Marriage of Exact Enumeration and 1/d Expansion Methods: Lattice Model of Dilute Polymers

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We consider the properties of a self-avoiding polymer chain with nearest-neighbor contact energy ε on a d-dimensional hypercubic lattice. General theoretical arguments enable us to prescribe the exact analytic form of the n-segment chain partition function C_n, and unknown coefficients for chains of up to 11 segments are determined using exact enumeration data in $d = 2$–6. This exact form provides the main ingredient to produce a large-n expansion in d^{-1} of the chain free energy through fifth order with the full dependence on the contact energy retained. The ε-dependent chain connectivity constant and free energy amplitude are evaluated within the d^{-1} expansion to $O(d^{-5})$. Our general formulation includes for the first time self-avoiding walks, neighbor-avoiding walks, theta, and collapsed chains as particular limiting cases.

KEY WORDS: Lattice model of polymers; self-avoiding walk; self-interacting walk; neighbor-avoiding walk; connectivity constant.

1. INTRODUCTION

Orr's pioneering work[1] studies the lattice model of a single polymer chain with excluded volume and nearest-neighbor contact interactions. This lattice model describes a flexible linear polymer as a self-avoiding random walk (SAW) on a regular d-dimensional lattice. The lattice model of polymers is very rich and completely describes the interesting temperature

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1083

and molecular weight dependence of a dilute polymer solution.[2,3] For example, as the contact energy ε increases in absolute value, the chain contracts. When ε reaches some critical value ε_θ (the Flory θ point), the effects of the repulsive (excluded volume) and attractive (contact) interactions cancel to a large extent. More negative ε causes the chain to collapse into a condensed state (the collapse transition). Positive ε corresponds to enhanced repulsion between neighboring nonsequential monomers, and a neighbor-avoiding walk (NAW) is obtained in the $\varepsilon \to \infty$ limit. Orr uses an exact enumeration method to evaluate the exact ε-dependent n-bond partition function C_n for chains with up to $n = 8$ ($n = 6$) bonds on a square (simple cubic) lattice and to extrapolate the results to the large-n limit.

The lattice model of polymer solutions has also been widely studied using a variety of numerical and analytic techniques. In particular, direct enumeration[4-7] and Monte Carlo methods[8-11] have been employed to evaluate, for example, the free energy per segment and other thermodynamic properties of SAWs, NAWs, theta chains, and the collapse transition.[4] A very extensive literature is devoted to describing the universal critical properties of these walks.[3-12] Analytical approximations to the lattice model of polymers are likewise numerous. In particular, the classic Flory–Huggins mean-field approximations[2,3] to the chain free energy is perhaps the most widely used theory in polymer science. Recently, the lattice cluster theory[13-16] (LCT) has enabled the systematic improvement of the Flory–Huggins approximation and has been employed to study a variety of lattice polymer thermodynamic properties.

Fisher and Gaunt[17] have derived an expansion of the lattice self-avoiding walk partition function in powers d^{-1} up to fifth order. They calculate the chain connectivity constant μ and the susceptibility critical index γ and study the dependence of these quantities on the spatial dimensionality d. In the process of calculating the d^{-1} expansion, ref. 17 obtains the exact n-bond SAW partition function C_n^{SAW} for short chains with up to $n = 11$ bonds in any dimension. They express C_n^{SAW} in terms of lower-order walks, polygons, simple and star figure eights, and dumbbells. These recurrence relations are obtained by adding one bond to an n-bond SAW, thus forming either an $(n + 1)$-step self-avoiding walk, a tadpole, or a polygon (closed walk).

