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Physica A 222 (1995) 155–160

PHYSICA A

New approaches to shapes of arbitrary random walks

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Received: 7 May 1995

Abstract

The problem of the shape of a random object such as a flexible polymer chain was first tackled by Kuhn nearly thirty years after the answer to the probability distribution of its size was publicly sought for by Pearson in 1905. Since then, significant progress in the field has been made, but the important task of evaluating both analytically and accurately averaged individual principal components of the shape or inertia tensor for a walk of a certain architectural type remains unfinished. We have recently developed a new and general formalism for both exact and approximate calculations of these and other averages such as asphericity and prolateness parameters, which is illustrated here for an end-looped random walk and a self-avoiding or Edwards chain. We find that this combined open and closed random walk has surprisingly larger shape asymmetry than a simply open walk despite its smaller size.

The shape of a random walk taking place in a d-dimensional space is often described by d principal components arranged in descending order, i.e., $S_1 \geqslant S_2 \geqslant \cdots \geqslant S_d$, of the shape or gyration tensor [7, 11, 15] **S** which registers precisely its vertices' positions and hence its spatial configuration. It is related to the inertia tensor **I** of an n-vertex walk by the equality $\mathbf{I} = n(s^2 \mathbf{1} - \mathbf{S})$ where unit mass is assumed for each vertex, **1** is the identity matrix, and s^2 is the trace of **S**, i.e., $s^2 = \mathrm{tr}(\mathbf{S})$ with s historically termed radius of gyration [3, 5], i.e., the square root of the arithmetic mean of n squared distances of the vertices from their centers of mass. For convenience, unit step length is further assumed for the walk.

A walk may be either self-intersecting [1–3, 5] (the large-n limit of the gaussian model) or self-avoiding (Edwards model) [1, 4, 10, 12–14] and may have different architectural types [19] usually specified by the architecture or Kirchhoff matrix **K**. Let $\mathbf{\Lambda}$ denote the diagonal matrix of all $n-1$ nonzero eigenvalues of **K** times n^2. The eigenpolynomials of $\mathbf{\Lambda}$, i.e., $P_{n-1}(x) = |\mathbf{1} + x\mathbf{\Lambda}^{-1}|$ for an end-looped or dumbbell-like walk, i.e., two identical large rings connected by a doubly-sized chain, may be written down with the use of graph theory, with the result that $D(x) \equiv P_\infty(x^2) = U(x)\,U^2(x/2)\,B(x, -1/3)\,B(x, 2/3)$, where $U(x) = 4\,\mathrm{sh}(x/4)/x$ and $B(x,a) = [\mathrm{ch}(x/4) - a]/(1 - a)$. From the above eigenpolynomial, one can easily

SSDI 0378-4371(95)00259-6

Table 1
Asphericity parameters and factors and exact values of shape and shape variance factors for open (I), closed (II) and end-looped (III) random walks in two dimensions

Type	$\langle A\rangle$	δ	Approximate		Exact		σ_1	σ_2
			δ_1	δ_2	δ_1	δ_2		
1	0.396400	0.571429	0.816228	0.183772	0.832938	0.167062	0.369214	0.009090
2	0.262553	0.333333	0.723607	0.276393	0.754323	0.245677	0.155901	0.014739
3	0.427009	0.632923	0.840212	0.159788	0.852352	0.147648	0.439593	0.006567

obtain an analytic expression for the function $S_m(x)$ defined as the large-n limit of $\mathrm{tr}(\mathbf{\Lambda} + x^2\mathbf{1})^{-m}$.

For arbitrary random walks in two dimensions, we find by using the method of Solc and Gobush [9] that shape factors, i.e., the δ_α defined as $\langle S_\alpha\rangle/\langle s^2\rangle$ or the ratio of averaged principal component to mean square radius of gyration, and shape variance factors, the σ_α defined as $(\langle S_\alpha^2\rangle - \langle S_\alpha\rangle^2)/\langle s^2\rangle^2$, are given by $\delta_\alpha = 1/2 + (-1)^\alpha \chi_1$, and $\sigma_\alpha = (1 + 3\mu_2)/4 + (-1)^\alpha \chi_2 - \delta_\alpha^2$, respectively, where $\mu_m = S_m(0)/S_1^m(0)$ and χ_m is defined as

$$\chi_m = S_1^{-m}(0) \int_0^\infty |xD(x+ix)|^{-1}\,\mathrm{Im}\,[F_m(x+ix)]\,\mathrm{d}x\,,$$

with $F_1(x) = S_1(x)$, $F_2(x) = S_2(x) + 2^{-1}S_1^2(x)$, and $\mathrm{Im}(x+\mathrm{i}y)$ denoting the imaginary part of $x + iy$. Numerical evaluations of δ_α and σ_α for three types of random walks, i.e., open, closed and end-looped walks, based on the above equalities have been made and the results are tabulated in Table 1. We note that our approach reproduces the results for rings first reported by Solc and Gobush [9]. Similarily, we can write down expressions for δ_α and σ_α for the $d = 3$ case. However, a complication occurs in this case as it involves triple integrals over the restricted domains of the rotation group SO(3), which are difficult to evaluate accurately even by numerical means. Therefore, for random walks in a space with $d \geqslant 3$ and for self-avoiding walks, methods for approximately evaluating $\langle S_\alpha^m\rangle$ must be sought.

