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The Gaussian Chain with Volume Exclusion

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ABSTRACT: The partition function and expansion factor α for the radius of gyration of linear and circular Gaussian chains is investigated by means of cluster theory. It is shown that use of the linearized δ function pseudopotential generates infinite cluster integrals for certain types of diagrams. These diagrams must be discarded, i.e., the theory must be renormalized. However, pathological behavior persists even though only finite integrals are retained, as is demonstrated by exact calculations for short chains. Both zeros and divergences are found for α^2 for short chains, and arguments are presented to suggest that this behavior persists as the chain length N increases. We have calculated the first and last terms of the partition function for both linear and circular chains. These results form the basis for an argument, independent of the short-chain results but in complete accord with them, which strongly suggests that the traditional expansion $\alpha^2 = 1 + \sum_{n=1}^{\infty} c_n z^n$ has a radius of convergence near $|z| \sim N^{-1/2}$. Alternative prenormalized cluster functions of a particular type may well generate similar problems. A simple function which avoids this multitude of problems is proposed, and calculation of c_1 in the above series with this alternative yields the same result as originally obtained by Zimm, Stockmayer, and Fixman for the linear chain, and by Casassa for the circular chain. We conclude that the δ function pseudopotential gives the correct slope for α^2 at $z = 0$, but that such a function cannot be generally used for finite z.

I. Introduction

The Gaussian chain with volume exclusion has been a useful model for polymer solutions for several years.[1,2] A configuration of the chain is pictured as a random walk of Gaussian steps which cannot intersect itself. Even with this simplification it is necessary to choose potential forms which permit evaluation of the configuration integral. It has become standard practice to prenormalize the potential in dealing with the cluster expansion, and the usual choice for the prenormalized cluster function is the d-dimensional Dirac δ function for a walk in d-dimensional space.

The cluster theory for such model chains has recently been brought to form[3] which permits exact (numerical) calculation of all coefficients of powers of the expansion parameter. We have pursued these calculations for short chains, and have unexpectedly found that the cluster theory is not well behaved for each chain length and topology considered. Our results are such as to strongly suggest that this mischievous behavior persists to very long chains.

Owing to the leading role that the cluster theory plays in the analysis of polymer solutions, it is important to understand the nature of the difficulties we, and others, have encountered. It is our contention, to be supported here, that prenormalizing must be avoided. Having done so, one can except to make a well-behaved theory of the excluded volume effect for all values of the binary cluster integral. Finally, the status of previous calculations is considered, particularly those of the slope of the expansion factor at vanishing volume exclusion. It appears to us that this slope has been firmly established,[4] even though the expansion factor for very long chains diverges if the binary cluster integral is only slightly different from zero.

II. General Approach

The partition function Q for a self-avoiding walk of Gaussian steps may be written as[3]

$$Q = \int \cdots \int \exp\left\{-\beta \sum_{i>j} V(\mathbf{r}_{ij})\right\} \times \exp\{-\gamma \tilde{\mathbf{R}}(\mathbf{A} \otimes \mathbf{E}_d)\mathbf{R}\}\delta(\tilde{\mathbf{J}}\mathbf{R})\, d\{\mathbf{R}\} \quad \text{(II.1)}$$

where $\mathbf{R}$ and its transpose $\tilde{\mathbf{R}} = (\tilde{\mathbf{r}}_1, \tilde{\mathbf{r}}_2, \ldots, \tilde{\mathbf{r}}_N)$ are Nd-dimensional vectors which specify the configuration of a particular walk. The coordinates $\mathbf{r}_i$ locate the N beads of the Rouse–Zimm chain. The $N \times N$ Rouse matrix $\mathbf{A}$ is known as the Kirchhoff matrix in graph theory; the direct product of $\mathbf{A}$ with the identity $\mathbf{E}_d$ of rank d expands $\mathbf{A}$ to conform with $\mathbf{R}$. In eq II.1, $\beta = 1/kT$, $\gamma = d/2\langle l^2\rangle_0$, where $\langle l^2\rangle_0$ represents the mean-square step length, and d = 1, 2, or 3 is the spatial dimensionality. The δ function of $\tilde{\mathbf{J}}\mathbf{R}$, where $\tilde{\mathbf{J}}$ is a row of ones, fixes the center of gravity at the origin of coordinates. The potential $V(\mathbf{r}_{ij})$ between beads i and j depends upon the distance $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, and since it is assumed pairwise additive the Ursell–Mayer method may be utilized to write

$$\exp\left\{-\beta \sum_{i>j} V(\mathbf{r}_{ij})\right\} = \prod_{i>j} (1 - f_{ij})$$

The cluster function f_{ij} has been approximated by Fixman[4b] and others[1,2] as $X'\langle f_{ij}\rangle$, where X' is the value of the binary cluster integral, and $\langle f_{ij}\rangle$ is a prenormalized function. Incorporation of the cluster functions in eq II.1 gives

$$Q = \int \ldots \int \exp\{-\gamma\tilde{\mathbf{R}}(\mathbf{A}\otimes\mathbf{E}_d)\mathbf{R}\} \times \prod_{i>j}(1 - X'\langle f_{ij}\rangle)\delta(\tilde{\mathbf{J}}\mathbf{R})\,\mathrm{d}\{\mathbf{R}\} \quad \text{(II.2)}$$

The expansion of $\Pi_{i>j}(1 - X'\langle f_{ij}\rangle)$ may be expressed as

$$\prod_{i>j}(1 - X'\langle f_{ij}\rangle) = \sum_{p=0}^{L}(-X')^p F_p \quad \text{(II.3)}$$

where

$$F_p = \sum_{\{(i,j)\neq(k,l)\neq\ldots\neq(m,n);i>j,k>l,\ldots,m>n\}} \langle f_{ij}\rangle\langle f_{kl}\rangle\ldots\langle f_{mn}\rangle$$

The restriction $\{(i,j) \neq (k,l)\ldots\}$ on the sum indicates that no two $\langle f\rangle$ functions have identical indices; the product $\langle f_{ij}\rangle \ldots \langle f_{mn}\rangle$ has p terms. Upon substituting eq II.3 in eq II.2 and reversing the order of summation and integration, one obtains

$$Q = \sum_{p=0}^{L}(-X')^p \int \times \exp\{-\gamma\tilde{\mathbf{R}}(\mathbf{A}\otimes\mathbf{E}_d)\mathbf{R}\}F_p\delta(\tilde{\mathbf{J}}\mathbf{R})\,\mathrm{d}\{\mathbf{R}\} \quad \text{(II.4)}$$

Note that for a given chain of N beads the maximum value of p cannot exceed $L = N(N-1)/2$, and so the partition function is a finite polynomial in X' if the chain is finite.