Ref. 17 also discuss a d^{-1} expansion for the critical temperature of the spin-1/2 Ising model with nearest-neighbor interactions. The further extension[18] to the classical N-vector model encompasses the self-avoiding walk, the Ising, and the spherical models as particular cases. A variety of lattice problems, such percolation processes,[19] lattice animals,[19,20] and dense self-avoiding self-interacting walks,[13-16] have been analyzed with diagrammatic d^{-1} expansion methods to obtain the (nonuniversal) critical points

and critical amplitudes. On the other hand, Gaunt *et al.*[21] study lattice trees with specified topologies and generate d^{-1} expansions for the tree connectivity constants using low-dimensional computer enumeration data.[4] In particular, they[21] evaluate μ for a neighbor-avoiding walk through third order. All of the available expansions in d^{-1} appear to be asymptotic,[5] as are the $4-d$ expansions in the renormalization group theory of critical phenomena.[24]

   This paper incorporates ingredients from the work of Orr,[1] Fisher and Gaunt,[17] Gaunt *et al.*,[21] and the lattice cluster theory[13–16] to produce a calculational scheme that fully includes the temperature dependence (i.e., ε) in the d-dimensional lattice model of dilute polymers and that enables all coefficients to be determined from computer enumeration data in lower dimensions. Section 2 evaluates the exact ε-*dependent* partition function C_n for $n \leqslant 11$ in *any dimension*. This result represents a considerable generalization of the classic work of refs. 1 and 17. SAWs, NAWs, theta, and collapsed chains are particular limiting cases of our general expression. The lengthy evaluation of many-body diagrams is not required to produce the exact short-chain d-dimensional partition function or the d^{-1} expansion of C_n in the large-n limit. Instead, we utilize only computer direct enumeration data in dimensions through 6. Section 3 rewrites C_n in a form valid for *all* $n \leqslant 11$, and this leads naturally to a d^{-1} expansion that is valid in the large-n limit. Section 4 derives a d^{-1} expansion for the free energy per segment through order d^{-5} but to all orders in ε. The chain connectivity constant μ and the free energy amplitude A are presented in Section 5 as series in d^{-1} to $O(d^{-5})$. Also, μ and A are determined in particular limiting cases such as the SAW ($\varepsilon = 0$), NAW ($\varepsilon = \infty$), and θ' chain. [A continuum limit estimate of the theta point starting from the lattice model of interacting SAWs indicates[25] $f = \exp(-\varepsilon/kT) - 1 \approx \sigma^{-1}$ with $\sigma = 2d - 1$ near the theta point. We thus define a θ' chain by taking $f = \sigma^{-1}$.]

2. THE EXACT PARTITION FUNCTION FOR SHORT SELF-AVOIDING CHAINS WITH CONTACT INTERACTIONS IN ANY DIMENSION

   The self-avoiding random walk with nearest neighbor contact interactions on d-dimensional hypercubic lattices is composed of $n + 1$ monomers

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[4] Computer enumeration data was used to produce a d^{-1} expansion in some percolation problems. See, e.g., Gaunt and Ruskin.[22]

[5] Ref. 18 shows that the d^{-1} expansion for the critical temperature of the N-vector model in the $N \to \infty$ limit (the spherical model) is asymptotic, and suggests that truncation after the term of the order $d^{-\lambda}$ with $\lambda = 1.62d$ is optimal.

joined by n bonds. An energy ε is assigned to each pair of monomers that are nearest neighbors on the lattice but are nonsequential along the chain. The energy may either be negative (attractive) or positive (repulsive).[1] Only hypercubic lattices are considered (i.e., square lattices in $d = 2$, simple cubic lattices in $d = 3$, etc.), but the extension to other lattices is straightforward. The model is illustrated in Fig. 1.

The lattice coordination number q is

$$q = \sigma + 1 = 2d \tag{1}$$

which also defines σ. The n-bond partition function C_n is defined as usual as[3]

$$C_n = \sum_{m=0} C_{n,m} \eta^m \tag{2}$$

where η is the Boltzmann factor

$$\eta = \exp \omega, \qquad \omega = -\varepsilon/kT \tag{2a}$$

and where $C_{n,m}$ is the number of configurations of an n-bond self-avoiding chain with m neighbor contacts. It is usually assumed that the large-n asymptotic behavior of C_n is of the form[3]