An analytic approximation to $\langle S_\alpha^m\rangle$ for an open walk has long been attempted [1, 15, 17, 20–23]. Here we present a method which is applicable to arbitrary walks in arbitrary $d \geqslant 2$ dimensions. It is based on the equality $S_\alpha^d = \Sigma_{1\leqslant m\leqslant d}(-1)^{m-1} S_\alpha^{d-m} M_m(\mathbf{S})$ which follows from the setting of the eigenpolynomial of $\mathbf{S}$ to zero, where the $M_m(\mathbf{S})$ are monomial symmetric functions of $S_1, \ldots, S_d$ corresponding to the partition $(1, \ldots, 1)$ of m, e.g., $M_1(\mathbf{S}) = \mathrm{tr}(\mathbf{S})$. Now by replacing S_α and $M_m(\mathbf{S})$ in the above-mentioned equality by $\langle S_\alpha\rangle$ and $\langle M_m(\mathbf{S})\rangle$, respectively, which is valid for $d = \infty$ or under the strong condition that the individual principal components are independent random variables, we can

Table 2
Asphericity and prolateness parameters and factors and approxiamte values of shape factors for open (I), closed (II) and end-looped (III) random walks in three dimensions

Type	$\langle A\rangle$	δ	$\langle P\rangle$	ζ	δ_1	δ_2	δ_3
1	0.394274	0.526316	0.237475	0.443740	0.750384	0.178522	0.071094
2	0.246368	0.294118	0.101430	0.153173	0.618805	0.265070	0.116125
3	0.433078	0.589635	0.282368	0.526900	0.783988	0.152818	0.063194

Table 3
Dimensionality dependence of asphericity and prolateness parameters and the first three shape factors for end-looped random walks

d	$\langle A\rangle$	$\langle P\rangle$	δ_1	δ_2	δ_3
4	0.437509	0.283849	0.755168	0.147947	0.062060
5	0.440845	0.285132	0.737623	0.144641	0.060354
30	0.457942	0.293616	0.677574	0.131787	0.051003
∞	0.462976	0.296674	0.665240	0.128910	0.047681

approximate shape factors as the roots of a polynomial of degree d for any walk and, for random walks in particular, the polynomial is

$$W_d(x) = x^d - x^{d-1} + \sum_{2 \leqslant m \leqslant d} \eta_m(d)\, x^{d-m},$$

$$\eta_m(d) = \gamma_m \prod\nolimits_{1 \leqslant j \leqslant m-1} (1 - j/d), \gamma_m = (-1)^m C_m / S_1^m(0),$$

and the C_m are the coefficients in the power series expansion of $D(x^{1/2})$. We note that γ_m satisfies the recurrence relation $\gamma_m = -\Sigma_{0 \leqslant j \leqslant m-1} \mu_{m-j} \gamma_j / m$ with $\gamma_0 = 1$ and that in obtaining $W_d(x)$ use is made of the analytic results of Wei and Eichinger [24] for $\langle M_m(\mathrm{S})\rangle$. We note that for $d = 3$, our method recovers the explicit expressions for the δ_α first obtained by Yang and Yu [22]. We have calculated shape factors for the three previously-mentioned types of random walks in two and three dimensions (see Tables 1 and 2) using the above method. For an Edwards chain or open self-avoiding walk, the $\varepsilon(=4-d)$-expansion results at $O(\varepsilon)$ for the $\langle M_m(\mathrm{S})\rangle$ have been obtained by Aronovitz and Nelson [13] and we may then proceed to calculate shape factors for the walk with the result that $\delta_1 = 0.854495$ and $\delta_2 = 0.145505$ for $d=2$; and $\delta_1 = 0.776017$, $\delta_2 = 0.164669$ and $\delta_3 = 0.059314$ for $d = 3$. We have also investigated the dependence on $d (2 \leqslant d \leqslant \infty)$ of shape factors for end-looped random walks (see Table 3).