The expansion factor of the radius of gyration s is formally calculated by means of a slight modification of eq II.4. If $\langle s^2\rangle$ denotes the mean-square radius of gyration with volume exclusion, and $\langle s^2\rangle_0$ denotes the similar quantity in its absence, the expansion factor α^2 may be defined as $\alpha^2 = \langle s^2\rangle/\langle s^2\rangle_0$. It is easily seen that

$$\langle s^2\rangle = -Q^{-1}\frac{\mathrm{d}}{\mathrm{d}a}\int \exp\{-as^2 - \gamma\tilde{\mathbf{R}}(\mathbf{A}\otimes\mathbf{E}_d)\mathbf{R}\} \times \prod_{i>j}(1 - X'\langle f_{ij}\rangle)\delta(\tilde{\mathbf{J}}\mathbf{R})\,\mathrm{d}\{\mathbf{R}\}|_{a=0} \quad \text{(II.5)}$$

where $s^2 = N^{-1}\tilde{\mathbf{R}}\mathbf{R}$. Use of eq II.3 in eq II.5 and reversal of the order of summation and integration leads to

$$\langle s^2\rangle = -Q^{-1}\sum_{p=0}^{L}(-X')^p\,(\mathrm{d}B_p(a)/\mathrm{d}a)_{a=0} \quad \text{(II.6)}$$

where

$$B_p(a) \equiv \int \exp\{-as^2 - \gamma\tilde{\mathbf{R}}(\mathbf{A}\otimes\mathbf{E}_d)\mathbf{R}\}F_p\delta(\tilde{\mathbf{J}}\mathbf{R})\,\mathrm{d}\{\mathbf{R}\} \quad \text{(II.7)}$$

Equation II.6, as well as subsequent formulas, may be rendered more succinct by defining

$$Q = Q_{X'}(a) = \sum_{p=0}^{L}(-X')^p B_p(a) \quad \text{(II.8)}$$

which reduces to $Q_0(a) = B_0(a)$ in the absence of volume exclusion. Thus

$$\langle s^2\rangle_0 = -\mathrm{d}\ln Q_0(a)/\mathrm{d}a|_{a=0} \quad \text{(II.9)}$$

and

$$\alpha^2 = \frac{\mathrm{d}\ln Q_{X'}(a)/\mathrm{d}a|_{a=0}}{\mathrm{d}\ln Q_0(a)/\mathrm{d}a|_{a=0}} \quad \text{(II.10)}$$

III. Renormalization

If the d-dimensional Dirac δ function[4] is used as the prenormalized cluster function, $Q_X(0)$ may be written[3] as

$$Q_X(0) = Q_0(0)A(X) \quad \text{(III.1a)}$$

where the function $A(X)$ is the polynomial

$$A(X) = \sum_{p=0}^{N(N-1)/2}(-X)^p A_p \quad \text{(III.1b)}$$

and a change of variables is made to $X = X'(d/2\pi\langle l^2\rangle_0)^{d/2}$. Here A_p is the sum of the determinants, each raised to the $-d/2$ power, of all principal minors of order p of a special matrix[3] $\mathbf{G}_0^{(-1)}$. The order of $\mathbf{G}_0^{(-1)}$ is $N(N-1)/2$, but its rank is $N-1$. Thus, terms of the sum with $p > N-1$ are divergent. However, there are also divergent terms in the A_p for $p \leq N - 1$; these must be removed, i.e., the function $A(X)$ must be renormalized.

In the terminology developed for imperfect gases, one finds that use of the δ function yields divergent cluster integrals for some irreducible diagrams. In particular, a closed circuit of chords joining beads on the polymer chain will lead to an infinity in A_p, and such terms are inevitably encountered for all $p \geq 3$. As an illustration, consider one term in A_3 arising from the three-body cluster $(i,j)(j,k)(i,k)$. These pairs of beads may be joined by chords which form a closed circuit. This circuit corresponds to the term

$$\begin{vmatrix} j-i & 0 & j-i \\ 0 & k-j & k-j \\ j-i & k-j & k-i \end{vmatrix}^{-d/2} \quad \text{(III.2)}$$

in A_3. The determinant is found to vanish, and as the determinant is raised to the $-d/2$ power, A_3 is infinite. The cluster expansion does not produce redundant interactions, e.g., $(i,j)(j,i)$. However, it does produce closed circuits, e.g., $(i,j)(j,k)(k,i)$ just considered, for $p \geq 3$. Since terms referring to clusters of the type $(i,j)(j,k)\ldots(k,i)$ are present in all the A_p for any $p \geq 3$, these coefficients in the expansion of $Q_X(0)$ are divergent.

Diagrams containing closed circuits have been excluded by Yamakawa[2] in his development of the cluster theory of the excluded volume effect. Furthermore, he seems to have been acutely aware of this inherent problem with the δ function in his work on a three-parameter theory of dilute solution properties.[5] The renormalization discussed here might be considered as an explicit and generalized formulation of these long known facts.[2,5,6]

The polynomial $A(X)$ in eq III.1b can be renormalized by suppressing those terms in the coefficients A_p which involve infinities. This requires suppression of the entire coefficient when $p > N-1$. Overall this leads to a redefinition of $A(X)$. By stipulation

$$A(X) = \sum_{p=0}^{N-1}(-X)^p A_p$$

where A_p *is now understood to represent the finite remainder of the original coefficient after terms involving closed circuits of chords have been deleted.* Derivatives of $Q_X(a)$ must also be renormalized. The numerator in eq II.10 may serve as an example; upon use of eq III.1a it may be cast into the form

$$\mathrm{d}\ln Q_X(a)/\mathrm{d}a|_{a=0} = [(\mathrm{d}Q_0(a)/\mathrm{d}a)_{a=0}A(X) + Q_0(\mathrm{d}A(X,a)/\mathrm{d}a)_{a=0}]/Q_X(a) \quad \text{(III.3)}$$

Here

$$A(X,a) = \sum(-X)^p A_p(a)$$

and $A(X) \equiv A(X,0)$. Use of eq III.1a and III.3 in eq II.10 leads to

$$\alpha^2 = 1 + \frac{Q_0(\mathrm{d}A(X,a)/\mathrm{d}a)_{a=0}}{(\mathrm{d}Q_0(a)/\mathrm{d}a)_{a=0}A(X)} \quad \text{(III.4)}$$

Both numerator and denominator in eq III.4 represent *renormalized* functions.

Table I
Coefficients of X in $A(X)$ [a]

Chain type	N	d	A_1	A_2	A_3	A_4	A_5
Linear	3	2	2.5000	3.0000			
		3	2.3536	3.0000			
	4	2	4.3333	10.8333	16.0000		
		3	3.8996	9.6673	16.0000		
	5	2	6.4167	24.9333	71.2500	125.0000	
		3	5.5706	20.3497	60.8369	125.0000	
	6	2	8.7000	46.5036	195.4071	644.3000	1296.0000
		3	7.3310	35.2810	146.5825	531.2265	1296.0000
Circular	3	2	4.5000	9.0000			
		3	5.5114	15.5885			
	4	2	7.3333	29.0000	64.0000		
		3	8.1584	40.5980	128.0000		
	5	2	10.4167	61.9048	256.2500	625.0000	
		3	10.7913	74.0024	396.4836	1397.5425	
	6	2	13.7000	109.3500	651.8571	2925.0000	7776.0000
		3	13.4173	115.4184	823.2731	4908.9903	19047.2322

[a] $A_0 = 1$ for every case.

Table II
Pathological Behavior in the Partition Function (Q) and α^2

Chain type	N	d	X	$z = N^{1/2}X$	Q	α^2
Linear	3	2	0.889	1.540		0
		3	0.919	1.591		0
	4	2	0.393	0.785	0	Diverges
		3	0.390	0.780	0	Diverges
	5	2	−1.068	−2.387		0
			0.318	0.711		0
		3	−1.002	−2.241		0
			0.326	0.728		0
	6	2	−0.386	−0.944		0
			0.239	0.586	0	Diverges
		3	−0.369	−0.904		0
			0.237	0.580	0	Diverges
Circular	3	2	0.444	0.770		0
		3	0.363	0.629		0
	4	2	−3.293	−6.585		0
			0.246	0.491	0	Diverges
		3	−2.356	−4.712		0
			0.196	0.391	0	Diverges
	5	2	−1.455	−3.254		0
			0.222	0.497		0
		3	−1.049	−2.345		0
			0.191	0.427		0
	6	2	−0.499	−1.221		0
			0.166	0.406	0	Diverges
		3	−0.374	−0.915		0
			0.139	0.340	0	Diverges

The ratio of polynomials in eq III.4 may be expressed in the traditional form

$$\alpha^2 = 1 + \sum_{n=1}^{\infty} c_n z^n \qquad \text{(III.5)}$$

if no attention is paid to convergence. Here $z = XN^{1/2}$ and the coefficients c_n are presumed to be finite when evaluated in the asymptotic limit $N \to \infty$. Previous calculations of c_3 which have given finite results have been implicitly renormalized.[6]

IV. Numerical Calculations

Equation III.4 was evaluated (after renormalization) for both two- and three-dimensional linear and circular chains composed of three to six beads on the University of Washington CDC 6400. Calculated coefficients A_p in the polynomial $A(X)$ are listed in Table I. A comprehensive list of points of pathological behavior found in the partition function (denoted by Q in the table) as well as in α^2 are given in Table II. It is clear from Table II that the qualitative behavior of α^2 is independent of dimensionality or chain type. Figure 1 displays the results obtained for α^2 for the linear chain in $d = 3$ dimensional space. The behavior of α^2 depicted in the figure is representative of the pattern of behavior found for both linear and circular short chains in two and three dimensions.