$$C_n \approx A\mu^n n^{\gamma - 1} \tag{3}$$

where γ, μ, and A are the η-dependent effective critical exponent, connectivity constant, and free energy amplitude, respectively. [$\mu = \exp(-\mathscr{F})$,
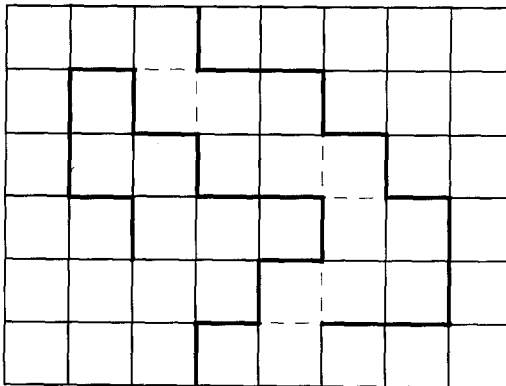

Fig. 1. Typical configuration of an n-segment self-interacting SAW on a square lattice. Nearest-neighbor sites that are not consecutive along the chain (indicated by dashed lines connecting both sites) interact with a contact energy ε. Periodic boundary conditions are assumed along all directions.

with $\mathscr{F}$ the dimensionless free energy per segment in the $n \to \infty$ limit.]
Temperature dependences enter in (2) only through the factors of η.

The quantity C_n is easily evaluated by direct enumeration for very short chains of $n = 1, 2,...$ bonds. For example, the $n = 1$ and 2 cases yield

$$C_1 = q = 2 \binom{d}{1} \tag{4a}$$

$$C_2 = q\sigma = 2 \binom{d}{1} + 8 \binom{d}{2} \tag{4b}$$

The factors of q and σ emerge in the middle of (4) because the first bond may be placed with q choices. Since walks cannot return to a previously visited site, the second bond only has $\sigma = q - 1$ choices. Alternatively, the above results may be obtained as follows: a one-step walk may only extend in one dimension. The factorial in the right-hand side of (4a) is the number of ways of choosing a given direction $(x_1, x_2,..., x_d)$ for this bond. The factor 2 appears because there are two possible orientations (along the positive or negative axis) for the bond. A two-step walk can either fully extend along a single direction, or it can occupy a two-dimensional subspace. The number of configurations with the walk lying in a single direction is also $2d = q$ as for a one-step walk. In fact, this result holds for chains of any length. The number of configurations that fully occupy two dimensions is eight, as the first bond may be placed with four directional choices, while the second has only two because it must be in an orthogonal direction to the first bond. The second factorial on the right-hand side of (4b) is the number of ways of choosing a plane in a d-dimensional space.

Similarly, for $n = 3$ we find

$$C_3 = [q\sigma^2 - q(\sigma - 1)] + q(\sigma - 1)\eta$$

$$= \left[2 \binom{d}{1} + 24 \binom{d}{2} + 48 \binom{d}{3} \right] + \left[8 \binom{d}{2} \right] \eta \tag{4c}$$

which is easily obtained as follows: The total number of configurations of a three-link self-avoiding chain on a d-dimensional hypercubic lattice is $q\sigma^2$. The number of one-contact configurations is $q(q - 2)$, since the first bond has $2d$ choices, the second bond, which must be orthogonal to the first one, has $q - 2$, while the third segment just has a single choice (it must be parallel to the first bond). Hence $[q\sigma^2 - q(\sigma - 1)]$ gives the total number of walks without contacts, while the $q(\sigma - 1)\eta$ term is the contribution

