Total Curvature and Total Torsion of a Freely Jointed Circular Polymer with $n \gg 1$ Segments

Alexander Y. Grosberg

Department of Physics, University of Minnesota, 116 Church Street SE, Minneapolis, Minnesota 55455, and Max Planck Institute for Polymer Research, 10 Ackermannweg, 55128 Mainz, Germany

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Introduction

Consider a random walk on a cubic lattice in 3D. Without volume exclusion constraints, at every step the walker has one possibility to continue straight, at 0 angle turn; four possibilities to make $\pi/2$ turn; and one possibility to make a turn of π (go back). This suggests that an average angle of turn should be $\pi/2$. For the polygon of n turns, this implies average total turn angle $n\pi/2$. Because of the obvious connection to the case of smooth curves, this quantity is also called total curvature.

Similar logic predicts that the average total torsion should also be linear in n, namely, $n\pi/2$.

Although illustrated above for the example of random walk on a cubic lattice, the argument is easily generalized and holds off-lattice as well.

In the work,[1] while looking at many geometrical characteristics of closed polymer loops modeled as polygons of $n \gg 1$ edges, the authors found, somewhat surprisingly, that both total curvature and total torsion deviate from the expected linear in n behavior. Corrections to both curvature and torsion do not depend on n, they have opposite signs, but apparently the same (or very close) absolute values: the curvature appears close to $n\pi/2 + 1.2$, while torsion $n\pi/2 - 1.2$.

The authors of the work[1] challenged theorists to explain their numerical finding. Here, I meet the challenge and show that total curvature and total torsion are asymptotically equal to $n\pi/2 + 3\pi/8 + \mathcal{O}(1/n)$ and $n\pi/2 - 3\pi/8 + \mathcal{O}(1/n)$, respectively. Note that $3\pi/8 \approx 1.178$. At the end of the work I discuss the multidimensional generalization of this result.

Notations

Consider a polygon of n sides, each of unit length, each represented by a vector $\vec{y}_i$, with closure condition

$$\sum_i \vec{y}_i = 0 \qquad (1)$$

and completely random otherwise.

Curvature. Angle θ_i is defined as the angle between consecutive vectors, such that

$$\cos\theta_i = \vec{y}_i \cdot \vec{y}_{i+1} \qquad (2)$$

$0 \le \theta_i < \pi$. The quantity of interest, total curvature, is defined as

$$\text{curv} = \sum_i \theta_i \qquad (3)$$

Torsion. Another quantity of interest is torsion which is defined in the following way. Consider three subsequent vectors $\vec{y}_{i-1}$, $\vec{y}_i$, and $\vec{y}_{i+1}$. Cross-products $\vec{p}_i = \vec{y}_{i-1} \times \vec{y}_i$ and $\vec{p}_{i+1} = \vec{y}_i \times \vec{y}_{i+1}$ define normals to the corresponding planes, and the angle between these normals is defined as φ_i:

$$\cos\varphi_i = (\vec{p}_i \cdot \vec{p}_{i+1})\ (|\vec{p}_i|\ |\vec{p}_{i+1}|) \qquad (4)$$

$0 \le \varphi_i < \pi$. Then, total torsion is defined by summation of all angles φ:

$$\text{torsion} = \sum_i \varphi_i \qquad (5)$$

There are some symmetry properties which will be important in our further calculations; in particular, note that renumbering of all bond vectors $\vec{y}_i$ in the opposite direction around the loop does not change the angle φ associated with a particular vertex of the polygon: each vector $\vec{y}$ flips the sign, but also the order in which two subsequent bond vectors enter in the definition of $\vec{p}$ changes; therefore, vectors $\vec{p}$ flip the sign, but the angle between them does not change.