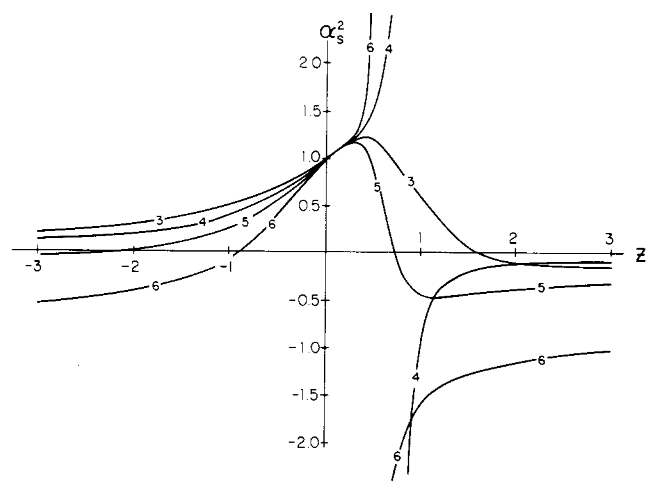

Figure 1. The expansion factor α^2 for three-dimensional linear Gaussian chains of N = 3–6 beads (two–five steps) plotted as functions of the parameter $z = N^{1/2}X$.

One notes that the results in Table I for A_{N-1} in the linear case may be reproduced upon setting

$$A_{N-1} = N^{N-2} \qquad \text{(IV.1)}$$

Similarly, the results listed for A_{N-1} in the circular case may be reproduced upon setting

$$A_{N-1} = N^{N-2+d/2} \qquad \text{(IV.2)}$$

as is readily verified by inspection of Table I. Furthermore, eq IV.1 and IV.2 are shown to be exact for all N in Appendix B. An extensive discussion of the results contained in Tables I and II and implications thereof will be deferred to the next section.

Values of the coefficient c_1 in eq III.5 have been calculated for larger values of N than those listed in Tables I and II. The

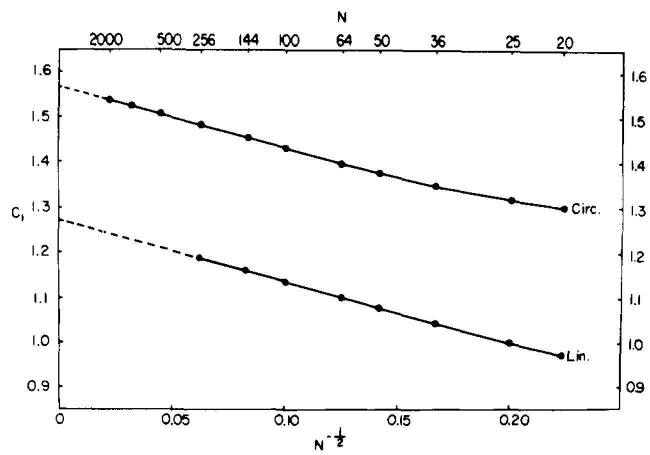

Figure 2. The coefficient $c_1(N)$ in the expansion $\alpha^2 = 1 + c_1(N)z + \ldots$ as a function of $N^{-1/2}$ for three-dimensional linear and circular Gaussian chairs.

calculation of c_1 for the linear chain was extended to $N = 256$, and for the circular chain to $N = 2000$. The results of these numerical calculations are depicted in Figure 2. For the linear and circular chains considered ($d = 3$), $c_1(N)$ may be expressed as the polynomial

$$c_1(N) = \sum_{i=0} b_i N^{-i/2} \tag{IV.3}$$

For computational purposes, the expansion was truncated at $i = 5$, and the coefficients b_i were determined by Cramer's rule. Results for the linear chain give

$$c_1(N) = 1.276\,190 - 1.460\,319N^{-1/2} - 0.001\,049N^{-1} + 2.835\,974N^{-3/2} - 2.222\,101N^{-2} - 0.288\,852N^{-5/2} \tag{IV.4}$$

The computed limiting value, $c_1(\infty)$, agrees with the exact result[4] $c_1(\infty) = 134/105 \doteq 1.276\,190$. The circular chain results reported in Table III may be similarly analyzed to give

$$c_1(N) = 1.570\,796 - 1.460\,305N^{-1/2} - 0.002\,266N^{-1} + 5.169\,494N^{-3/2} + 1.074\,883N^{-2} - 3.904\,806N^{-5/2} \tag{IV.5}$$

The exact limiting value for the circular chain is known[7] to be $c_1(\infty) = \pi/2 \doteq 1.570\,796$. This result is also derived analytically in Appendix C.

V. Asymptotic Forms

A. Behavior of the Configuration Integral. The extrapolation to large N offered in this section is based upon analysis of very small systems. For this reason, a segment of the arguments to be presented is inductive. The general trends found for the configuration integrals of the various small chains investigated must first be elucidated.

As noted in eq III.1a, the configuration integral calculated by use of the pseudopotential takes the form $Q_X(0) = Q_0(0)A(X)$, where the renormalized $A(X)$ is a polynomial of degree $N - 1$ in X. The renormalized coefficients, A_p, in $A(X)$ are positive definite. Hence $A(X)$ may be written as the product

$$A(X) = \prod_{j=1}^{N-1} (1 - XM_j) \tag{V.1}$$

where the constants M_i are chosen so that $\Sigma M_i = A_1$, $\Sigma_{i>j} M_i M_j = A_2$, etc. For $N = 3$, the results of calculations listed in Table I may be expressed in terms of eq V.1 with the $M_j \rightarrow M^{\pm} = A_2^{1/2} \exp(\pm i\theta)$, where the angle θ is chosen to give the appropriate value for A_1. Inspection of Table II reveals that the configuration integral possesses a real root only for

Table III
Machine Calculated Coefficients $c_1(N)$ [a]

Chain type	N	$c_1(N)$	Chain type	N	$c_1(N)$
Linear	36	1.044 152 18	Circular	100	1.429 980 70
	64	1.098 621 45		256	1.480 792 77
	100	1.132 758 50		500	1.505 950 54
	144	1.156 022 34		900	1.522 309 20
	196	1.172 851 29		1444	1.532 459 95
	256	1.185 574 16		2000	1.538 199 42

[a] See eq IV.3.

Table IV
Real Roots of $A(X)$ for N = 4 and 6

Chain type	N	d	X	$z = N^{1/2}X$ [a]	z(exact) [b]
Linear	4	2	0.397	0.794	0.785
		3	0.397	0.794	0.780
	6	2	0.239	0.584	0.586
		3	0.239	0.584	0.580
Circular	4	2	0.250	0.500	0.491
		3	0.198	0.397	0.391
	6	2	0.167	0.408	0.406
		3	0.139	0.341	0.340

[a] Calculated from the approximate eq V.5. [b] Values taken from Table II.

