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SPANS OF POLYMER CHAINS

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Abstract—The span of an N-segment chain in a given direction, e, is defined as the maximum distance between parallel planes normal to e which contain segments of the chain. We present a simple derivation of Daniel's result for the span of a random chain. We have generalized this simple derivation and have calculated: (1) $\langle X_{\text{ring}}\rangle$, the average span of an N-segment random polymer ring; (2) $\langle X_{\text{surf.}}\rangle$, the average span in the direction normal to the solution surface of an N-segment chain which is attached at one end to the surface; (3) In addition, we have obtained the exact solution of a problem treated by Hollingsworth, the calculation of $\langle R_{\text{Holl.}}\rangle$, the average distance between the first segment and the most distant segment in an N-segment polymer chain. The results are:

$$\langle X_{\text{ring}}\rangle = (\pi N/6)^{1/2} \cong 0.724N^{1/2}$$

$$\langle X_{\text{surf.}}\rangle = 2\ln 2(\pi N/6)^{1/2} \cong 1.003N^{1/2}$$

$$\langle R_{\text{Holl.}}\rangle = \tfrac{1}{2}\pi(\pi N/6)^{1/2} \cong 1.137N^{1/2}.$$

For reference purposes we note that the average span calculated by Daniels for an N-segment polymer chain is $\langle X\rangle = 2(2N/3\pi)^{1/2} \cong 0.921N^{1/2}$ and the root-mean-square end-to-end distance is $\langle r_N^2\rangle^{1/2} = N^{1/2}$.

The spans of each chain configuration in the directions defined by the principal components of the square radius of gyration of the chain have been determined. The relative values of the average squares of the spans in the directions of the largest, intermediate, and smallest components of the square radius of gyration are found to be 6.7 : 2.2 : 1 in the case of the unrestricted polymer chain model. For the same model, Solč and Stockmayer obtained the following set of relative values of the ordered principal components of the square radius of gyration, 11.7 : 2.7 : 1. We have determined that the apparent difference between these two sets of relative average dimensions arises from a different segment density distribution in the different principal directions.

I. INTRODUCTION

Spans of polymer chains are useful measures of their size and shape. The span of an N-segment chain in a given direction, e, is defined as the maximum distance between parallel planes normal to e which contain segments of the chain. The span was first introduced by Daniels[1] in 1941 and later was discussed independently by Kuhn[2,3] and, in a different context, by Feller.[4] A set of spans in three orthogonal directions serves to define the dimensions of a rectangular box occupied by a polymer chain. The relative proportions of the box and the disposition of segments of the polymer chain within the box influences the solution properties of these chains. For example, properties such as viscosity, streaming birefringence, dielectric relaxation, and rates of diffusion and sedimentation are related to movements of the entire chain, or parts of it, relative to the solvent. Recently, Mazur and Rubin[5] have shown that the typical or average shape of the circumscribing box for a polymer chain is significantly noncubic. They investigated spans based on space-fixed axes[6] and on chain-fixed axes[7] and ordered each set of three spans according to their magnitude. The relative dimensions based on chain-fixed axes associated with the maximum span of the entire chain were found to be respectively, 2.42 : 1.48 : 1 and 2.73 : 1.55 : 1 for unrestricted lattice-random-walk and self-avoiding lattice-random-walk models of polymer chains. The result that the typical shape is asymmetric is not new. Kuhn,[8] Hollingsworth[9,10] and Kuhn[2] came to similar conclusions. Asymmetric configurations are simply more numerous than symmetric ones. More recently, Koyama[11,12], Solč and Stockmayer,[13] Solč[14] and Mazur, Guttman, and McCrackin[15] investigated the ordered principal components of the square radius of gyration tensor of model polymer chains and found evidence for an even more asymmetric form than that indicated by the values of the ordered spans cited above. The origin of this apparent discrepancy lies in the distribution of polymer segments within the spanning prism and will be discussed in Section 3.

The effect of the asymmetric shape of polymer chain molecules on their solution properties has been recognized for some time.[16,17] However, detailed knowledge of the average shape of the molecule and detailed knowledge of the average disposition of segments of the molecule with respect to its center of gravity has been lacking. This type of information is important in any discussion of the gradient dependence of the intrinsic viscosity of chain molecules.[18,19]

In Section 2, the random flight model of a random walk[20] is adopted as a model of a polymer chain. We present a simple derivation of the joint probability distribution function of three orthogonal spans of the polymer chain. The derivation uses ideas implicit in the work of Daniels[1] and Kuhn[3] and is easily modified to treat the following problems: (1) the span of an N-segment ring; (2) the span in the direction normal to the solution surface of an N-segment chain which is attached at one end to the surface; and (3) the exact solution of a problem treated by Hollingsworth,[9] the determination of the average distance between the first segment and the most distant segment in an N-segment polymer chain.