Apart from shape factors, there are other parameters which are widely used in characterizing average shapes of a walk, e.g., asphericity factor δ and parameter $\langle A\rangle$ and prolateness factor ζ and parameter $\langle P\rangle$. δ and ζ are defined as the ratio of the statistical average of the numerator to the denominator of A and P, respectively. A and P are defined as $A = d\ \mathrm{tr}(\mathbf{\Delta}^2)/[(d-1)s^4]$ and $P = d^2\ \mathrm{tr}(\mathbf{\Delta}^3)/[(d-1)(d-2)s^6]$, where $\mathbf{\Delta} = \mathbf{S} - (s^2/d)\mathbf{1}$, $0 \leqslant A \leqslant 1$ and $-(d-1)^{-3} \leqslant P \leqslant 1$. A value of zero for A or P corresponds to spherical shape and a value of 1 to rodlike shape in the interval $[-(d-1)^{-3}, 0)$ or $(0, 1]$ for values of P in the region of oblate or prolate shape [13, 15, 24]. Simple analytic expressions for δ and ζ are readily obtained for arbitrary random walks by use of the Wei-Eichinger method [24]. For analytic calculations of the statistical averages of A and P, i.e., $\langle A \rangle$ and $\langle P \rangle$, use is made first of the Laplace–deGennes transformation of the factors $1/s^4$ and $1/s^6$ as first done by Diehl and Eisenriegler [25] for evaluating $\langle A \rangle$ for chains and rings, and then of the Wei–Eichinger method [24]. The final results for self-intersecting walks are $\langle A \rangle = \varphi_2$ and $\langle P \rangle = \varphi_3$, with φ_m given by

$$\varphi_m = d\,\omega_m(d) \int_0^\infty X^{2m-1}\, S_m(x)\, D^{-d/2}(x)\, \mathrm{d}x\,,$$

where $\omega_2(x) = 1 + x/2$ and $\omega_3(x) = (1 + x/4)\omega_2(x)$. We note that analytic evaluations of δ, ζ, $\langle A \rangle$ and $\langle P \rangle$ for self-avoiding walks are much more involved and can nonetheless be carried out [13, 26]. Numerical evaluations of $\langle A \rangle$ and $\langle P \rangle$ based on the above equalities for open, closed and end-looped random walks in two and three dimensions have been made and the results are tabulated in Tables 1 and 2 which also include values of δ and ζ for these walks for comparison. In Table 3 are numerical values of $\langle A \rangle$ and $\langle P \rangle$ for an end-looped random walk in higher dimensions. Finally, we note that for large d, $\langle A \rangle$ or $\langle P \rangle$ may be expanded as an asymptotic series in $1/d$ for arbitrary random walks and that a similar $1/d$-expansion for δ_α or σ_α can also be carried out as in the case of an open random-walk [15, 17, 23, 27]. We have obtained the $1/d$-expansion of $\langle A \rangle$ at $\mathrm{O}(d^{-2})$ which recovers the results at $\mathrm{O}(d^{-1})$ for chains and rings [15, 25] (the details of which are to be published elsewhere), and the results of $\langle P \rangle$ at $\mathrm{O}(d^{-1})$, i.e., $\langle P \rangle = \mu_3[1 + 6\beta_3/d + \mathrm{O}(d^{-2})]$ with $\beta_3 = 1 + 2\mu_2 - 3\mu_4/\mu_3$.

From Table 1, it is seen that our approximation method of analytically evaluating shape factors is satisfactory, especially for the largest shape factor, for the three selected types of random walks confined to a plane, with relative errors of δ_1 being between 1.4% and 4.1%. It is also found that the simulation results of Bishop and Michels [28] for shape factors of 2D chains and rings of finite length ($n = 64$), i.e., 0.839 and 0.161 for chains and 0.755 and 0.245 for rings, are very close to the exact values given in Table 1 and that shape variance factors are in descending order, i.e., $\sigma_1 > \sigma_2$, for all three types of random walks, implying a broader distribution of the largest principal component. In three dimensions, our approximate values of shape factors for chains (see Table 2) are close to those of Zifferer and Olaj [29] by use of simulation (0.7646, 0.1721 and 0.06333, extrapolated to $n = \infty$) while the results for Edwards chains are in agreement with the simulation results of Mazur, Guttman and McCrackin [8], i.e., 0.785, 0.162 and 0.053. Our approximation is also seen to be an improvement to that of Doi and Nakajima [20] (0.7386, 0.1814 and 0.08004) and that of Gaspari, Rudnick and Beldjenna [23] (0.7599, 0.1900 and 0.08443, see also Refs. [15, 17, 27]) for open self-intersecting walks; (to the approximation) and of Minato and Hatano [21] (0.7658, 0.1667 and 0.06753) for open self-avoiding walks. It is further noted that a self-avoiding walk is more extended than a self-intersecting one in both two and three dimensions. For an end-looped random walk, it is found from Tables 1–3 that it is more elongated than simply open or closed random walks though its average size is smaller than that of a chain (with a shrinking factor, i.e., the ratio of its mean square radius of gyration to that of a chain, of $51/64 \cong 0.796875$); as d increases from 2 to ∞, its shape asymmetry decreases slowly, reaching a limit at $d = \infty$.

Finally, we notice that although no experimental determination of shape factors for randomly coiled macromolecules has been done so far, there are available [30] numerical values which completely specify the equivalent ellipsoids of globular proteins as calculated from small-angle X-ray scattering data. This should stimulate future experimental work on shapes of polymers modeled as either self-avoiding or self-intersecting walks.

Acknowledgements

The author thanks Professors Yuliang Yang and Xuexian Zhu for useful discussions. This work was supported in part by Peking University Excellent Scholar Fund and by National Natural Science Foundation and State Education Commission of China.

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