Correlations between $\vec{y}$

Consider the correlation $\langle \vec{y}_i \cdot \vec{y}_j \rangle$; how does it depend on i and j, particularly when $i \neq j$? While it obviously does not depend on i and j separately, one could have thought that the correlation depends on the chemical distance $i-j$. In fact, it does not depend even on the distance, so it is a constant independent of i and j as long as $i \neq j$. This can be established through the following argument: any given set of vectors with zero sum, eq 1, gives rise to a closed polygon; arbitrary reshuffling of these vectors produces a different polygon which, therefore, in the full ensemble has the same weight (or probability) as the original one. Therefore, closeness of vectors $\vec{y}_i$ and $\vec{y}_j$ in terms of their labeling by indices i and j has no bearing on their statistical properties.

With this result in mind, let us now square the ring closure condition (1) and average the result. We should remember that $\vec{y}_i \cdot \vec{y}_i = 1$, while for $i \neq j$, the quantity $\langle \vec{y}_i \cdot \vec{y}_j \rangle$ does not depend on i and j:

$$n\langle \vec{y}^2 \rangle + n(n-1)\langle \vec{y} \cdot \vec{y}' \rangle = 0 \qquad (6)$$

which means that

$$\langle \vec{y}_i \cdot \vec{y}_j \rangle = -\frac{1}{n-1} \quad \text{for } i \neq j \qquad (7)$$

Thus, every $\vec{y}$ is slightly against any other particular $\vec{y}$, because they have to sum up to zero. This weak ($\mathcal{O}(1/n)$) negative correlation is what gives rise to the corrections to both total curvature and total torsion. Notice, however, that the correlation rule (7) is naturally formulated in terms of dot product, or cosine of the angle θ, not the angle itself. For the dot product, the correlation is $1/n$ with coefficient 1; it is when we average the angle that a nontrivial factor appears.

Curvature, Method 1

The results of this section will be reproduced in the next section by a more general method. It is nevertheless useful to present first the simpler calculation revealing the underlying physics.

Consider the probability distribution of the angle θ_i. Actually, it does not depend on i, so let us look for the probability density $P(\theta)$. It is convenient to start from probability density $P(\vec{y})$, defined of course on the sphere. I assume that $\vec{y}$ is $\vec{y}_i$ and that vectors $\vec{y}_{i-1}$ and $\vec{y}_{i-2}$ form a coordinate system with respect to which $P(\vec{y})$ will be written.

How do we find $P(\vec{y})$? Let us make an *assumption* that $P(\vec{y})$ is such that it maximizes entropy

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$$\int P(\vec{y})\ln\frac{P(\vec{y})}{e}d^2y \tag{8}$$

subject to the two constraints that $P(\vec{y})$ is properly normalized

$$\int P(\vec{y})d^2y = 1 \tag{9}$$

and that it satisfies the correlations-due-to-closure condition (7):

$$\int \cos\theta P(\vec{y})d^2y = -\frac{1}{n-1} \tag{10}$$

in all three cases, integration runs around the sphere. Introducing proper Lagrange multipliers λ and μ, we arrive then at

$$P(\vec{y}) = \exp[\lambda + \mu(n-1)\cos\theta] \tag{11}$$

We should now remember that solid angle integration previously denoted as d^2y involves factor 2π for the integration over φ and involves $\int_0^\pi$ ...sin θ dθ. With this in mind, we have then two equations for λ and μ:

$$\begin{cases} 2\pi\int_0^\pi e^{\lambda+\mu\cos\theta}\sin\theta\,d\theta = 1 \\ 2\pi\int_0^\pi e^{\lambda+\mu\cos\theta}\cos\theta\sin\theta\,d\theta = -\dfrac{1}{n-1}\end{cases} \tag{12}$$

These are simple integrals, and so we arrive at

$$\begin{cases} 2\pi\dfrac{e^{\mu}-e^{-\mu}}{\mu}e^{\lambda} = 1 \\ 2\pi\dfrac{(\mu-1)e^{\mu}+(\mu+1)e^{-\mu}}{\mu^2}e^{\lambda} = -\dfrac{1}{n-1}\end{cases} \tag{13}$$

