integrals which are not R-I is questionable in general [23, 46]. Nevertheless, it is common in the polymer literature where, for example, the R-I nematic interaction term  $\int_0^N d\tau \int_0^N d\tau' \left| \frac{dr}{d\tau} \times \frac{dr'}{d\tau'} \right|$  is used in combination with the K–P action (e.g. (2.8)) which is *not* R-I. This disrespect of R-I sometimes leads to erroneous physical predictions (e.g. for polyelectrolytes) as discussed in [23, 45]. Since according to [17] (and the analysis of section 3), any value of  $\alpha$  between 1 and 3 is acceptable, the requirement of R-I may not be very stringent. At the same time, since for the *individual* torus knots calculations were made with  $\alpha = 2$  [47] so that the resulting energies are manifestly  $N$ -independent, the issue of R-I for knot-related problems requires much more study if path integrals are used.

The reparametrization invariance cannot always be a guiding principle. Indeed, the knot complexity which we calculated in section 3 makes *physical* sense only with respect to the length of the polymer. This can be seen already in computations of  $l_T$ . For  $N < l_T$  we still anticipate crossings in knot-projections onto some chosen plane(s). The minimal number of crossings to produce a non-trivial knot should be at least 3. Hence for  $N \simeq l_T$  we expect to have at least three crossings. This naturally reintroduces the lower cut-off into the knot problem. On another hand, if we keep the number of crossings  $n$  fixed but let  $N \rightarrow \infty$ , then the knot complexity  $\langle c[\gamma] \rangle \sim n$  does not mean much because  $n/N \rightarrow 0$ . At the same time, since  $\langle c[\gamma] \rangle$  grows faster than the length  $N$  according to numerical experiments [1], we formally obtain infinity  $N^{\alpha-1} \rightarrow \infty$ . However, this infinity is not physically relevant. Indeed, if we were to ignore for the moment the excluded volume effects, then we would have to consider  $\langle c[\gamma] \rangle$  crossings in the volume  $V \sim R^3 \propto N^{3/2}$ . This would create a ratio  $P = \langle c[\gamma] \rangle / N^{3/2}$  (packing capacity of a knot) and, according to our estimate (3.37), this ratio will go *at most* to the constant. This would require us to have no more than about one crossing per unit volume, which is physically sensible.

The excluded volume effects will create some obstacles to the knot formation leading to reduced  $\langle c[\gamma] \rangle$ . Because the volume exponent  $\alpha_V$  will be larger than  $\frac{3}{2}$  while  $\alpha_c$  will be smaller than 1.5 (see (4.3) below); this will produce  $P \rightarrow 0$  for  $N \rightarrow \infty$ . Since  $N$  is

never infinite, the finite-size effects are always important (e.g. see the result (2.6) which was obtained mainly because of the finite-size effects) and, hence represent real physical interest.

This argument naturally provides an upper bound for  $\alpha_c$ . If, in addition, one considers the collapsed state, where  $R \sim N^{\frac{1}{3}}$ , then one arrives at the lower bound  $\alpha_c \geq 1$  by requiring the ratio  $P$  to be a constant. A previously obtained estimate for  $K(n)$  indicates that the collapsed state for quasi-knots [4] should be glass-like with  $K(n)$  being the number of possible quasi-equilibrium states.

Third, in section 3 we noticed that the bounds (3.35) are obtained with disregard of the excluded volume effects. Our experience with polymers [39] allows us easily to correct this deficiency. Indeed, in the case of polymers, calculation of the diffusion coefficient for the individual polymer chain (using Kirkwood approximation) involves averages like

$$D = \frac{k_B T}{6\pi\eta_s} \int_0^N \frac{d\tau}{N} \int_0^N \frac{d\tau'}{N} \left\langle \frac{1}{|\mathbf{r}(\tau) - \mathbf{r}(\tau')|} \right\rangle \tag{4.1}$$

see e.g. equation (4.1) of [39]. We have used in (4.1) the same averaging procedure as in (3.23) (averages similar to (4.1) were considered much earlier by Feynman [40] in connection with the polaron problem) and have introduced the temperature factor  $k_B T$  and the viscosity of the solvent  $\eta_s$ . Upon calculation of the average in (4.1), we obtain the Stokes–Einstein formula [48]

$$D = \frac{k_B T}{6\pi\eta_s \sqrt{\langle \mathbf{R}^2 \rangle}} \tag{4.2}$$

where  $\langle \mathbf{R}^2 \rangle \propto N$  as is always the case for Gaussian chains [49, 50].

In the light of the earlier introduced ratio  $P$ , it is not totally unusual that the diffusion coefficient  $D$  for polymers formally resembles that for hard spheres. At the same time, any departure of  $P$  from the constant value should immediately affect  $D$  [11]. The ratio  $P$  is ultimately responsible for the ‘porosity’ of the ‘hard’ sphere (D’arcy law). This observation leads to separation of different knots with the help of chromatography or centrifugation. All these observations, of course, require much more study.

The account of the excluded volume effects will formally produce  $\langle \mathbf{R}^2 \rangle \propto N^{2\nu}$  with  $2\nu \simeq \frac{6}{5}$  as is well known [24]. Using this fact in (3.34), we would obtain instead

$$\langle E[\gamma] \rangle \propto N^{2-\alpha\nu} \equiv N^{\alpha_c}. \tag{4.3}$$

For  $\alpha$  close to 1 this would produce the exponent

$$\alpha_c = 2 - \alpha\nu \leq 1.4 \tag{4.4}$$

while for the upper permissible value of  $\alpha = 2$ , the lower bound for the exponent  $\alpha_c$  should remain unchanged, i.e.  $\alpha_c = 1$ , in view of (3.35). Hence, accounting for the excluded volume effects brings our results much closer to the experimentally observed [1].

The above calculations were based on the inequality (3.21). In principle, there is a better way to find knot-complexity. It is based on the use of manifestly reparametrization-invariant path integrals with the action  $S$  given by

$$S = \gamma_1 \int_0^N d\tau |k(\tau)| + \gamma_2 \int_0^N d\tau |T(\tau)| \tag{4.5}$$

where  $\gamma_1$  and  $\gamma_2$  are some constants while  $k(\tau)$  and  $T(\tau)$  are, respectively, the local curvature and the local torsion of the curve. For  $2 + 1$  dimensions the path integrals of this sort were recently considered in [51] while in [52] the more general case of the action in  $d + 1$  dimensions was considered (but either with  $\gamma_1 = 0$  or  $\gamma_2 = 0$ , etc) with results which are

less detailed than in [51]. The above path integrals are also closely related to the strings with rigidity [30] so that the detailed solutions of these integrals may shed some new light both on knot and string theories.

*Note added in proof.* After this work was completed we found reference [53] which relates our results to further physical applications.

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