N even. Therefore, most of the M_j occur as pairs $M_l^{\pm} = |M_l| \exp(\pm i\theta_l)$ of complex conjugates. Hence, eq V.1 may be written as

$$\begin{aligned} \prod_{j=1}^{N-1} (1 - XM_j) &= (1 - XM_0) \prod_{l=1}^{(N-2)/2} [1 - X|M_l| \exp(i\theta_l)] \\ &\quad \times [1 - X|M_l| \exp(-i\theta_l)] \qquad N \text{ even} \\ \prod_{j=1}^{N-1} (1 - XM_j) &= \prod_{l=1}^{(N-1)/2} [1 - X|M_l| \exp(i\theta_l)] \\ &\quad \times [1 - X|M_l| \exp(-i\theta_l)] \qquad N \text{ odd} \end{aligned} \tag{V.2}$$

The product representation is now extended beyond $N = 3$ by means of the assumption

$$|M_1| = |M_2| = \ldots = |M_l| = (A_{N-1})^{1/(N-1)} \tag{V.3}$$

where the coefficient A_{N-1} is given alternatively by eq IV.1 or IV.2 for the linear or circular chain, respectively. It is convenient to set $r = (A_{N-1})^{1/(N-1)}$. Use of this approximation for the $|M_l|$ in eq V.2 leads to the result

$$\prod_{i=1}^{N-1} (1 - XM_i) = \prod_{l=1}^{(N-1)/2} [1 - Xr \exp(i\theta_l)][1 - Xr \exp(-i\theta_l)] \tag{V.4a}$$

when N is odd and

$$\prod_{i=1}^{N-1} (1 - XM_i) = (1 - Xr) \prod_{l=1}^{(N-2)/2} [1 - Xr \exp(i\theta_l)][1 - Xr \exp(-i\theta_l)] \tag{V.4b}$$

when N is even. Now, if the form assumed for r were exact for small N, then for even N the polynomial $A(X)$ would possess a real root at

$$X = 1/r = (A_{N-1})^{-1/(N-1)} \tag{V.5}$$

Thus, the location of the zero in the partition function for a linear chain with even N would be independent of the spatial dimensionality. Reference to Table II shows that this is only approximately true. However, the overall agreement between

Table V
The Coefficients A_p and the Appropriate θ_k Values [a]

Chain type	N	d	A_1	A_2	θ_0 [b,c]	θ_1 [c]	θ_2 [c]
Linear	4	2	4.2993		0	69.33	
		3	3.8365		0	74.85	
	5	2	6.3728			27.35	86.29
		3	5.4414			30.05	92.98
	6	2	8.7400	46.6032	0	45.76	98.94
		3	7.2064	34.9589	0	49.97	106.49
Circular	4	2	7.2500		0	69.89	
		3	8.0558		0	72.59	
	5	2	10.2500			26.94	82.33
		3	10.6058			29.17	90.34
	6	2	13.5417	108.6429	0	44.57	94.81
		3	13.2770	114.7067	0	48.65	103.64

[a] Calculations based on the approximate eq V.3 and V.4a,b. [b] Refers only to $N = 4, 6$. [c] The values for the angles θ_0, θ_1, and θ_2 are in degrees.

eq V.5 and the location of zeros obtained from exact calculations is excellent, as inspection of Table IV reveals. The disparity between the exact and approximate ordinates of zeros is less than 2% for $N = 4$ and decreases to less than 1% for the linear chain and less than 0.5% for the circular chain with $N = 6$ (see Table IV).

The approximate forms for $A(X)$ given by eq V.4a,b establish relationships amongst various A_p. Application of eq V.4b to a chain of four beads gives

$$A(X) = 1 - Xr[1 + 2\cos\theta_1] + X^2r^2[1 + 2\cos\theta_1] - X^3r^3$$

Hence, $A_1 = A_2/r$; similarly, for $N = 5$, $A_1 = A_3/r^2$; for $N = 6$, $A_1 = A_4/r^3$, and $A_2 = A_3/r$. The various coefficients calculated by means of these relations are given in Table V along with the corresponding angles θ_k. The approximate coefficients listed in Table V are in good agreement with the exact values listed in Table I.

It is concluded that the assumed form of r, i.e., $r = (A_{N-1})^{1/(N-1)}$, is a very good approximation for small N, and that it is reasonable to assume that the trend in agreement continues for larger N.

The next point to be considered is the behavior of the θ_k as N increases. (Here the discussion will be confined to $d = 3$.) It is shown in Appendix A that $A_1 = O(N)$ for both linear and circular chains. From eq V.3 and the approximation to the M_i, one finds

$$\begin{aligned} A_1 &= r + 2r\sum_{k=1}^{(N-2)/2}\cos\theta_k \qquad N \text{ even} \\ &= 2r\sum_{k=1}^{(N-1)/2}\cos\theta_k \qquad N \text{ odd} \end{aligned} \tag{V.6}$$

Now, as $N \to \infty$, $r \to N$ and the distinction between even and odd N must vanish, so that $A_1(N \text{ odd}) \to A_1(N \text{ even})$. Hence, in the limit $N \to \infty$, at least one root for odd N must move to the real axis. Equation V.6, as well as Table V, reveal that the θ_k are not confined to the region $(0,\pi/2)$. If the θ_k were indeed confined to $(0, \pi/2)$, then $\Sigma \cos\theta_k \propto N$, and in consequence, $A_1 \propto N^2$, since $r \sim N$. This is not the case. In order that $\lim_{N\to\infty} \Sigma \cos\theta_k = \sigma$, where σ is a constant of order unity and independent of N, most of the $\cos\theta_k$ terms must cancel. In this spirit one is led to make the plausible assertion that the θ_k are distributed throughout the entire region $(0,\pi)$ as $N \to \infty$. Inspection of eq V.5 leads to the conclusion that the partition functions $Q_X(0)$ for both linear and circular chains have zeros for finite even N at $X \sim 1/N$. In terms of $z = N^{1/2}X$ the zero occurs at $z \sim N^{-1/2}$. In light of this result and the discussion above concerning the behavior of the roots of the partition function for odd N, it is evident that in the infinite chain limit $Q_X(0)$ has zero radius of convergence. This is in accord with the results of Edwards,[8] Domb and Joyce,[9] and Gordon, Ross-Murphy, and Suzuki.[10] More recently, Oono[11] has shown that $\alpha^2 = 0$ for $z \to 0$ along with the negative axis in the infinite chain limit. His proof is based upon the assumption that α^2 exists for some finite z as $N \to \infty$, and that the coefficients c_n [eq III.5] are finite in this limit. Both conjectures are questionable in view of our exact results for finite N.

Further insight into the nature of the zero of $A(X)$ for the linear chain in three dimensions may be obtained from the magnitudes of A_1 and A_{N-1}. In Appendices A and B we show that A_1 is of order N, and A_{N-1} is of order N^{N-1} (roughly speaking) for all N. Hence, the polynomial $A(X)$ might be approximated as

$$A(X) = B(X)[1 - (-XN)^N]/(1 + XN)$$

where $B(X)$ is expected to vary slowly with N. This form for $A(X)$ ensures that A_p is of order N^p. From this equation it is seen that $A(X)$ has a zero for even N near $XN = 1$ (the function $B(X)$ can be expected to perturb the root). It is also apparent that for odd $N \to \infty$ there is a root which approaches the real axis as $\exp(i\pi/N)$.