I do not know how to move forward with no approximations, but since $n \gg 1$, it is easy to realize that the solution for μ must be small: $\mu \ll 1$. Indeed, formula 7 implies that there is only a small correlation between vectors $\vec{y}$ and, therefore, the distribution of $\vec{y}$ should be close to isotropic. If μ is small, then Taylor expansion gives me $(e^{\mu} - e^{-\mu})/\mu \simeq 2 + \mathcal{O}(\mu^2)$ and $\{(\mu - 1)e^{\mu} + (\mu + 1)e^{-\mu}\}/\mu^2 \simeq 2\mu/3 + \mathcal{O}(\mu^3)$. Therefore, the equations simplify dramatically:

$$\begin{cases} 4\pi e^{\lambda} = 1 \\ 4\pi\dfrac{\mu}{3}e^{\lambda} = -\dfrac{1}{n}\end{cases} \tag{14}$$

yielding

$$e^{\lambda} \simeq \frac{1}{4\pi} \quad \text{and} \quad \mu \simeq -\frac{3}{n} \tag{15}$$

In other words, the distribution P now reads

$$P(\vec{y}) = \frac{1}{4\pi}\left[1 - \frac{3}{n}\cos\theta\right] \tag{16}$$

It is a rewarding exercise to check that this distribution does satisfy the conditions 9 and 10.

Once we have the distribution P, we can also calculate the average total curvature. We write

$$\langle \text{curv} \rangle = n\langle\theta\rangle \tag{17}$$

and compute average angle as

$$\begin{aligned}\langle\theta\rangle &= \int \theta P(\vec{y})\,d^2y \\ &= 2\pi\int_0^\pi \theta P(\theta)\sin\theta\,d\theta \\ &= \frac{1}{2}\int_0^\pi \theta\left[1 - \frac{3}{n}\cos\theta\right]\sin\theta\,d\theta \\ &= \frac{1}{2}\int_0^\pi \theta\sin\theta\,d\theta - \frac{3}{2n}\int_0^\pi \theta\cos\theta\sin\theta\,d\theta \\ &= \frac{\pi}{2} + \frac{3\pi}{8n}\end{aligned} \tag{18}$$

in other words,

$$\langle \text{curv} \rangle = n\frac{\pi}{2} + \frac{3\pi}{8} \tag{19}$$

Notice that $3\pi/8 \approx 1.178$.

Curvature, Method 2

This method is totally independent of the previous one. The main idea is to write down the joint probability distribution of all n vectors $\vec{y}_i$; let us denote it $P(\vec{y}_1, \ldots, \vec{y}_n)$.

The convenient starting point is the so-called Green's function $G_k(\vec{r})$, which is the probability density that a linear chain of k segments has end-to-end vector $\vec{r}$. In order to write down Green's function, let us treat the $\vec{y}$ -vectors as the 3D vectors, even though each of them has length unity and, therefore, is located on the sphere. This approach is more readily generalized for the cases when sticks are not of the same length but somehow distributed in length. We will operate in terms of $g(\vec{y})$, the "bare" distribution of vector $\vec{y}$ in 3D; "bare" means unaffected by other y's, in particular, unaffected by the ring closure condition. In particular, if all y's are of the same length, then

$$g(\vec{y}) = \frac{1}{4\pi l^2}\delta(|\vec{y}| - l) \tag{20}$$

where $l = 1$ is the length of one segment. Of course, g is the normalized spherically symmetric distribution of the unit length vector. In terms of g, Green's function is written as

$$G_k(\vec{r}) = \int g(\vec{y}_1)\ldots g(\vec{y}_k)\delta(\vec{y}_1 + \ldots + \vec{y}_k - \vec{r})\,d^3y_1\ldots d^3y_k \tag{21}$$

Consider now the joint probability distribution of all vectors in the closed polygon. We can treat it as a conditional probability of a certain set of vectors $\vec{y}_1,\ldots,\vec{y}_n$ conditioned by the closure constraint (1). This conditional probability is written as

$$P(\vec{y}_1, \ldots, \vec{y}_n) = \frac{g(\vec{y}_1)\ldots g(\vec{y}_n)\delta(\vec{y}_1 + \ldots + \vec{y}_n)}{C_n} \tag{22}$$

where the denominator

$$C_n \equiv G_n(0) = \int g(\vec{y}_1)\ldots g(\vec{y}_n)\delta(\vec{y}_1 + \ldots + \vec{y}_n)\,d^3y_1\ldots d^3y_n \tag{23}$$

ensures the correct normalization and arises as the probability of the condition.