Table I. Number of Configurations $C_{n,m}$ for Linear

n	$C_{n,0}$	$C_{n,1}$	$C_{n,2}$	$C_{n,3}$	$C_{n,4}$	$C_{n,5}$
$d = 2$						
1	4	0	0	0	0	0
2	12	0	0	0	0	0
3	28	8	0	0	0	0
4	68	32	0	0	0	0
5	164	88	32	0	0	0
6	396	256	128	0	0	0
7	940	736	344	152	0	0
8	2244	2032	1072	528	40	0
9	5324	5376	3400	1384	784	0
10	12,668	14,224	9832	4608	2384	384
11	29.940	36,976	27,600	15,552	6424	3552
$d = 3$						
1	6	0	0	0	0	0
2	30	0	0	0	0	0
3	126	24	0	0	0	0
4	534	192	0	0	0	0
5	2214	1032	288	0	0	0
6	9246	5376	2112	192	0	0
7	38,142	26,688	11,928	4488	0	144
8	157,974	128,880	66,192	29,424	4632	864
9	649,086	605,664	353,544	168,504	65,472	7680
10	2,675,022	2,802,576	1,817,208	956,832	412,416	116,928
11	10,966,470	12,755,136	9,092,592	5,269,920	2,435,256	1,059,120
$d = 4$						
1	8	0	0	0	0	0
2	56	0	0	0	0	0
3	344	48	0	0	0	0
4	2120	576	0	0	0	0
5	12,872	4752	960	0	0	0
6	78,392	36,864	11,136	768	0	0
7	472,952	271,680	98,256	27,792	0	576
8	2,861,768	1,931,808	820,896	289,632	36,336	5760
9	17,223,224	13,384,320	6,523,248	2,587,248	777,120	87,168
10	103,835,096	91,133,664	49,672,560	22,079,616	7,785,120	1,843,968
11	623,927,912	610,863,072	367,817,184	180,499,968	71,331,408	25,164,288

Chains with n Bonds and m Contacts in $d = 2\text{--}6$

$C_{n,6}$	$C_{n,7}$	$C_{n,8}$	$C_{n,9}$	C_n^{SAW}	C_n^{NRRW}
0	0	0	0	4	4
0	0	0	0	12	12
0	0	0	0	36	36
0	0	0	0	100	108
0	0	0	0	284	324
0	0	0	0	780	972
0	0	0	0	2172	2916
0	0	0	0	5916	8748
0	0	0	0	16,268	26,244
0	0	0	0	44,100	78,732
248	0	0	0	120,292	236,196
0	0	0	0	6	6
0	0	0	0	30	30
0	0	0	0	150	150
0	0	0	0	726	750
0	0	0	0	3534	3750
0	0	0	0	16,926	18,750
0	0	0	0	81,390	93,750
0	0	0	0	387,966	468,750
3936	0	0	0	1,853,886	2,343,750
24,288	4608	0	0	8,809,878	11,718,750
257,880	94,272	0	3504	41,934,150	58,593,750
0	0	0	0	8	8
0	0	0	0	56	56
0	0	0	0	392	392
0	0	0	0	2696	2744
0	0	0	0	18,584	19,208
0	0	0	0	127,160	134,456
0	0	0	0	871,256	941,192
0	0	0	0	5,946,200	6,588,344
31,488	0	0	0	40,613,816	46,118,408
345,216	55,296	0	0	276,750,536	322,828,856
5,442,192	1,610,880	85,248	42,048	1,886,784,200	2,259,801,992

n	$C_{n,0}$	$C_{n,1}$	$C_{n,2}$	$C_{n,3}$	$C_{n,4}$	$C_{n,5}$
$d=5$						
1	10	0	0	0	0	0
2	90	0	0	0	0	0
3	730	80	0	0	0	0
4	5930	1280	0	0	0	0
5	47,690	14,320	2240	0	0	0
6	384,090	148,480	35,840	1920	0	0
7	3,075,610	1,459,840	433,040	95,600	0	1440
8	24,663,210	13,835,680	4,862,560	1,389,600	135,760	20,160
9	197,117,210	127,784,640	51,759,280	17,005,840	4,048,960	393,600
10	1,576,845,050	1,158,460,000	527,313,040	195,416,640	56,686,400	10,919,040
11	12,589,411,530	10,342,876,480	5,218,528,800	2,143,264,320	708,980,560	204,737,760
$d=6$						
1	12	0	0	0	0	0
2	132	0	0	0	0	0
3	1332	120	0	0	0	0
4	13,452	2400	0	0	0	0
5	134,892	33,960	4320	0	0	0
6	1,353,732	441,600	88,320	3840	0	0
7	13,536,612	5,436,960	1,357,800	244,200	0	2880
8	135,457,932	64,509,840	19,183,440	4,573,680	361,560	51,840
9	1,352,852,292	745,845,120	256,222,200	71,229,720	13,934,640	1,207,680
10	13,517,235,732	8,461,348,080	3,274,749,720	1,030,869,120	251,783,280	40,740,480
11	134,908,128,732	94,558,053,840	40,628,931,120	14,200,593,600	3,996,066,600	972,131,040

to C_3 from single contacts. Figure 2 depicts all no-contact and single-contact chain configurations contributing to the partition function for $n = 3$, and the caption explains the alternative form of expressing C_3. Direct counting can also be applied to longer chains. However, as is well known, it becomes impractical for n about 5 or 6, and computer assistance is required.