II. SPANS OF SOME RANDOM FLIGHT CHAINS

In this Section we first derive an expression for $p(R_1, R_2, R_3; N)$ the joint probability distribution function (p.d.f.) of three spans of a random flight chain in the directions of the orthogonal space-fixed axes, x_1, x_2, x_3. The quantity, $p(R_1, R_2, R_3)\,dR_1\,dR_2\,dR_3$, is the probability that a random flight chain of N steps has a span in the x_i-direction which lies between R_i and $R_i + dR_i$, $i = 1, 2, 3$. The terms random flight, polymer chain, and random walk are used interchangeably. In the limit of large N, the p.d.f. of the position of the random walk after N steps is governed by the equation:[20]

$$\frac{\partial v}{\partial N} = \frac{1}{6}\left(\frac{\partial^2 v}{\partial x_1^2} + \frac{\partial^2 v}{\partial x_2^2} + \frac{\partial^2 v}{\partial x_3^2}\right) \qquad (1)$$

where $v = v(x_1, x_2, x_3; N)$. The solution of this equation which is the normalized probability that a random walk starts at ξ_1, ξ_2, ξ_3 and arrives at x_1, x_2, x_3 after N steps is given by the expression

$$v_{\xi_1,\xi_2,\xi_3}(x_1, x_2, x_3) = (2\pi N/3)^{-3/2}\exp\{-3[(x_1-\xi_1)^2 + (x_2-\xi_2)^2 + (x_3-\xi_3)^2]/2N\}. \qquad (2)$$

The mean square displacement in N steps is

$$\langle (x_1-\xi_1)^2 + (x_2-\xi_2)^2 + (x_3-\xi_3)^2 \rangle = N. \qquad (3)$$

To determine $p(R_1, R_2, R_3; N)$, consider the auxiliary random flight problem governed by eqn (1) in the box-like region $\Omega(R_1, R_2, R_3)$ where $0 \leq x_i \leq R_i$, $i = 1, 2, 3$ and where the boundary conditions on the walls of the box are absorbing. That is, $v(x_1, x_2, x_3; N) = 0$ on the walls of the box. The probability that the random walk starts in the box at ξ_1, ξ_2, ξ_3 and is located at x_1, x_2, x_3 at step N is[21]

$$v_{\xi_1,\xi_2,\xi_3}(x_1, x_2, x_3; N) = \prod_{i=1}^{3}\left\{\frac{2}{R_i}\sum_{n_i=1}^{\infty}\sin\left(\frac{n_i\pi\xi_i}{R_i}\right)\sin\left(\frac{n_i\pi x_i}{R_i}\right)e^{-n_i^2\pi^2 N/6R_i^2}\right\}. \qquad (4)$$

From eqn (4), we derive an expression which is proportional to the total number of distinct N-step random walks which are contained in $\Omega(R_1, R_2, R_3)$,

$$\Psi(R_1, R_2, R_3; N) = \int_0^{R_1} dx_1 \int_0^{R_2} dx_2 \int_0^{R_3} dx_3 \int_0^{R_1} d\xi_1 \int_0^{R_2} d\xi_2 \times \int_0^{R_3} d\xi_3 v_{\xi_1,\xi_2,\xi_3}(x_1, x_2, x_3; N) = \prod_{i=1}^{3}\psi(R_i; N) \qquad (5)$$

where

$$\psi(R_i; N) = \frac{8R_i}{\pi^2}\sum_{n=0}^{\infty}(2n+1)^{-2}\exp[-(2n+1)^2\pi^2 N/6R_i^2]. \qquad (6)$$

Included among the distinct N-step walks in $\Omega(R_1, R_2, R_3)$, $\Psi(R_1, R_2, R_3; N)$, there are exactly

$$(R_1-\rho_1)(R_2-\rho_2)(R_3-\rho_3)p(\rho_1, \rho_2, \rho_3; N)\,d\rho_1\,d\rho_2\,d\rho_3$$

walks whose spanning box is $\Omega(\rho_1, \rho_2, \rho_3)$ where $0 \leq \rho_i \leq R_i$, $i = 1, 2, 3$. Thus, the following relation exists between $\Psi(R_1, R_2, R_3; N)$ and $p(\rho_1, \rho_2, \rho_3; N)$

$$\Psi(R_1, R_2, R_3; N) = \int_0^{R_1} d\rho_1 \int_0^{R_2} d\rho_2 \int_0^{R_3} d\rho_3 (R_1-\rho_1)(R_2-\rho_2)(R_3-\rho_3)p(\rho_1, \rho_2, \rho_3; N). \qquad (7)$$