Once we have the joint distribution of all vectors, we can extract the joint probability distribution of the two subsequent vectors, $P(\vec{y}_i, \vec{y}_{i+1})$ in the polygon. Notice that it does not depend on i (nor does $P(\vec{y}_i, \vec{y}_j)$ depend on i and j as long as $i \neq j$). Integrating out all but two of y vectors, we arrive at

$$P(\vec{y}_1, \vec{y}_2) = g(\vec{y}_1)g(\vec{y}_2)\frac{G_{n-2}(-\vec{y}_1 - \vec{y}_2)}{C_n} \tag{24}$$

This result has the transparent physical or geometrical meaning: for the two sticks, the remaining $n - 2$ sticks form a chain which must connect their ends and acts like a little entropic spring.

So far, all equations were exact. Now, since $n \gg 1$, we can resort to the central limit theorem to write down the explicit expressions for both G_{n-2} and C_n:

$$G_{n-2}(\vec{r}) = (2\pi(n-2)l^2/3)^{-3/2}e^{-3r^2/2(n-2)l^2} \tag{25}$$

$$C_n = (2\pi n l^2/3)^{-3/2} \tag{26}$$

This produces now

$$P(\vec{y}_1, \vec{y}_2) = g(\vec{y}_1)g(\vec{y}_2)\left(\frac{n}{n-2}\right)^{3/2} e^{-3(\vec{y}_1+\vec{y}_2)^2/2(n-2)l^2} \qquad (27)$$

Furthermore, in the region where $g(\vec{y}_1)$ and $g(\vec{y}_2)$ are nonzero, the quantity $(\vec{y}_1 + \vec{y}_2)^2/(n-2)l^2$ is very small, so exponential can be expanded. Also $(n/(n-2))^{3/2} \simeq 1 + (3/n)$. Therefore, we get

$$P(\vec{y}_1, \vec{y}_2) = g(\vec{y}_1)g(\vec{y}_2)\left[1 + \frac{3}{n} - \frac{3\vec{y}_1^2}{2nl^2} - \frac{3\vec{y}_2^2}{2nl^2} - \frac{3\vec{y}_1 \cdot \vec{y}_2}{nl^2}\right] \qquad (28)$$

which is valid up to the terms $o(1/n)$. Since all y are of the same length $l = 1$, this is further simplified

$$P(\vec{y}_1, \vec{y}_2) = g(\vec{y}_1)g(\vec{y}_2)\left[1 - \frac{3\cos\theta}{n}\right] \qquad (29)$$

Apart from notations, it is the same answer as formula 16, so it implies the same result for the total curvature. Indeed, in order to do the integration, we can introduce the spherical coordinates for vector $\vec{y}_2$ using $\vec{y}_1$ as the z-axis. Integration over $\vec{y}_1$ then produces 4π, so we get

$$\begin{aligned}\langle\theta\rangle &= \int \theta P(\vec{y}_1, \vec{y}_2)\, d^3y_1\, d^3y_2 \\ &= \frac{1}{4\pi}\int_0^{\pi} \sin\theta\, d\theta \int_0^{2\pi} d\phi\left[1 - \frac{3\cos\theta}{n}\right] \\ &= \frac{1}{2}\int_0^{\pi} \theta \sin\theta\left[1 - \frac{3}{n}\cos\theta\right] \\ &= \frac{\pi}{2} + \frac{3\pi}{8n}\end{aligned} \qquad (30)$$

