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LETTER TO THE EDITOR

Universal shape ratios for open and closed random walks: exact results for all d

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Abstract. The mean asphericities $\langle A_d \rangle$ of open and closed Gaussian polymer chains are computed exactly and analytically (up to simple quadratures) for arbitrary space dimensions d. Excellent agreement is found with existing simulation data for $d = 2$, 3, and 4. Our technique can also be used to compute other averages of ratios of fluctuating variables as well as extended to include the effects of self-avoiding walk interactions.

As has been known for several decades, the gross shapes of polymers are not spherical (Kuhn 1934, Solc 1971). This anisotropy plays an important role in the interpretation of viscous flow and other hydrodynamic phenomena of dilute polymeric solutions. (Kramers 1946, Abernathy *et al* 1980). Recently several groups of authors have undertaken efforts to define and compute universal numbers by which the shapes of polymers can be characterised (Bishop and Michels 1985, Theodorou and Suter 1985, Aronovitz and Nelson 1986, Rudnick and Gaspari 1986, Bishop and Saltiel 1987, Gaspari *et al* 1987). Consider a linear polymer consisting of N repeat units ('monomers') in d dimensions. We assume that on semi-microscopic scales this polymer chain can be modelled as an $(N-1)$-step walk in $\mathbb{R}^d$. Let $\boldsymbol{R}_j = (X_{j,\alpha}\,;\ \alpha = 1, \ldots, d)$ be the position vector of the jth monomer. The shape of a specified conformation $\{\boldsymbol{R}_j\}$ of the chain can be conveniently characterised by the invariants of the radius of gyration tensor $\boldsymbol{Q}$ with elements

$$Q_{\alpha\beta} = N^{-1} \sum_{i>j} (X_{i,\alpha} - X_{j,\alpha})(X_{i,\beta} - X_{j,\beta}) \tag{1}$$

(Solc 1971, Rudnick and Gaspari 1986). One familiar such invariant is the so-called *asphericity*

$$A_d = \frac{d}{d-1} \frac{\mathrm{tr}(\hat{\boldsymbol{Q}}^2)}{(\mathrm{tr}\, \boldsymbol{Q})^2} \tag{2}$$

where $\hat{\boldsymbol{Q}}$ means the traceless tensor

$$\hat{\boldsymbol{Q}} = \boldsymbol{Q} - \frac{1}{d} \mathbf{1}\, \mathrm{tr}\, \boldsymbol{Q}. \tag{3}$$

The quantity A_d ranges from 0 for a spherically symmetric object to 1 for a completely elongated chain. Hence the *mean asphericity* $\langle A_d \rangle$ one obtains by averaging

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$A_d = A_d\{\boldsymbol{R}_j\}$ over all conformations $\{\boldsymbol{R}_j\}$ is an adequate measure of how much its shape deviates on average from a spherical one. However, the computation of $\langle A_d \rangle$ requires the averaging of a *ratio of fluctuating variables.* This is a non-trivial task even for Gaussian (or random walk, RW) chains. In fact, except in the limit $d \to \infty$ (Gaspari *et al* 1987), no exact analytical results for $\langle A_d \rangle_{\mathrm{RW}}$ have been obtained so far. In the existing analytical approaches (Aronovitz and Nelson 1986, Rudnick and Gaspari 1986, Gaspari *et al* 1987) the above difficulty is usually bypassed by considering simpler—albeit less natural—measures of the mean asphericity, such as the ratio of averages

$$a_d = \frac{d}{d-1} \langle \mathrm{tr}(\hat{\boldsymbol{Q}}^2) \rangle / \langle (\mathrm{tr}\, \boldsymbol{Q})^2 \rangle. \tag{4}$$

The only exception is the work of Gaspari *et al* (1987) who worked out the first two terms of the expansion of $\langle A_d \rangle_{\mathrm{RW}}$ in powers of d^{-1}, claiming that an exact analytical evaluation of $\langle A_d \rangle_{\mathrm{RW}}$ for general d was impossible.

In this letter we will present *exact analytical results* for $\langle A_d \rangle_{\mathrm{RW}}$. Both *open* and *closed* chains will be considered. Although detailed results will only be worked out for the RW case, our technique can also be utilised in conjunction with perturbation theory to compute the ε expansion of $\langle A_d \rangle$ for *self-avoiding* walks in $4-\varepsilon$ dimensions (Diehl *et al* 1989). Furthermore, there exist other interesting universal averages of ratios that can be evaluated in the same manner (Diehl *et al* 1989).