A rigorous argument showing that the cluster theory with δ function is badly behaved as $N \to \infty$ may be formulated as follows. Since

$$\prod_{j=1}^{N-1} M_j = N^{N-2}$$

there is at least one $|M_j| \geq N^{1-1/(N-1)}$. Hence,

$$A(X) = \prod_{j=1}^{N-1}(1 - XM_j)$$

has at least one zero at

$$|X| \leq N^{-1+1/(N-1)}$$

This zero might not be located on the real axis, but in the limit $N \to \infty$, the zero converges to the origin as N^{-1}. Therefore, the radius of convergence of both $A(X)$ and $\alpha^2(z)$ go to zero as $N \to \infty$.

This argument is independent of machine calculations, but is in complete agreement with them. There is little doubt that this root, planted by the prenormalized cluster function, poses an unavoidable obstacle to continued use of all such functions which have the property[12] that the parameters (if any) which describe $\langle f_{ij}\rangle$ are independent of $X' = \int f_{ij}\,d\mathbf{r}_{ij}$. To further argue the case, we go on to consider the equation for α^2.

B. Behavior of α^2. As noted in section III, a concise expression for α^2 is obtained upon generalizing Q. Here $Q \to$

$Q_X(a)$, where $Q_X(a) = Q_0(a)A(X,a)$ and $A(X,a) \equiv \Sigma(-X)^p A_p(a)$. The generalization of eq V.1 is straightforward upon recalling that the coefficients M_i are directly related to the coefficients A_p. It is clear that one may cast $A(X,a)$ into the form

$$A(X,a) = \prod_{j=1}^{N-1} [1 - XM_j(a)] \quad \text{(V.7)}$$

and, by use of eq II.9 and III.4,

$$\alpha^2 = 1 + (X/\langle s^2\rangle_0) \sum_{j=1}^{N-1} [\mathrm{d}M_j(a)/\mathrm{d}a)_{a=0}/(1 - XM_j(0))] \quad \text{(V.8)}$$

where

$$M_j(a) = |M_j(a)| \exp[i\theta_j(a)] \quad \text{(V.9)}$$

The terms $[\mathrm{d}M_j(a)/\mathrm{d}a]_{a=0}$ are independent of X; hence eq V.8 yields a convergent series

$$\alpha^2 = 1 + \sum_{n=1}^{\infty} b_n X^n$$

if, and only if, $|XM_j(0)| < 1$ for all $M_j(0)$. Since there is at least one $|M_j(0)| \geq N^{1-1/(N-1)}$, the radius of convergence of this traditional series for α^2 can be no greater than $X = N^{-1+1/(N-1)}$, i.e., $z \cong N^{-1/2}$. This result is in complete agreement with the conclusions of others previously cited.[8-11] One sees from eq V.7 and the results discussed in section V.A that the power series for α^2 can only be valid for $|X| \lesssim 1/N$, or equivalently $|z| \lesssim N^{-1/2}$. For larger values of X, at least one denominator in eq V.8 will vanish for N even.[12] For X larger still, the term $X|M_j(0)|$ dominates unity.

For large X, use of the approximation offered above [eq V.3] gives

$$XM_j(0) = X|M_j(0)| \exp[i\theta_j(0)] \approx XN \times \exp[i\theta_j(0)] = zN^{1/2} \exp[i\theta_j(0)]$$

and the asymptotic relation reduces to

$$[\mathrm{d}M_j(a)/\mathrm{d}a]_{a=0}/[1 - XM_j(0)] \sim -[\mathrm{d}M_j(a)/\mathrm{d}a]_{a=0}/XM_j(0) \quad \text{(V.10)}$$

which is also valid for $N \to \infty$, $X \to 0$, z = constant. When eq V.10 is inserted into eq V.8 and the limit is taken one finds that

$$\lim_{N\to\infty} \alpha^2 = 1 + \lim_{N\to\infty} \{[Q_0/(\mathrm{d}Q_0(a)/\mathrm{d}a)_{a=0}] \times \sum_i (\mathrm{d}M_i(a)/\mathrm{d}a)_{a=0}/M_i(0)\} \quad \text{(V.11)}$$

Since

$$A_{N-1}(a) = \prod_{j=1}^{N-1} M_j(a)$$

it is seen that

$$\sum_i \{(\mathrm{d}M_i(a)/\mathrm{d}a)_{a=0}/M_i(0)\} = (\mathrm{d}A_{N-1}(a)/\mathrm{d}a)_{a=0}/A_{N-1}(0) \quad \text{(V.12)}$$

With use of the definition of r discussed in section V.A, eq V.11 may be written

$$\lim_{N\to\infty} \alpha^2 = 1 + \lim_{N\to\infty} \{NQ_0(\mathrm{d}r(a)/\mathrm{d}a)_{a=0}/ r(0)(\mathrm{d}Q_0(a)/\mathrm{d}a)_{a=0}\} \quad \text{(V.13)}$$

In the approximation $r(0) \sim N$, eq V.13 may be further simplified to

$$\lim_{N\to\infty} \alpha^2 = 1 + \lim_{N\to\infty} [Q_0(\mathrm{d}r(a)/da)_{a=0}/ (\mathrm{d}Q_0(a)/\mathrm{d}a)_{a=0}] \quad \text{(V.14)}$$

or

$$\lim_{N\to\infty} \alpha^2 = 1 - \lim_{N\to\infty} \langle s^2\rangle_0^{-1}(\mathrm{d}r(a)/\mathrm{d}a)_{a=0}$$

This important result states that α^2 is a constant, independent of X, in the limit $N \to \infty$. This limit is attained for both positive and negative X, exclusive of $X = 0$. Reference to Table VI suggests that α^2 might become a large negative number in the limit $N \to \infty$. Order of magnitude estimates (not given here) of α^2 in this limit suggest, in fact, that $\alpha^2 \to -\infty$.

Table VI
Numerical Results for the Function[a] $f(N) = 1 - (dA_{N-1}(a)/da)_{a=0}/A_{N-1}(0)\langle s^2\rangle_0$

N	d	$f(N)$\{linear\}	$f(N)$\{circular\}
3	2, 3	0	0
4	2, 3	0	−0.0500
5	2, 3	−0.1888	−0.0848
6	2, 3	−0.7746	−0.2526

[a] The function $f(N)$ may be obtained upon taking $\lim_{|X|\to\infty} \alpha^2$, which is a limit similar to $N \to \infty$, z = constant, discussed in the text.

VI. An Alternative to the δ Function Pseudopotential

The δ function pseudopotential is clearly in a precarious position for two reasons. Renormalization is required to remove infinite terms in the A_p for $p \geq 3$; this alone suffices to discourage use of the δ function cluster function for calculation of higher order terms in the cluster expansion. Second, the renormalized functions display an impressive range of pathological behavior which include simple divergences and zeros in α^2. This behavior occurs in the "physical realm" and is present for vanishingly small values of the expansion parameter in the large N limit.

It is clearly necessary to devise an alternative approximate, yet integrable, cluster function which circumvents the problems inherent in the δ function if one hopes to press the cluster theory to a satisfactory conclusion. A function satisfying these criteria is

$$1 - \exp[-\beta V(\mathbf{r}_{ij})] = f(\mathbf{r}_{ij}) = \eta \exp(-\mathbf{r}_{ij}\cdot\mathbf{r}_{ij}/4\psi) \quad \text{(VI.1)}$$

where $\psi > 0$. This approximation has been chosen for three reasons. (i) If one sets $\eta = X'(4\pi\psi)^{-d/2}$ and allows $\psi \to 0$ at the end of calculations, results identical with those obtained with the δ function are recovered. This version of the cluster function is prenormalized since the independent parameter X' is taken to be the value of the binary cluster integral. Hence, this choice for η does not eliminate pathological behavior.[12] (ii) If $\eta = 1$, then $0 \leq \exp[-\beta V(r_{ij})] \leq 1$. Thus, the configuration integral (see eq II.1) is nonnegative definite for all nonnegative ψ (positive definite for $0 < \psi < \infty$), and bounded from above by the partition function for the unperturbed chain. (iii) Integrals are readily evaluated.