Torsion

To work out the results for torsion, one has to look at the joint probability distribution of three segments. Such probability reads

$$\begin{aligned}P(\vec{y}_1,\vec{y}_2,\vec{y}_3) &= g(\vec{y}_1)g(\vec{y}_2)g(\vec{y}_3)\frac{G_{n-3}(-\vec{y}_1 - \vec{y}_2 - \vec{y}_3)}{C_n} \\ &\simeq g(\vec{y}_1)g(\vec{y}_2)g(\vec{y}_3)\left[1 + \frac{9}{2n} - \frac{3\vec{y}_1^2}{2nl^2} - \frac{3\vec{y}_2^2}{2nl^2} - \frac{3\vec{y}_3^2}{2nl^2} - \frac{3\vec{y}_1 \cdot \vec{y}_2}{nl^2} - \frac{3\vec{y}_1 \cdot \vec{y}_3}{nl^2} - \frac{3\vec{y}_3 \cdot \vec{y}_2}{nl^2}\right] \\ &\simeq g(\vec{y}_1)g(\vec{y}_2)g(\vec{y}_3)\left[1 - \frac{3}{n}(\vec{y}_1 \cdot \vec{y}_2 + \vec{y}_1 \cdot \vec{y}_3 + \vec{y}_3 \cdot \vec{y}_2)\right]\end{aligned} \qquad (31)$$

From here, to facilitate integration, we introduce spherical coordinates using vector $\vec{y}_2$ as the z-axis. Then, integration over $\vec{y}_2$ simply gives 4π. Furthermore, we can choose the spherical coordinate system based on vector $\vec{y}_1$. In such coordinates, the azimuthal integration over $\vec{y}_1$ leaves just 2π. We are now left with angles θ_1, θ_3, and ϕ, the latter being the angle between projections of the two vectors $\vec{y}_1$ and $\vec{y}_3$ on the plane perpendicular to $\vec{y}_2$. Obviously, we have

$$\vec{y}_1 \cdot \vec{y}_2 = \cos\theta_1 \quad \text{and} \quad \vec{y}_3 \cdot \vec{y}_2 = \cos\theta_3 \qquad (32)$$

as well as

$$\vec{y}_1 \cdot \vec{y}_3 = \cos\theta_1 \cos\theta_2 + \sin\theta_1 \sin\theta_3 \cos\phi \qquad (33)$$

Angle ϕ is closely related to the above-defined torsion angle φ, see (4). Remembering in particular the discussion of the symmetry properties of the angle φ, one can realize that $\varphi = \pi - \phi$ as long as $\phi < \pi$ and $\varphi = \phi - \pi$ when $\phi > \pi$. Thus, we define the function

$$\varphi(\phi) = \begin{cases}\pi - \phi & \text{when } 0 < \phi < \pi \\ \phi - \pi & \text{when } \pi < \phi < 2\pi\end{cases} \qquad (34)$$

One can derive this formally, by using the above-defined coordinate system and explicitly computing cross products and vectors $\vec{p}$ and then their dot product (4), yielding $\cos\varphi = -\cos\phi$; given further the bounds of φ and ϕ, this results in (34). Taking advantage of the thus defined function $\varphi(\phi)$, we obtain

$$\begin{aligned}\langle\varphi\rangle &= \int \varphi P(\vec{y}_1,\vec{y}_2,\vec{y}_3)\, d^3y_1\, d^3y_2\, d^3y_3 \\ &= \frac{2\pi}{(4\pi)^2}\int_0^{\pi} \sin\theta_1\, d\theta_1 \int_0^{\pi} \sin\theta_3\, d\theta_3 \int_0^{2\pi} d\phi\, \varphi(\phi)\left[1 - \frac{3Q}{n}\right]\end{aligned} \qquad (35)$$

where for brevity

$$Q = \cos\theta_1 + \cos\theta_3 + \cos\theta_1 \cos\theta_2 + \sin\theta_1 \sin\theta_3 \cos\phi \qquad (36)$$

The rest is the straightforward integration which yields

$$(\varphi) \simeq \frac{\pi}{2} - \frac{3\pi}{8n} \qquad (37)$$

This further implies

$$\langle\text{torsion}\rangle \simeq n\frac{\pi}{2} - \frac{3\pi}{8} \qquad (38)$$

Generalization

The above results can be generalized for a closed polygon in the space of dimension d.