Let us write the reduced Hamiltonian of the chain as

$$\begin{aligned} \mathcal{H}\{\boldsymbol{R}_j\} &= \mathcal{H}_{\mathrm{RW}}\{\boldsymbol{R}_j\} + \mathcal{V}\{\boldsymbol{R}_j\} \\ &= \sum_{\alpha=1}^{d} [h_{\mathrm{RW}}\{X_{j,\alpha}\}] + \mathcal{V}\{\boldsymbol{R}_j\}. \end{aligned} \tag{5}$$

Here $\mathcal{H}_{\mathrm{RW}}$ is the Gaussian part with

$$h_{\mathrm{RW}}\{X_j\} = (2l)^{-2} \sum_{j=2(1)}^{N} (X_j - X_{j-1})^2 \tag{6}$$

where the summation over j starts at $j=2$, if the chain is open, and at $j=1$, if it is closed. $\mathcal{V}$ stands for two-body and higher interaction terms which need not be specified here. The crucial trick of our approach is to use the identity

$$x^{-2} = \int_0^\infty y\, \mathrm{e}^{-xy}\, \mathrm{d}y \tag{7}$$

with $x = \mathrm{tr}\, \boldsymbol{Q}$. This enables us to cast $\langle A_d \rangle$ in the form

$$\begin{aligned} \frac{d-1}{d} \langle A_d \rangle &= \int_0^\infty \mathrm{d}y\, y \langle \mathrm{tr}(\hat{\boldsymbol{Q}}^2)\, \mathrm{e}^{-y\, \mathrm{tr}\, \boldsymbol{Q}} \rangle \\ &= \int_0^\infty \mathrm{d}y\, y \langle \mathrm{tr}(\hat{\boldsymbol{Q}}^2) \rangle_{\mathcal{H}_y} Z[\mathcal{H}_y]/Z[\mathcal{H}]. \end{aligned} \tag{8}$$

Here $\mathcal{H}_y$ means the Hamiltonian

$$\mathcal{H}_y\{\boldsymbol{R}_j\} = \mathcal{H} + y\, \mathrm{tr}\, \boldsymbol{Q} \tag{9}$$

$Z[\mathcal{H}_y] = \mathrm{Tr}\, \exp(-\mathcal{H}_y\{\boldsymbol{R}_j\})$ the corresponding partition function, and $\langle \cdot \rangle_{\mathcal{H}_y}$ a respective average.

Writing $\mathcal{H}_y = \mathcal{H}_{\mathrm{RW},y} + \mathcal{V}$ we have from (1) and (6) $\mathcal{H}_{\mathrm{RW},y}\{\boldsymbol{R}_j\} = \Sigma_\alpha\, h_{\mathrm{RW},y}\{X_{j,\alpha}\}$ with

$$h_{\mathrm{RW},y}\{X_j\} = (2l)^{-2} \sum_{j=2(1)}^{N} (X_j - X_{j-1})^2 + yN^{-2} \sum_{i>j} (X_i - X_j)^2. \tag{10}$$

Thus the RW analogue of $\mathcal{H}_y$ is *Gaussian*, a fact which enables us to compute analytically the partition functions and the average required in (8) if $\mathcal{V} \equiv 0$, as well as to compute the perturbation series of these quantities by means of Wick's theorem in the general case $\mathcal{V} \neq 0$. In the following we will set $\mathcal{V} \equiv 0$.

We introduce normal coordinates Ξ_ν to obtain

$$h_{\mathrm{RW},y}\{X_j = \sum_\nu \varphi_\nu(j)\Xi_\nu\} = \sum_\nu \varepsilon_\nu(y)|\Xi_\nu|^2 \tag{11}$$

where the eigenfunctions $\varphi_\nu(j)$ and the eigenvalues $\varepsilon_\nu(y)$ depend on the boundary conditions. For ring polymers (RP) we have periodic boundary conditions and the eigenfunctions are $\varphi_\nu^{\mathrm{RP}}(j) = N^{-1/2}\exp(\mathrm{i}2\pi\nu j/N)$ with $\nu = 0, \pm 1, \pm 2, \ldots, \pm(N-1)/2$, provided N is uneven. For open chains (OC) the eigenfunctions are identical to those of a harmonic chain with free ends and given by $\varphi_{\nu=0}^{\mathrm{OC}}(j) = N^{-1/2}$ and $\varphi_\nu^{\mathrm{OC}}(j) = (2/N)^{1/2}\cos[\pi\nu(j-\frac{1}{2})/N]$ for $\nu = 1, \ldots, N-1$. The associated eigenvalues are

$$\begin{aligned} \varepsilon_\nu^{\mathrm{RP}}(y) &= l^{-2}\left[\sin^2\left(\frac{\pi\nu}{N}\right) + \frac{y}{N}\right] \\ \varepsilon_\nu^{\mathrm{OC}}(y) &= l^{-2}\left[\sin^2\left(\frac{\pi\nu}{2N}\right) + \frac{y}{N}\right]. \end{aligned} \tag{12}$$

In terms of these $\varepsilon_\nu(y)$ the required ratio of partition function reads

$$\frac{Z[\mathcal{H}_{\mathrm{RW},y}]}{Z[\mathcal{H}_{\mathrm{RW}}]} \equiv \langle \mathrm{e}^{-y\,\mathrm{tr}\,\boldsymbol{Q}}\rangle_{\mathrm{RW}} = \left[\prod_{\nu\neq 0} \frac{\varepsilon_\nu(y)}{\varepsilon_\nu(0)}\right]^{-d/2}. \tag{13}$$