Equation VI.1 is only a crude approximation and should not be considered in any other light. With that disclaimer noted, use of the function with $\eta = 1$ eliminates the pathological behavior found with use of the δ function. However, in the following η will be left variable so as to comprehend alternative choices.

The cluster function $f(\mathbf{r})$ given by eq VI.1 has a Fourier transform $g(\mathbf{k})$:

$$f(\mathbf{r}) = [\eta/(2\pi)^d]\int g(\mathbf{k})\, exp(i\mathbf{k}\cdot\mathbf{r})\mathrm{d}\mathbf{k} \quad \text{(VI.2)}$$

where

$$g(\mathbf{k}) = (4\pi\psi)^{d/2} \exp(-\psi\mathbf{k}\cdot\mathbf{k})$$

The evaluation of the configuration integral for Gaussian chains with the Gaussian cluster function has been accomplished previously.[3] The result of that calculation is

$$Q(a) = (\pi/\gamma)^{(N-1)d/2}|\mathbf{\Lambda}_0 + (a/\gamma N)\mathbf{E}_{N-1}|^{-d/2} \left\{ \sum_{p=0}^{L} [-\eta \times (4\gamma\psi)^{d/2}]^p \sum_{\text{all } \mathbf{J}_p} |\tilde{\mathbf{J}}_p(\mathbf{G}_a{}^{(-1)} + 4\gamma\psi\mathbf{E}_L)\mathbf{J}_p|^{-d/2}\right\} \quad \text{(VI.3)}$$

The diagonal matrix $\mathbf{\Lambda}_0$ is comprised of the nonvanishing eigenvalues of the Rouse–Zimm matrix $\mathbf{A}$ and is of order $N - 1$. The upper limit in the first sum is $L = N(N-1)/2$. The matrix

$$\mathbf{G}_a{}^{(-1)} = \tilde{\mathbf{C}}\tilde{\mathbf{T}}_0[\mathbf{\Lambda}_0 + (a/\gamma N)\mathbf{E}_{N-1}]^{-1}\mathbf{T}_0\mathbf{C}$$

where $\mathbf{C}$ is the incidence matrix of the complete graph on N nodes. [An explicit representation for $\mathbf{C}$ is given in eq A.1, Appendix A.] The matrix $\mathbf{T}_0$ of dimension $(N-1)N$ is related to the orthogonal matrix $\mathbf{T}$ which diagonalizes $\mathbf{A}$. Specifically, $\mathbf{T}_0$ is obtained from $\mathbf{T}$ by deletion of its constant column. The matrices $\mathbf{E}_{N-1}$ and $\mathbf{E}_L$ are identity matrices of order $N-1$ and $N(N-1)/2$, respectively. The superscript tilde denotes the transpose. The operation $\tilde{\mathbf{J}}_p(\mathbf{G}_a{}^{(-1)} + 4\gamma\psi\mathbf{E}_L)\mathbf{J}_p$ selects a submatrix of order p from $\mathbf{G}_a{}^{(-1)} + 4\gamma\psi\mathbf{E}_L$ which in turn becomes a principal minor upon forming its determinant.

We now set $Y \equiv \eta(4\gamma\psi)^{d/2}$ so as to write

$$Q_Y(a) = Q_0(a)A(Y,a) \quad \text{(VI.4a)}$$

where

$$Q_0(a) = (\pi/\gamma)^{(N-1)d/2}|\mathbf{\Lambda}_0 + (a/\gamma N)\mathbf{E}_{N-1}|^{-d/2} \quad \text{(VI.4b)}$$

and

$$A(Y,a) = \sum_{p=0}^{L} (-\mathrm{Y})^p \sum_{\text{all } \mathbf{J}_p} |\tilde{\mathbf{J}}_p(\mathbf{G}_a{}^{(-1)} + 4\gamma\psi\mathbf{E}_L)\mathbf{J}_p|^{-d/2} \quad \text{(VI.4c)}$$

Hence, the expansion factor α^2 may be expressed in terms similar to those of eq III.4 as

$$\alpha^2 = 1 - \langle s^2\rangle_0{}^{-1}\partial \ln A(Y,a)/\partial a|_{a=0} \quad \text{(VI.5)}$$

The choice $\eta = X'(4\pi\psi)^{-d/2}$ gives $Y = X'(\gamma/\pi)^{d/2} = X$. Upon taking the limit $\psi \rightarrow 0$ in eq VI.4c, a result identical with that obtained with use of the δ function is reclaimed. In this case, as before, summation over p in eq VI.3 and VI.4c must be terminated at $p = N - 1$, and terms associated with diagrams with closed circuits will be infinite.

If we make the alternative choice for η suggested above, i.e., $\eta = 1$, then $Y = (4\gamma\psi)^{d/2}$. Examination of eq VI.4c or the configuration integral itself reveals that as $Y \rightarrow 0$, $A(Y,a) \rightarrow 1$ and that when $Y \rightarrow \infty$, $A(Y,a) \rightarrow 0$. Hence, for any finite value of N, both the partition function and the expansion factor α^2 will *not* exhibit pathological behavior when $Y < \infty$.

The most interesting result concerning the Gaussian cluster function is revealed when the expansion

$$\alpha^2 = 1 + c_1(N)N^{1/2}Y + \ldots$$

is examined. The coefficient $c_1(N)$ is evaluated in Appendix C for the *circular* chain, where it is shown that, if

$$4\gamma\psi \leq N^{1-\xi} \qquad \xi > 0$$

then $\lim_{N\rightarrow\infty} c_1(N)$ is the same as the value Casassa[7] obtained using the δ function. Similar calculations for the *linear* chain (not demonstrated here) yield the value obtained by Fixman.[4] That is to say, the prenormalized δ function cluster function appears to give the correct slope for α^2 at $z = 0$, even though the prenormalizing approximation cannot be used for the general theory. The Gaussian cluster function is only slightly closer to physical reality than is the δ function, but the fact that the coefficients c_1 are independent of the precise form of the potential argues strongly in favor of the general validity of Zimm's, Stockmayer's, and Fixman's original calculation of c_1. Although we have not yet calculated c_2 with this alternative cluster function, we expect it to generate the same value as obtained with the δ function. Higher order terms are certain to be different, however.

The very weak bound that we place on $4\gamma\psi$ may be translated to the form: if the range of the Gaussian cluster function, $(6\psi)^{1/2}$, does not grow with N as fast as the root-mean-square end-to-end distance of the unperturbed chain, $(3N/2\gamma)^{1/2}$, then the precise range of the potential is immaterial. In the infinite chain limit the range relative to the rms dimension shrinks to zero. We cannot at this time assert that the same conclusion holds if the potential of mean force possesses one or more minima.

There is another feature of the expansion III.5 for α^2 which deserves comment. Division of the polynomial $\mathrm{d}A(Y,a)/\mathrm{d}a|_{a=0}$ by $A(Y,0)$ in eq VI.5 to yield an expression of the form of eq III.5 will yield a convergent polynomial if and only if $1 - A(Y,0) = A_1Y - A_2Y^2 + \ldots$ is bounded from above by unity. Since A_1 is of order N [see eq A.7 of Appendix A], Y cannot be of order greater than N^{-1} if the first few terms of the expansion are expected to yield an accurate representation for the behavior of α^2. We have already shown that $A(Y,0)$ is bounded by unity by the simple observation that the Gaussian cluster function is bounded. Hence, the power series will work in general, but there is no guarantee that a great many terms will not have to be calculated for this representation to work for large values of Y. Our current feeling is that a Padé approximant will be the best representation for α^2, short of a complete solution.