To begin with, formula 29 is generalized as

$$P(\vec{y}_1, \vec{y}_2) = g(\vec{y}_1)g(\vec{y}_2)\left[1 - \frac{d\cos\theta}{n}\right] \qquad (39)$$

Indeed, the only novelty in d dimensions is that there is coefficient d instead of just 3. This is derived easily because the only place where changes are necessary is the implementation of central limit theorem, where dimension d comes in into the exponential, replacing the 3/2 coefficient with $d/2$. In d dimensions we have

$$G_{n-2}(\vec{r}) = (2\pi(n-2)l^2/d)^{-d/2} e^{-dr^2/2(n-2)l^2} \qquad (40)$$

$$C_n = (2\pi nl^2/d)^{-d/2} \qquad (41)$$

resulting in

$$\begin{aligned}P(\vec{y}_1, \vec{y}_2) &= g(\vec{y}_1)g(\vec{y}_2)\left(\frac{n}{n-2}\right)^{d/2} e^{-d[(\vec{y}_1+\vec{y}_2)^2]/[2(n-2)l^2]} \\ &\simeq g(\vec{y}_1)g(\vec{y}_2)\left[1 + \frac{d}{n}q\right]\end{aligned} \qquad (42)$$

where for brevity

$$q = 1 - \frac{\vec{y}_1^{\,2}}{2l^2} - \frac{\vec{y}_2^{\,2}}{2l^2} - \frac{\vec{y}_1 \cdot \vec{y}_2}{l^2} \qquad (43)$$

Qualitatively, it seems to make sense that the effect of correlations due to the closure condition increases with increasing d, because in large d the chances of random walk returning to the point of start decrease dramatically with increasing d.

From eq 39, it is straightforward to find the generalization of formula 19 which reads

$$\langle\text{curv}\rangle = \frac{n\pi}{2} + \frac{d\pi}{8} \qquad (44)$$

Surely, there is also generalization for torsion. In general, the higher the dimension, the more quantities like curvature and torsion exist there describing how the curve bends; specifically, in addition to curvature, there are $d - 2$ more quantities. I have computed the first one of them for arbitrary d; the result reads

$$\langle \text{torsion} \rangle \simeq n\frac{\pi}{2} - \Gamma^2\left(\frac{d}{2}\right) 2^{5-2d}\pi^{d-3}d \qquad (45)$$

Not surprisingly, in $d = 3$ we have our previous results. As an example, in $d = 4$ we get $\langle \text{curv} \rangle = n\pi/2 + \pi/2$ and $\langle \text{torsion} \rangle \simeq n\pi/2 - \pi/2$, while in $d = 5$ the results are $\langle \text{curv} \rangle = n\pi/2 + 5\pi/8$ and $\langle \text{torsion} \rangle \simeq n\pi/2 - 45\pi^3/512$.

To conclude, this paper explains the finding of the work (ref 1) that both total curvature and total torsion of the closed random polygon, on average, are not equal to $\pi/2$ per bond, but have corrections proportional to $1/n$ with mysterious yet universal coefficients close to 1.2. The mysterious number 1.2 is established to be a $3\pi/8$ in disguise. The underlying purpose of the work is to reinforce the view point that there are no seriously unclear open questions for the polymer rings as long as both excluded volume and topological constraints are ignored.

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References and Notes

(1) Plunkett, P.; Piatek, M.; Dobay, A.; Kern, J.; Millett, K.; Stasiak, A.; Rawdon, E. *Macromolecules* **2007**, *40*, 3860.

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