The solution of this simple integral equation is

$$p(R_1, R_2, R_3; N) = \prod_{i=1}^{3}\left\{\frac{d^2}{dR_i^2}\psi(R_i; N)\right\}. \qquad (8)$$

Daniels[1] obtained the product form in eqn (8) for the joint p.d.f. of the spans in the limit $N \gg 1$. Recently, Weiss and Rubin[22] evaluated correction terms to this asymptotic result.

The average value of the span in the x_i-direction, $\langle X_i \rangle$, is obtained from the expression

$$\langle X_i \rangle = \frac{\int_0^\infty dR_1 \int_0^\infty dR_2 \int_0^\infty dR_3 R_i p(R_1, R_2, R_3; N)}{\int_0^\infty dR_1 \int_0^\infty dR_2 \int_0^\infty dR_3 p(R_1, R_2, R_3; N)} = \frac{\int_0^\infty dR\, R\frac{d^2}{dR^2}\psi(R; N)}{\int_0^\infty dR\frac{d^2}{dR^2}\psi(R; N)} = \frac{\left[R\frac{d}{dR}\psi(R; N) - \psi(R; N)\right]\Big|^\infty}{\frac{d}{dR}\psi(R; N)\Big|^\infty}. \qquad (9)$$

The functions $(d/dR)\psi(R; N)$ and $\psi(R; N)$ in eqn (9) are equal to zero at $R = 0$. At $R = \infty$, the numerator and denominator in eqn (9) must be evaluated by taking the limit $R \to \infty$. The results obtained in Appendix 1 are:

$$\lim_{R\to\infty}\frac{d}{dR}\psi(R; N) = 1 \qquad (10)$$

and

$$\lim_{R\to\infty}\left[R\frac{d}{dR}\psi(R; N) - \psi(R; N)\right] = 2(2N/3\pi)^{1/2}. \qquad (11)$$

Thus the average span of an N-step polymer chain in the x_i-direction is[1,3,4]

$$\langle X \rangle = 2(2N/3\pi)^{1/2}. \qquad (12)$$

1. *Span of an* N-*segment ring*

The calculation of the joint p.d.f. of the spans of an N-segment ring requires only a slight modification of the foregoing calculation. We consider the same auxiliary random flight problem governed by eqn (1) in the box, $\Omega(R_1, R_2, R_3)$, with absorbing boundary conditions on the walls of the box. Then the probability that a ring of N steps is contained in the box and passes through the point ξ_1, ξ_2, ξ_3 can be obtained from eqn (4) by setting $x_i = \xi_i$, $i = 1, 2, 3$. This probability is proportional to

$$v_{\xi_1,\xi_2,\xi_3}(\xi_1, \xi_2, \xi_3) = \prod_{i=1}^{3}\left\{\frac{2}{R_i}\sum_{n_i=1}^{\infty}\sin^2\left(\frac{n_i\pi\xi_i}{R_i}\right)e^{-n_i^2\pi^2 N/6R_i^2}\right\}. \qquad (13)$$

Then the total number of distinct N-segment rings which are contained in $\Omega(R_1, R_2, R_3)$ is proportional to

$$\Psi_{\text{ring}}(R_1, R_2, R_3; N) = \int_0^{R_1} d\xi_1 \int_0^{R_2} d\xi_2 \int_0^{R_3} d\xi_3 v_{\xi_1,\xi_2,\xi_3}(\xi_1, \xi_2, \xi_3; N) = \prod_{i=1}^{3} \chi(R_i; N) \tag{14}$$

where

$$\chi(R_i; N) = \sum_{n=1}^{\infty} \exp[-n^2\pi^2 N/6R_i^2]. \tag{15}$$

The joint p.d.f. of the spans of an N-segment ring, $p_{\text{ring}}(R_1, R_2, R_3; N)$, and $\Psi_{\text{ring}}(R_1, R_2, R_3; N)$ satisfy an integral equation which is identical with eqn (7). Thus, the expression for $p_{\text{ring}}(R_1, R_2, R_3; N)$ is

$$p_{\text{ring}}(R_1, R_2, R_3; N) = \prod_{i=1}^{3} \left\{\frac{d^2}{dR_i^2} \chi(R_i; N)\right\}. \tag{16}$$