VII. Conclusion

The slope of α^2, determined by Zimm, Stockmayer, and Fixman[4] and by Casassa[7] for linear and circular chains, respectively, appears to be valid at $z = 0$ for a general class of potential forms. However, use of the linearized δ function pseudopotential for calculation of cluster integrals beyond second order generates infinite terms. Upon discarding these integrals, finite values for the partition function are obtained. Yet the theory is still not well behaved, because the partition function now contains a real zero for finite even N and for infinite odd N. This zero occurs near $z \sim N^{-1/2}$ for finite even N; in the infinite chain limit α^2 has zero radius of convergence. These difficulties are associated with any of a class of prenormalized cluster functions. An alternative cluster function has been suggested, which can be exploited to develop the cluster theory with the assurance that finite results will be obtained.

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Appendix A

Let $\mathbf{C}$ be an $N \times N(N-1)/2$ matrix whose nonzero elements c_{ij} are given by

$$c_{i,i+l} = 1 \qquad c_{i+k,i+l} = -1 \quad \text{(A.1)}$$

where $k = 1, \ldots, N-1$, $i = 1, \ldots, N-k$, $l = N(k-1) - k(k-1)/2 = (N - k/2)(k-1)$. Let $\mathbf{W}$ be an $N \times N$ matrix whose elements w_{ij} are given by

$$w_{ij} = N - j \qquad i \le j$$
$$w_{ij} = N - i \qquad i \ge j \qquad \text{(A.2)}$$

It has been shown for the linear chain that[14]

$$\mathbf{G}^{(-1)} = \tilde{\mathbf{C}}\mathbf{W}\mathbf{C}$$

where the superscript tilde indicates the transpose. The coefficient A_1 in eq III.1b is related to $\mathbf{G}^{(-1)}$ by

$$A_1 = \sum_{m=1}^{N(N-1)/2} (g_{mm}{}^{(-1)})^{-d/2} \qquad \text{(A.3)}$$

The diagonal elements of $\mathbf{G}^{(-1)}$ are readily calculated from eq A.1 and A.2. If i, k, and l are defined as in eq A.1, then

$$g_{i+l,i+l}{}^{(-1)} = w_{ii} - w_{i+k,i} - w_{i,i+k} - w_{i+k,i+k} = k \qquad \text{(A.4)}$$

Since $i = 1, \ldots, N - k$, there are $N - k$ identical elements for each value of k. Thus, eq A.3 becomes

$$A_1 = \sum_{k=1}^{N-1} (N - k)k^{-d/2} \qquad \text{(A.5)}$$

For $d = 2$, one finds[15] that

$$A_1 = N \ln N - (1 - C)N + \tfrac{1}{2} + 0(N^{-1}) \qquad \text{(A.6)}$$

where C is Euler's constant. For the case $d = 3$ it is convenient to define

$$2\sigma \equiv \sum_{k=1}^{\infty} k^{-3/2} = \xi(\tfrac{3}{2})$$

where $\xi(\frac{3}{2})$ is the Riemann ζ function. Then $\sigma \doteq 1.3062$. One finds[13] that

$$A_1 = 2\sigma N - 4N^{1/2} - \xi(\tfrac{1}{2}) + 0(N^{-1/2}) \qquad \text{(A.7)}$$

For the circular chain $\mathbf{G}_0{}^{(-1)} = \tilde{\mathbf{C}}\mathbf{V}\mathbf{C}$, where $\mathbf{V}$ is an $N \times N$ matrix whose elements v_{ij} are given by

$$v_{ij} = (N - j)(1 - (N - i)/N) \qquad i < j$$
$$v_{ij} = (N - i)(1 - (N - j)/N) \qquad i > j \qquad \text{(A.8)}$$

The diagonal elements of this $\mathbf{G}_0{}^{(-1)}$ are given by

$$g_{i+l,i+l}{}^{(-1)} = v_{ii} - v_{i+k,i} - v_{i,i+k} + v_{i+k,i+k} = k(N - k)/N \qquad \text{(A.9)}$$

Here the variables i, k, and l are defined as in eq A.1. Since $i = 1, \ldots, N - k$, there are N identical diagonal elements if $k = N - s$ and $k = s$ are taken together. (For even N there is a single unpaired element.) This observation allows eq A.3 to be evaluated for the circular chain as

$$A_1 = N \sum_{s=1}^{(N-1)/2} (s(1 - x))^{-d/2} \qquad N = \text{odd integer}$$

$$A_1 = N \sum_{s=1}^{(N-2)/2} (s(1 - x))^{-d/2} + 2^{(d-1)}N^{(2-d)/2} \qquad N = \text{even integer} \qquad \text{(A.10)}$$

where $x = s/N$. When $d = 2$,

$$A_1 \sim N \ln (N) + 0(N) \qquad \text{(A.11)}$$

Since $0 < s/N < \frac{1}{2}$ for all s, expansion of the denominators in eq A.10 about $s/N = 0$ is valid for all s. Negligible error is introduced upon extending the upper limit of s to $N/2$ for any N. The expansion

$$(1 - x)^{-3/2} = \sum_{k=0}^{\infty} [(2k + 1)!/2^{2k}(k!)^2]x^k$$

has a radius of convergence of unity and may be directly applied to eq A.10 to yield

$$A_1 = N \sum_{s=1}^{N/2} s^{-3/2} + N \sum_{s=1}^{N/2} \sum_{k=1}^{\infty} [(2k + 1)!/2^{2k}(k!)^2][s^{(2k-3)/2}/N^k] \qquad \text{(A.12)}$$

The double sum on the right-hand side of eq A.12 is evaluated by interchanging orders of summation and by converting the various $\Sigma s^{(2k-3)/2}/N^k$ to integrals, to give

$$\sum_{s=1}^{N/2} s^{(2k-3)/2}/N^k \sim N^{-1/2} \int_0^{1/2} x^{(2k-3)/2}\, dx \sim 2N^{-1/2}(2k - 1)^{-1}2^{-(2k-1)/2} \qquad k \ge 1 \qquad \text{(A.13)}$$

The second term on the right-hand side of eq A.12 is of order $N^{1/2}$, since

$$2 \sum_{k=1}^{\infty} [(2k + 1)!/(2k - 1)2^{(6k-1)/2}(k!)^2] < 2^{3/2} \sum_{k=1}^{\infty} [(2k + 1)!/2^{3k}(k!)^2] = 2^{3/2}(2^{3/2} - 1)$$

by substitution from eq A.13. The last expansion is obtained from the closed form $2^{3/2}[(1 - x)^{-3/2} - 1]$ when $x = \frac{1}{2}$. The first term on the right-hand side of eq A.12 approaches the expression encountered for the linear chain as $N \to \infty$.[13b] Thus, when $d = 3$,

$$A_1 \sim 2\sigma N + 0(N^{1/2}) \qquad \text{(A.14)}$$

and one sees that the lead terms in A_1 for linear and circular chains are asymtotically equal.