The partition function $C_{n,m}$ in any dimension can, in general, be written as

$$C_{n,m} = \sum_{l=1}^{n} 2^l l! \binom{d}{l} p_{n,m}^{(l)} \tag{5}$$

Equation follows because the total number of configurations for chains with n bonds and m contacts on d-dimensional hypercubic lattices may be computed by summing the polymer configurations $[2^l l!\, p_{n,m}^{(l)}]$ that *only*

(Continued)

n	$C_{n,6}$	$C_{n,7}$	$C_{n,8}$	$C_{n,9}$	C_n^{SAW}	C_n^{NRRW}
	0	0	0	0	10	10
	0	0	0	0	90	90
	0	0	0	0	810	810
	0	0	0	0	7210	7290
	0	0	0	0	64,250	65,610
	0	0	0	0	570,330	590,490
	0	0	0	0	5,065,530	5,314,410
	0	0	0	0	44,906,970	47,829,690
	118,080	0	0	0	398,227,610	430,467,210
	1,821,120	230,400	0	0	3,527,691,690	3,874,204,890
	37,732,880	9,358,080	426,240	175,200	31,255,491,850	34,867,844,010
	0	0	0	0	12	12
	0	0	0	0	132	132
	0	0	0	0	1452	1452
	0	0	0	0	15,852	15,972
	0	0	0	0	173,172	175,692
	0	0	0	0	1,887,492	1,932,612
	0	0	0	0	20,578,452	21,258,732
	0	0	0	0	224,138,292	233,846,052
	314,880	0	0	0	2,441,606,532	2,572,306,572
	6,234,240	645,120	0	0	26,583,605,772	28,295,372,292
	156,415,560	33,870,720	1,278,720	490,560	289,455,960,492	311,249,095,212

span l dimensions with $1 \leqslant l \leqslant n$, multiplied by the number of ways $\binom{d}{l}$ of selecting l dimensions in a d-dimensional space. The factor 2^l arises because when a bond enters a previously unvisited dimension, the bond may be placed in either direction. The $l!$ factor appears because the l dimensions may be chosen in any order. These considerations imply that the $p_{n,m}^{(l)}$ must be positive integers. The quantity $[2^l l! \binom{d}{l}]$ can be alternative written as $q(q-2)(q-4)\cdots[q-(2l-2)]$.

For given n and m, the coefficients $p_{n,m}^{(l)}$ may be obtained from the partition functions $\{C_{n,m}\}$ in $d = 1, 2,..., n$ by just inverting Eq. (5) if the latter functions are known exactly. This is possible because the $p_{n,m}^{(l)}$ are independent of d and the combinatorial factors $\binom{d}{l}$ are linearly independent. In fact, this information is redundant, and, as later shown, enumeration data are required only for dimensions through $d = n/2$ $[d = (n+1)/2]$ for n even $[n$ odd$]$. Table I presents exact enumeration results for the total number of
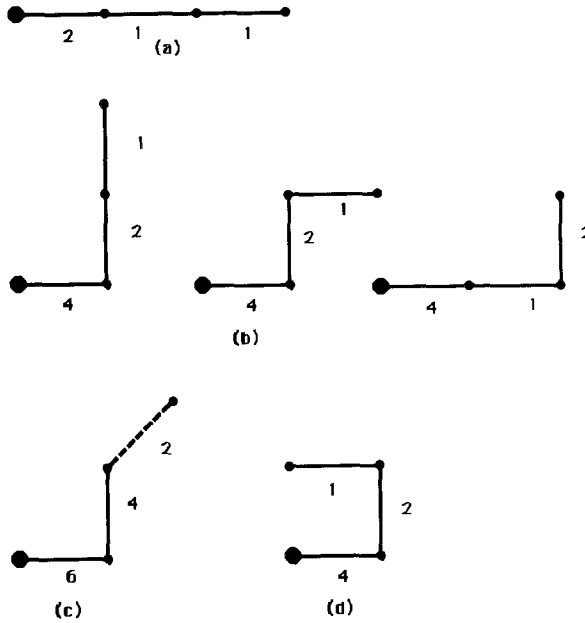
Fig. 2. Configurations of a three-segment chain: Starting at a given lattice site there are two configurations (a) that fully extend in one dimension, as the rods can be oriented in either direction. There are $3 \times (4 \times 2)$ no-contact configurations spanning two dimensions because the first bond in b1 and b2 (b3) has four choices, the second (third) has two, and the third (second) segment has just one choice. The number of configurations (c) that span three dimensions is $6 \times 4 \times 2$, as all bonds are placed in mutually orthogonal directions. There are 4×2 one-contact, two-dimensional configurations (d), as the first bond has four choices, the second only has two because it must be orthogonal to the first one, and the third bond has just one choice to produce the contact.