The average value of the span of the ring in the x_i-direction is obtained from an expression which is identical in form with eqn (9)

$$\langle X_{\text{ring}} \rangle = \frac{\left[R\frac{d}{dR}\chi(R; N) - \chi(R; N)\right]\Big|^{\infty}}{\frac{d}{dR}\chi(R; N)\Big|^{\infty}}. \tag{17}$$

The values of the numerator and denominator in the limit $R \to \infty$ are obtained in Appendix 2. The results are

$$\lim_{R\to\infty} \frac{d}{dR}\chi(R; N) = (3/2\pi N)^{1/2} \tag{18}$$

and

$$\lim_{R\to\infty} \left[R\frac{d}{dR}\chi(R; N) - \chi(R; N)\right] = \frac{1}{2}. \tag{19}$$

Thus the average span of an N-segment polymer chain in the x_i-direction is

$$\langle X_{\text{ring}} \rangle = (\pi N/6)^{1/2}. \tag{20}$$

2. *Span in the direction normal to the solution surface of an* N-*segment chain which is attached at one end to the surface*

We assume that the solution surface corresponds to the plane $x_1 = 0$. The calculation of the joint p.d.f. of the spans in this case $p_{\text{surf.}}(R_1, R_2, R_3; N)$ requires further modification. We must proceed indirectly in the calculation of $\Psi_{\text{surf.}}(R_1, R_2, R_3; N)$, a quantity which is proportional to the total number of distinct N-step walks which originate on the surface $x_1 = 0$ and lie in the region $0 \le x_i \le R_i$, $i = 1, 2, 3$. There is a complication because the walks originate on an absorbing surface. To circumvent this difficulty, we first calculate $\Psi_\epsilon(R_1, R_2, R_3; N)$, a quantity proportional to the total number of distinct N-step walks which originate anywhere on the plane $x_1 = \epsilon$ inside the region $\Omega(R_1, R_2, R_3)$ and remain in $\Omega(R_1, R_2, R_3)$. Subsequently we calculate

$$\Psi_{\text{surf.}}(R_1, R_2, R_3; N) = \lim_{\epsilon\to 0} \epsilon^{-1}\Psi_\epsilon(R_1, R_2, R_3; N). \tag{21}$$

The value of $\Psi_\epsilon(R_1, R_2, R_3; N)$ is

$$\Psi_\epsilon(R_1, R_2, R_3; N) = \int_0^{R_1} dx_1 \int_0^{R_2} dx_2 \int_0^{R_3} dx_3 \int_0^{R_2} d\xi_2 \int_0^{R_3} d\xi_3 v_{\epsilon,\xi_2,\xi_3}(x_1, x_2, x_3; N) = \psi_\epsilon(R_1; N)\psi(R_2; N)\psi(R_3; N) \tag{22}$$

where

$$\psi_\epsilon(R_1; N) = \frac{4}{\pi}\sum_{n=0}^{\infty} (2n+1)^{-1} \sin[(2n+1)\pi\epsilon/R_1] \times \exp[-(2n+1)^2\pi^2 N/6R_1^2] \tag{23}$$

and $\psi(R; N)$ is given in eqn (6). Substituting (22) and (23) in eqn (21), we obtain

$$\Psi_{\text{surf.}}(R_1, R_2, R_3; N) = \psi_{\text{surf.}}(R_1; N)\psi(R_2; N)\psi(R_3; N) \tag{24}$$

where

$$\psi_{\text{surf.}}(R_1; N) = \frac{4}{R_1}\sum_{n=0}^{\infty} \exp[-(2n+1)^2\pi^2 N/6R_1^2]. \tag{25}$$

Included among the number of distinct N-step walks in $\Omega(R_1, R_2, R_3)$ which originate on $x_1 = 0$, $\Psi_{\text{surf.}}(R_1, R_2, R_3; N)$, there are exactly

$$(R_2 - \rho_2)(R_3 - \rho_3)p_{\text{surf.}}(\rho_1, \rho_2, \rho_3)\, d\rho_1\, d\rho_2\, d\rho_3$$

walks whose spanning box has the dimensions ρ_1, ρ_2, ρ_3. Thus the relation between $\Psi_{\text{surf.}}(R_1, R_2, R_3; N)$ and $p_{\text{surf.}}(\rho_1, \rho_2, \rho_3)$ is

$$\Psi_{\text{surf.}}(R_1, R_2, R_3; N) = \int_0^{R_1} d\rho_1 \int_0^{R_2} d\rho_2 \int_0^{R_3} d\rho_3 (R_2 - \rho_2) \times (R_3 - \rho_3)p_{\text{surf.}}(\rho_1, \rho_2, \rho_3). \tag{26}$$