Appendix B

It has been shown elsewhere[14] that if $\mathbf{D}$ denotes the $(N - 1) \times N(N - 1)/2$ petrie matrix whose only nonzero elements are

$$d_{j+m-1,j+l} = 1 \qquad \text{(B.1)}$$

where $k = 1, \ldots, N - 1$, $j = 1, \ldots, N - k$, $l = (N - k/2)(k - 1)$, $m = 1, \ldots, k$, then,

$$\mathbf{G}_0{}^{(-1)} = \tilde{\mathbf{D}}\mathbf{D} \qquad \text{(B.2)}$$

for the linear chain. The matrix $\mathbf{D}$ represents the $N(N - 1)/2$ possible combinations of pair contacts. Let $\mathbf{J}_{N-1(r)}$ denote a $[N(N - 1)/2] \times (N - 1)$ matrix, each of whose $N - 1$ columns contains a single nonzero element equal to unity. It is further stipulated that no two columns in $\mathbf{J}_{N-1(r)}$ are identical. One then sees that $\tilde{\mathbf{J}}_{N-1(r)}\mathbf{G}_0{}^{(-1)}\mathbf{J}_{N-1(r)}$ selects a submatrix from $\mathbf{G}_0{}^{(-1)}$ which becomes a principal minor upon forming its determinant as required to construct the coefficient A_{N-1} of the partition function. The subscript r in $\mathbf{J}_{N-1(r)}$ denotes the rth combination of nonzero elements. There are $(N(N - 1)/2)!/(N - 1)!((N - 1)(N - 2)/2)!$ such combinations. The matrix product $\mathbf{D}\mathbf{J}_{N-1(r)}$ is a square matrix of dimension $(N - 1) \times (N - 1)$; thus

$$|\tilde{\mathbf{J}}_{N-1(r)}\mathbf{G}_0{}^{(-1)}\mathbf{J}_{N-1(r)}| = |\mathbf{D}\mathbf{J}_{N-1(r)}|^2 \qquad \text{(B.3)}$$

Since the determinant of the transpose of a matrix equals the determinant of that matrix.

The important feature of the matrix $\mathbf{D}\mathbf{J}_{N-1(r)}$ is that it is a square petrie matrix. It has been shown[16] that the value of the determinant of a square petrie matrix can be only 0, +1, or −1. In consequence, the left-hand side of eq B.3 is

$$|\tilde{\mathbf{J}}_{N-1(r)}\mathbf{G}_0{}^{(-1)}\mathbf{J}_{N-1(r)}| = 0 \text{ or } 1 \qquad \text{(B.4)}$$

Thus all the nonvanishing principal minors of order $N - 1$ of $G_0{}^{(-1)}$ are equal to 1. The number of nonvanishing principal minors of order $N - 1$ may be obtained by use of a famous theorem in graph theory. It was shown by Cayley that the number of trees in a complete graph is N^{N-2}, where all the trees in a connected graph of N nodes contain $N - 1$ edges.

This is just the number of diagrams in the $(N-1)$th term in the cluster expansion which do not possess a circuit. This result, together with eq B.4, establishes that

$$A_{N-1} = N^{N-2} \tag{B.5}$$

for the linear chain.

The circular chain will now be considered. As has been noted in Appendix A [eq A.8],

$$\mathbf{G}_0^{(-1)} = \tilde{\mathbf{C}}\mathbf{V}\mathbf{C}$$

Manipulation of this equation gives

$$\mathbf{G}_0^{(-1)} = \tilde{\mathbf{D}}\mathbf{F}\mathbf{D} \tag{B.6}$$

where the $(N-1) \times (N-1)$ matrix $\mathbf{F} = \mathbf{E} - N^{-1}\mathbf{U}$.

The matrix $\mathbf{D}$ and its transpose $\tilde{\mathbf{D}}$ have been encountered in eq B.2. In essence, the matrix $\mathbf{F}$ displays the degeneracy introduced upon closing the linear chain. Substitution of eq B.6 for $\mathbf{G}_0^{(-1)}$ in the left-hand side of eq B.3 yields

$$|\tilde{\mathbf{J}}_{N-1(r)}\mathbf{G}_0^{(-1)}\mathbf{J}_{N-1(r)}| = |\mathbf{D}\mathbf{J}_{N-1(r)}|^2|\mathbf{F}| \tag{B.7}$$

Here $|\mathbf{D}\mathbf{J}_{N-1(r)}|^2$ is either zero or unity, as before. There are N^{N-2} nonvanishing determinants. The determinant $|\mathbf{F}|$ is readily evaluated after observing that $\mathbf{U}$ possesses only one nonzero eigenvalue, equal to $N-1$. Thus, $|\mathbf{F}| = 1/N$, so that

$$|\tilde{\mathbf{J}}_{N-1(r)}\mathbf{G}_0^{(-1)}\mathbf{J}_{N-1(r)}|^{-d/2} = N^{d/2} \tag{B.8}$$

The observation that for the *circular* chain there are exactly $N^{N-2}(r)$ assignments satisfying eq B.8 leads to

$$A_{N-1} = N^{d/2}N^{N-2} \tag{B.9}$$

for all N.

Appendix C

The coefficient $c_1(N)$ in the expansion

$$\alpha^2 = 1 + c_1(N)N^{1/2}Y + \ldots$$

for the circular chain will be evaluated in the limit as $N \to \infty$. Here, direct use is made of the cluster function defined by eq VI.1. The results for large N are independent of whether N is odd or even; since expressions for odd N are somewhat simpler than for even N, only odd N will be treated. One may show for three dimensions that

$$c_1(N) = 6[(N^{3/2})(N^2-1)]^{-1} \sum_{l=1}^{(N-1)/2} [(N-l)(l/N) + 4\gamma\psi]^{-5/2} \left\{ \sum_{i=1}^{N} (N-i)^2(i-2)^2 - \sum_{j=1}^{l+1} (N-j) \times (N+j-l-2)(l-j)(j-2) - \sum_{k=1}^{N-l-1} (N-k-l-1) \times (N-k-1)(k+l-1)(k-1) \right\} \tag{C.1}$$

Set, $w \equiv i/N$, $x \equiv j/N$, $y \equiv k/N$, $z \equiv l/N$, $\delta \equiv 4\gamma\psi/N$. Upon converting the expressions in eq C.1 to integrals, one finds (to the highest power in N as $N \to \infty$) that

$$c_1(N) \sim 6\int_0^{1/2} dz \left\{ [z(1-z)+\delta]^{-5/2} \times \left[\int_0^1 (1-w)^2 w^2\, dw - \int_0^z (1-x)(1+x-z)(z-x)x \times dx - \int_0^{1-z} (1-y-z)(1-y)(y+z)y\, dy \right] \right\} \tag{C.2}$$

The evaluation of the integrals contained within the large square brackets in eq C.2 results in

$$c_1(N) \sim \int_0^{1/2} dz\{z^2(1-z)^2/(z(1-z)+\delta)^{5/2}\} \tag{C.3}$$

Consider the more general form $B(a)$, where

$$B(a) = \int_0^{1/2} dz/(az(1-z)+\delta)^{1/2} \tag{C.4}$$

The right-hand side of eq C.3 is related to $B(a)$ by

$$\int_0^{1/2} dz\{z^2(1-z)^2/(z(1-z)+\delta)^{5/2}\} = (4/3)(d^2B(a)/da^2)_{a=1} \tag{C.5}$$

The tabulated integral (eq C.4) is

$$B(a) = a^{-1/2}\sin^{-1}\{[a/(a+4\delta)]^{1/2}\} \tag{C.6}$$

Use of eq C.5 and C.6 in eq C.3 leads to

$$c_1(N) \sim \sin^{-1}\{(1+4\delta)^{-1/2}\} - (2/3)\delta^{1/2}\{(1+4\delta)^{-1} + 2(1+4\delta)^{-2} - (1+4\delta)^{-3}\} \tag{C.7}$$

If $4\gamma\psi \leq N^{1-\xi}$, where $\xi > 0$, then $\delta = N^{-\xi}$ and one finds

$$\lim_{N\to\infty} c_1(N) = \sin^{-1}(1) = \pi/2 \tag{C.8}$$

This result is identical with that obtained by Casassa, who used the three-dimensional Dirac δ function.[7]

References and Notes

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