configurations $C_{n,m}$ for chains of n links with m nearest-neighbor contacts ($m = 0, 1, 2,...$) in $d = 2$–6 for $n \leqslant 11$. For convenience, Table I also provides the n-bond SAW partition function $C_n^{SAW} = C_n(\eta = 1)$ and the number C_n^{NRRW} of n-step nonreversal random walks

$$C_n^{NRRW} = q\sigma^{n-1}, \qquad n = 1, 2, 3,... \tag{6}$$

The values for some of the $\{p_{n,m}^{(l)}\}$ are obtained by simple counting arguments. For example, the number of one-dimensional fully extended configurations for an n-bond chain is $2d$, which equals the number of possible orientations for the first bond, as the direction of the others is then determined. This gives $p_{n,0}^{(1)} = 1$. Similarly, the number of fully extended zero-contact configurations in $d = n$ dimensions is $(2d)(2d-2)(2d-4)(2d-6) \cdots 2$,

since, once the direction of the first bond is specified, the subsequent ones must be in directions orthogonal to all previous bonds. This produces $p_{n,0}^{(n)} = 1$. Similar arguments may be employed for cases with m contacts ($m = 1, 2, 3,...$). It is clear that there must be sufficient chain folding to produce contacts. For example, extended one-dimensional chains cannot have contacts. These facts are summarized by the relations

$$p_{n,0}^{(1)} = p_{n,0}^{(n)} = 1 \tag{7a}$$

$$p_{n,m}^{(1)} = 0, \qquad p_{n,m}^{(n-m+1)} = p_{n,m}^{(n-m+2)} = \cdots = p_{n,m}^{(n)} = 0, \qquad m = 1, 2,... \tag{7b}$$

Table II provides the computed $\{p_{n,m}^{(l)}\}$ for all m with n (and l) $\leqslant 11$ as determined from (5) and Table I with the assumptions discussed at the end of Section 4. The fact that the $\{p_{n,m}^{(l)}\}$ must be positive integers provides a very useful check of the enumeration data. In addition, direct enumeration through $d = 8$ has checked the consistency of our scheme. We stress that the above result applies to any d. As discussed by Baker and Benofy,[23] this analytic continuation is the same as that of the $4 - d$ expansions in the renormalization group theory.[24] It is interesting to compare

Table II. Coefficients $p_{n,m}^{(l)}$ of Eq. (5) for All m with n and $l \leqslant 11$

n \ m	0	1	2	3	4	5	6	7	8	9
$l = 2$										
3	3	1								
4	8	4								
5	20	11	4							
6	49	32	16							
7	117	92	43	19						
8	280	254	134	66	5					
9	665	672	425	173	98					
10	1583	1778	1229	576	298	48				
11	3742	4622	3450	1944	803	444	31			
$l = 3$										
4	7	2								
5	36	16	4							
6	168	96	36	4						
7	736	510	227	84	0	3				
8	3151	2558	1312	580	94	18				
9	13,190	12,282	7153	3424	1315	160	82			
10	54,938	57,498	37,244	19,646	8443	2412	506	96		
11	226,597	263,421	187,704	108,818	50,333	21,843	5357	1964	0	73