The expression for $p_{\text{surf.}}(R_1, R_2, R_3; N)$ is

$$p_{\text{surf.}}(R_1, R_2, R_3; N) = \frac{d}{dR_1}\psi_{\text{surf.}}(R_1; N)\frac{d^2}{dR_2^2}\psi(R_2; N) \times \frac{d^2}{dR_3^2}\psi(R_3; N). \tag{27}$$

The average value of the span normal to the surface is

$$\langle X_{\text{surf.}} \rangle = \frac{\int_0^\infty dR_1 \int_0^\infty dR_2 \int_0^\infty dR_3 R_1 p_{\text{surf.}}(R_1, R_2, R_3; N)}{\int_0^\infty dR_1 \int_0^\infty dR_2 \int_0^\infty dR_3 p_{\text{surf.}}(R_1, R_2, R_3; N)} = \frac{\left[R\psi_{\text{surf.}}(R; N) - \int_0^R d\rho\psi_{\text{surf.}}(\rho; N)\right]\Big|^{\infty}}{\psi_{\text{surf.}}(R; N)\Big|^{\infty}}. \tag{28}$$

The values of the numerator and denominator in eqn (28) in the limit $R \to \infty$ are obtained in Appendix 3. The results are

$$\lim_{R\to\infty} \psi_{\text{surf.}}(R; N) = (6/\pi N)^{1/2} \tag{29}$$

and

$$\lim_{R\to\infty}\left[R\psi_{\text{surf.}}(R;N)-\int_0^R \mathrm{d}\rho\psi_{\text{surf.}}(P;N)\right]=2\ln 2. \tag{30}$$

Thus the average span normal to the surface of a surface-attached N-segment polymer chain is

$$\langle X_{\text{surf.}}\rangle = \ln 2(2\pi N/3)^{1/2}. \tag{31}$$

3. *Exact solution of a problem posed by Hollingsworth*[9]

We next treat the problem of calculating for an N-step random walk the average largest excursion from its starting point. The problem of calculating the p.d.f. of the largest excursion in an N-step walk, $p_{\text{Holl.}}(R)$, can be treated in a manner which is exactly analogous to the calculation of the joint p.d.f. of the spans R_1, R_2, R_3 in eqn (8). We consider the auxiliary random flight problem governed by eqn (1) in a sphere of radius R with an absorbing boundary condition on the surface of the sphere. The appropriate coordinate system for treating this problem is spherical polar with the origin and starting point of the random walk located at the center of the sphere. In spherical polar coordinates, for a walk starting at the origin, eqn (1) takes the form

$$\frac{\partial v}{\partial N}=\frac{1}{6}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial v}{\partial r} \tag{32}$$

with $v(R,N)=0$ and $v(r,0)=\delta(0)$. The solution is[21]

$$v_0(R,N)=\frac{1}{2R^2}\sum_{n=1}^{\infty}\frac{n}{r}\sin\left(\frac{\pi n r}{R}\right)\exp(-\pi^2n^2N/6R^2). \tag{33}$$

The total number of random walks which start at the origin and remain in the sphere after N steps is proportional to

$$\begin{aligned}\Psi_{\text{Holl.}}(R;N)&=\int_0^R \mathrm{d}\rho 4\pi\rho^2 v_0(\rho;N)\\ &=2\sum_{n=1}^{\infty}(-1)^n\exp(-\pi^2n^2N/6R^2).\end{aligned} \tag{34}$$

The total number of walks represented in $\Psi_{\text{Holl.}}(R;N)$ is related to the p.d.f., $p_{\text{Holl.}}(\rho;N)$, that the maximum excursion is ρ by the relation

$$\Psi_{\text{Holl.}}(R;N)=\int_0^R \mathrm{d}\rho\, p_{\text{Holl.}}(\rho;N) \tag{35}$$

so

$$p_{\text{Holl.}}(R;N)=\frac{\mathrm{d}}{\mathrm{d}R}\Psi_{\text{Holl.}}(R;N). \tag{36}$$

The average value of the maximum excursion is

$$\begin{aligned}\langle R_{\text{Holl.}}\rangle&=\frac{\int_0^\infty \mathrm{d}RRp_{\text{Holl.}}(R;N)}{\int_0^\infty \mathrm{d}Rp_{\text{Holl.}}(R;N)}\\ &=\frac{\left[R\Psi_{\text{Holl.}}(R;N)-\int_0^R \mathrm{d}\rho\Psi_{\text{Holl.}}(\rho;N)\right]\Big|_0^\infty}{\Psi_{\text{Holl.}}(R;N)\Big|_0^\infty}.\end{aligned} \tag{37}$$