The result simplifies considerably in the continuum limit $l \to 0$, $N \to \infty$, with $Nl^2 \equiv L$ fixed, in which one finds

$$\langle \mathrm{e}^{-y\,\mathrm{tr}\,\boldsymbol{Q}}\rangle_{\mathrm{RW}}^{(\mathrm{RP})} = \left[\frac{y_L/2}{\sinh(y_L/2)}\right]^d \tag{14}$$

and

$$\langle \mathrm{e}^{-y\,\mathrm{tr}\,\boldsymbol{Q}}\rangle_{\mathrm{RW}}^{(\mathrm{OC})} = \left[\frac{y_L}{\sinh(y_L)}\right]^{d/2} \tag{15}$$

with $y_L \equiv 2(yL)^{1/2}$.

The other average $\langle \mathrm{tr}(\hat{\boldsymbol{Q}}^2)\rangle_{\mathcal{H}_{\mathrm{RW},y}}$ can be expressed in terms of the propagator

$$G_{j,j'} = \langle (X_j - X_1)(X_{j'} - X_1)\rangle_{\mathcal{H}_{\mathrm{RW},y}} \tag{16}$$

by applying Wick's theorem. In the continuum limit one finds for $G(t, t') \equiv \lim G_{j=t/l^2, j'=t'/l^2}$ the results

$$\begin{aligned} G^{(\mathrm{RP})}(t, t') = \frac{L}{y_L \sinh(y_L/2)} \{&\cosh[\tfrac{1}{2}y_L - |\tau - \tau'|] - \cosh[\tfrac{1}{2}y_L - \tau] \\ &- \cosh[\tfrac{1}{2}y_L - \tau'] + \cosh[\tfrac{1}{2}y_L]\} \end{aligned} \tag{17}$$

and

$$G^{(\mathrm{OC})}(t,t') = \frac{2L}{y_L \sinh(y_L)} \{\tfrac{1}{2}[\cosh(y_L - \tau - \tau') + \cosh(y_L - |\tau - \tau'|)]$$
$$- \cosh(y_L - \tau) - \cosh(y_L - \tau') + \cosh(y_L)\} \tag{18}$$

where $\tau = y_L t/L$ and $\tau' = y_L t'/L$. The remaining calculation is straightforward, though lengthy and tedious. The final result can be written in the remarkably simple form

$$\langle A_d \rangle_{\mathrm{RW}}^{(\mathrm{RP})} = \frac{d+2}{2d+2} \langle A_{2d} \rangle_{\mathrm{RW}}^{(\mathrm{OC})}$$
$$= \frac{d(d+2)}{4(d+1)} \left[3 + \frac{2}{d} - dM_d \right] \tag{19}$$

with

$$M_d = \int_0^\infty x^{d+1} \sinh^{-d} x \, \mathrm{d}x. \tag{20}$$

When these results are expanded in powers of d^{-1}, one obtains

$$\langle A_d \rangle_{\mathrm{RW}}^{(\mathrm{RP})} = \tfrac{1}{5} + \tfrac{32}{175} d^{-1} + \mathrm{O}(d^{-2}) \tag{21}$$
$$\langle A_d \rangle_{\mathrm{RW}}^{(\mathrm{OC})} = \tfrac{2}{5} - \tfrac{12}{175} \mathrm{d}^{-1} + \mathrm{O}(d^{-2}) \tag{22}$$

which agrees with the results of Gaspari *et al* (1987) up to a sign error in their equation (3.44). In table 1 we list the explicit results for $\langle A_d \rangle_{\mathrm{RW}}$ with $d = 2, 3$, and 4 and compare them with those obtained by Bishop and Saltiel (1988) through numerical simulations. The agreement is very good.

Table 1. Comparison between our exact results and the simulation results by Bishop and Saltiel (1988). Here $\zeta(\cdot)$ is the Riemann zeta function.

	$\langle A_d \rangle_{\mathrm{RW}}^{(\mathrm{RP})}$		$\langle A_d \rangle_{\mathrm{RW}}^{(\mathrm{OC})}$	
d	Exact	Simulations	Exact	Simulations
2	$(8/3) - 2\zeta(3) = 0.2625\ldots$	0.279 ± 0.014	$[10 - 7\zeta(3)]/4 = 0.3964\ldots$	0.411 ± 0.031
3	$\frac{5}{16}\{11 - 27[7\zeta(3) - \frac{31}{4}\zeta(5)]\} = 0.2464\ldots$	0.252 ± 0.020	$0.394\,27\ldots$	0.390 ± 0.004
4	$\frac{6}{5}\{\frac{7}{2} - 20[\zeta(3) - \zeta(5)]\} = 0.2369\ldots$	0.234 ± 0.009	$4 - 3\zeta(3) = 0.3937\ldots$	0.388 ± 0.014

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