The values of the numerator and denominator in eqn (37) in the limit $R\to\infty$ are obtained in Appendix 4. The results are

$$\lim_{R\to\infty}\Psi_{\text{Holl.}}(R;N)=1 \tag{38}$$

and

$$\lim_{R\to\infty}\left[R\Psi_{\text{Holl.}}(R;N)-\int_0^R \mathrm{d}\rho\Psi_{\text{Holl.}}(\rho;N)\right]=\tfrac{1}{2}\pi(\pi N/6)^{1/2}. \tag{39}$$

Thus the average largest excursion from the starting point of an N-step walk is

$$\langle R_{\text{Holl.}}\rangle=\tfrac{1}{2}\pi(\pi N/6)^{1/2}. \tag{40}$$

The numerical value of $\langle R_{\text{Holl.}}\rangle$ which Hollingsworth[9] obtained agrees with (40) to the first two decimal places.

III. ASYMMETRIC DISPOSITION OF SEGMENTS IN RANDOM FLIGHT CHAINS

Solč and Stockmayer[13] have studied the asymmetric shape of random flight polymer chains by determining the average ordered principal components of the square radius of gyration. If $u_i(n)$, $i=1,2,3$, are the coordinates of the nth segment with respect to the center of gravity of the chain in the principal axis directions of the square radius of gyration, then the ordered components of the square radius of gyration are

$$S_i^2(N)=(N+1)^{-1}\sum_{n=0}^{N}u_i^2(n),\quad i=1,2,3 \tag{41}$$

where $S_3^2(N)\geq S_2^2(N)\geq S_1^2(N)$. The relative average values obtained by Solč and Stockmayer[13] are

$$\langle S_3^2\rangle:\langle S_2^2\rangle:\langle S_1^2\rangle=11.7:2.7:1. \tag{42}$$

Rubin and Mazur[7] have determined the square spans $r_3^2(N)$, $r_2^2(N)$, $r_1^2(N)$ associated with the set of values $S_3^2(N)$, $S_2^2(N)$, $S_1^2(N)$ for each polymer chain. The span $r_i^2(N)$ is simply

$$\max_{n,m}\{[u_i(n)-u_i(m)]^2\}$$

where $\max_{n,m}\{\ \}$ denotes the maximum value in the set of all intersegment distance components. The relative values of the average square spans are

$$\langle r_3^2\rangle:\langle r_2^2\rangle:\langle r_1^2\rangle=6.7:2.2:1. \tag{43}$$

Rubin and Mazur[7] verified that the distribution of values of $u_i^2(n)$, $n=0,\ldots,N$, within the spanning box is, on the average, significantly different in the different directions, $i=1,2,3$. The distribution is flattest in the direction $i=3$ and the distributions in the directions $i=2$ and $i=1$ fall off progressively more rapidly from the center to the faces of the box. This type of variation accounts for the apparent discrepancy between the two measures of asymmetry listed in eqns (42) and (43).

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APPENDIX

1. Evaluation of

$$\lim_{R\to\infty}\frac{d}{dR}\psi(R;N)$$

and

$$\lim_{R\to\infty}\left[R\frac{d}{dR}\psi(R;N)-\psi(R;N)\right]$$

where

$$\psi(R;N)=8R\pi^{-2}\sum_{n=1}^{\infty}(2n+1)^{-2}\exp\left[-(2n+1)^2\pi^2N/6R^2\right].$$

The expression for

$$\frac{d}{dR}\psi(R;N)$$

is

$$\begin{aligned}\frac{d}{dR}\psi(R;N)&=8\pi^{-2}\sum_{n=0}^{\infty}(2n+1)^{-2}\exp\left[-(2n+1)^2\pi^2N/6R^2\right]\\&\quad+(8N/3R^2)\sum_{n=0}^{\infty}\exp\left[-(2n+1)^2\pi^2N/6R^2\right]\\&=8\pi^{-2}\sum_{n=0}^{\infty}(2n+1)^{-2}\exp\left[-(2n+1)^2\pi^2N/6R^2\right]\\&\quad+(4N/3R^2)\theta_2(0,i2\pi N/3R^2),\end{aligned}\tag{44}$$

where $\theta_2(0, i2\pi N/3R^2)$ is a Theta Function.[23] The Theta Function,

$$\theta_2(0,i2\pi N/3R^2)=2\sum_{n=0}^{\infty}\exp\left[-\pi\left(\frac{2\pi N}{3R^2}\right)(n+\tfrac{1}{2})^2\right],\tag{45}$$

is related to another Theta Function by the transformation[23]

$$\theta_2(0,i2\pi N/3R^2)=(3R^2/2\pi N)^{1/2}\theta_0(0,i3R^2/2\pi N)\tag{46}$$

where

$$\theta_0,(0,i3R^2/2\pi N)=1+2\sum_{n=1}^{\infty}(-1)^n\exp(-3R^2n^2/2N).\tag{47}$$

Combining eqns (46) and (47) with (44), it can be seen that the second term on the right-hand side of eqn (44) is negligible compared to the first term in the limit $R\to\infty$, so

$$\lim_{R\to\infty}\frac{d}{dR}\psi(R;N)=8\pi^{-2}\sum_{n=0}^{\infty}(2n+1)^{-2}=1.\tag{48}$$

The expression for $R\frac{d}{dR}\psi(R;N)-\psi(R;N)$ is

$$\begin{aligned}R\frac{d}{dR}\psi(R;N)-\psi(R;N)&=8R\pi^{-2}\sum_{n=0}^{\infty}(2n+1)^{-2}\\&\quad\times\exp\left[-(2n+1)^2\pi^2N/6R^2\right]\\&\quad+(4N/3)(3/2\pi N)^{1/2}\theta_0(0,i3R^2/2\pi N)-\psi(R;N)\\&=2(2N/3\pi)^{1/2}\theta_0(0,i3R^2/2\pi N).\end{aligned}\tag{49}$$

In the limit $R\to\infty$, we have

$$\lim_{R\to\infty}\left[R\frac{d}{dR}\psi(R;N)-\psi(R;N)\right]=2(2N/3\pi)^{1/2}.\tag{50}$$

2. Evaluation of

$$\lim_{R\to\infty}\frac{d}{dR}\chi(R;N)$$

and

$$\lim_{R\to\infty}\left[R\frac{d}{dR}\chi(R;N)-\chi(R;N)\right]$$

where

$$\chi(R;N)=\sum_{n=1}^{\infty}\exp(-n^2\pi^2N/6R^2).$$

The function $\chi(R;N)$ can be expressed in terms of a Theta Function

$$\chi(R;N)=-\tfrac{1}{2}+\tfrac{1}{2}\theta_3(0,i\pi N/6R^2)\tag{51}$$

where

$$\theta_3(0,i\pi N/6R^2)=1+2\sum_{n=1}^{\infty}\exp\left[-\pi\left(\frac{\pi N}{6R^2}\right)n^2\right].\tag{52}$$

Equation (51) can be rewritten using the transformation[23]

$$\theta_3(0,i\pi N/6R^2)=(6R^2/\pi N)^{1/2}\theta_3(0,i6R^2/\pi N)\tag{53}$$

so

$$\chi(R;N)=-\tfrac{1}{2}+(3/2\pi N)^{1/2}R\theta_3(0,i6R^2/\pi N).\tag{54}$$

The derivative with respect to R of the expression for $\chi(R;N)$ in eqn (54) leads to the following result in the limit $R\to\infty$

$$\lim_{R\to\infty}\frac{d}{dR}\chi(R;N)=(3/2\pi N)^{1/2}.\tag{55}$$

The expression for

$$R\frac{d}{dR}\chi(R;N)-\chi(R;N)$$

is

$$\begin{aligned}R\frac{d}{dR}\chi(R;N)-\chi(R;N)&=(3/2\pi N)^{1/2}\Big[R\theta_3(0,i6R^2/\pi N)\\&\quad+R^2\frac{d}{dR}\theta_3(0,i6R^2/\pi N)\Big]\\&\quad+\tfrac{1}{2}-(3/2\pi N)^{1/2}R\theta_3(0,i6R^2/\pi N)\\&=\tfrac{1}{2}+(3/2\pi N)^{1/2}R^2\frac{d}{dR}\theta_3(0,i6R^2/\pi N).\end{aligned}\tag{56}$$

In the limit $R \to \infty$, the second term in eqn (56) is negligible so

$$\lim_{R\to\infty}\left[R\frac{d}{dR}\chi(R;N)-\chi(R;N)\right]=\tfrac{1}{2}. \tag{57}$$

3. Evaluation of $\lim_{R\to\infty}\psi_{\text{surf.}}(R;N)$ and

$$\lim_{R\to\infty}\left[R\psi_{\text{surf.}}(R;N)-\int_0^R d\rho\,\psi_{\text{surf.}}(\rho;N)\right]$$

where

$$\psi_{\text{surf.}}(R;N)=4R^{-1}\sum_{n=0}^{\infty}\exp\left[-(2n+1)^2\pi^2N/6R^2\right].$$

The function $\psi_{\text{surf.}}(R;N)$ can be expressed in terms of Theta Functions as

$$\psi_{\text{surf.}}(R;N)=2R^{-1}\theta_2(0,i2\pi N/3R^2) \tag{58}$$

or

$$\psi_{\text{surf.}}(R;N)=(6/\pi N)^{1/2}\theta_0(0,i3R^2/2\pi N). \tag{59}$$

In the limit $R \to \infty$, we have

$$\lim_{R\to\infty}\psi_{\text{surf.}}(R;N)=(6/\pi N)^{1/2}. \tag{60}$$

The expression for $[R\psi_{\text{surf.}}(R;N)-\int_0^R d\rho\,\psi_{\text{surf.}}(\rho;N)]$, which is obtained by using eqns (59) and (47), is

$$\begin{aligned}R\psi_{\text{surf.}}(R;N)&-\int_0^R d\rho\,\psi_{\text{surf.}}(\rho;N)\\
&=(6/\pi N)^{1/2}R\left\{1+2\sum_{n=1}^{\infty}(-1)^n\exp\left[-3R^2n^2/2N\right]\right\}\\
&\quad-\int_0^R d\rho\,(6/\pi N)^{1/2}\left\{1+2\sum_{n=1}^{\infty}(-1)^n\exp\left[-3\rho^2n^2/2N\right]\right\}\\
&=2R(6/\pi N)^{1/2}\sum_{n=1}^{\infty}(-1)^n\exp(-3R^2n^2/2N)\\
&\quad+2(6/\pi N)^{1/2}\sum_{n=1}^{\infty}(-1)^{n+1}\int_0^R d\rho\,\exp(-3\rho^2n^2/2N).\end{aligned} \tag{61}$$

In the limit $R \to \infty$, we have

$$\lim_{R\to\infty}\left[R\psi_{\text{surf.}}(R;N)-\int_0^R \psi_{\text{surf.}}(\rho;N)\,d\rho\right]=2\ln 2. \tag{62}$$

4. Evaluation of $\lim_{R\to\infty}\psi_{\text{Holl.}}(R;N)$ and

$$\lim_{R\to\infty}\left[R\psi_{\text{Holl.}}(R;N)-\int_0^R d\rho\,\psi_{\text{Holl.}}(\rho;N)\right]$$

where

$$\psi_{\text{Holl.}}(R;N)=2\sum_{n=1}^{\infty}(-1)^{n+1}\exp(-\pi^2n^2N/6R^2).$$

The function $\psi_{\text{Holl.}}(R;N)$ is expressed in terms of Theta Functions as

$$\psi_{\text{Holl.}}(R;N)=1-\theta_0(0,i\pi N/6R^2) \tag{63}$$

or

$$\psi_{\text{Holl.}}(R;N)=1-(6/\pi N)^{1/2}R\theta_2(0,i6R^2/\pi N). \tag{64}$$

In the limit $R \to \infty$

$$\lim_{R\to\infty}\psi_{\text{Holl.}}(R;N)=1. \tag{65}$$

The expression for $R\psi_{\text{Holl.}}(R;N)-\int_0^R d\rho\,\psi_{\text{Holl.}}(\rho;N)$ is

$$\begin{aligned}R\psi_{\text{Holl.}}(R;N)&-\int_0^R d\rho\,\psi_{\text{Holl.}}(\rho;N)\\
&=R-(6/\pi N)^{1/2}R^2\theta_2(0,i6R^2/\pi N)\\
&\quad-\int_0^R d\rho\left[1-(6/\pi N)^{1/2}\rho\theta_2(0,i6\rho^2/\pi N)\right]\\
&=-(6/\pi N)^{1/2}R^2\theta_2(0,i6R^2/\pi N)\\
&\quad+2(6/\pi N)^{1/2}\sum_{n=0}^{\infty}\int_0^R d\rho\,\rho\,\exp\left[-(n+\tfrac{1}{2})^2 6\rho^2/N\right].\end{aligned} \tag{66}$$

In the limit $R \to \infty$, we have

$$\lim_{R\to\infty}\left[R\psi_{\text{Holl.}}(R;N)-\int_0^R d\rho\,\psi_{\text{Holl.}}(\rho;N)\right]=\tfrac{1}{2}\pi(\pi N/6)^{1/2}. \tag{67}$$