Table II. (*Continued*)

m n	0	1	2	3	4	5	6	7	8	9
$l = 4$										
5	13	3								
6	114	44	9							
7	849	441	137	28						
8	5842	3720	1465	456	47	6				
9	38,174	28,630	13,358	5004	1354	147	41			
10	242,737	208,356	110,580	47,604	16,015	3590	646	96		
11	1,511,046	1,458,501	863,574	415,400	160,492	54,555	11,490	3213	222	73
$l = 5$										
6	21	4								
7	282	94	15							
8	3102	1418	367	60						
9	30,583	17,413	5897	1495	211	9				
10	282,368	190,280	77,350	24,620	5693	746	88			
11	2,494,567	1,931,183	903,670	336,799	98,076	23,300	3411	585		
$l = 6$										
7	31	5								
8	592	172	22							
9	9019	3643	792	101						
10	120,668	61,236	17,790	3700	439	12				
11	1,486,799	898,637	318,003	85,576	16,570	2171	141			
$l = 7$										
8	43	6								
9	1108	284	30							
10	22,312	8036	1490	152						
11	388,271	176,875	44,570	7711	743	15				
$l = 8$										
9	57	7								
10	1906	436	39							
11	48,993	15,881	2551	214						
$l = 9$										
10	73	8								
11	3074	634	49							
$l = 10$										
11	91	9								

Fig. 3. The number of configurations of an 11-bond chain C_{11} as a function of the spatial dimensionality d of the hypercubic lattice for SAWs, NAWs, and θ' chains. C_{11} of a NRRW is quite close to that of a θ' chain, so we also present the difference $\Delta C_{11} = C_{11}(\theta') - C_{11}(\text{NRRW})$.

Eq. (5) with the number of configurations for a simple random walk (RW) of n steps as a function of d. The RW yields the simple power-law behavior $C_n^{RW} = q^n$. Equations (2)–(5) indicate that the partition function of an n-step self-avoiding, self-interacting walk is also a polynomial in d (or in q) of degree n. Figure 3 presents C_n vs. d for a SAW, NAW, θ' chains, and NNRW with $n = 11$.

The results of this section can be used in conjunction with the ratio or other extrapolation methods to extract long-chain limit information such as the effective critical index γ, the critical amplitude A, and the free energy per segment $\mathscr{F}$ as functions of the contact energy ε in any dimension. This is the subject of a forthcoming work.[26] Alternatively, our results may be used to generate a d^{-1} expansion for some of these quantities, and this is described in the next sections.

3. ON THE n DEPENDENCE OF THE PARTITION FUNCTION C_n

Equations (2) and (5) are now recast in a manner that leads naturally to d^{-1} expansions of polymer properties for *any n*. In fact, forms for $\{C_n(\eta)\}$ are introduced that are valid for any n and that are exact for integer n with $n \leqslant 11$.

The n-bond partition functions $\{C_n(\eta)\}$ are polynomials in d of degree n as indicated by Eqs. (2) and (5). Section 2 and Table II express these polynomials in terms of the quantities $[2^l l! \binom{d}{l}]$, with $l = 1, 2,..., n$. We now expand the combinatorial factors and rewrite them in terms of $q\sigma^l$, $l = 0, 1, 2,..., n-1$. This choice of variables is suited for describing the packing of dilute self-avoiding walks and was used by Fisher and Gaunt.[17] An alternative choice is to expand C_n in terms of q^l, $l = 1, 2,..., n$, the form employed by Freed and co-workers[13,14] in the treatment of many dense polymer properties and by Nemirovsky and co-workers[15,16] in work on dilute polymers. Define the Mayer f-bond energy as[2,3]

$$f = \eta - 1 = \exp(-\varepsilon/kT) - 1 \tag{8}$$

Then Eqs. (4) are readily rewritten as

$$C_n = q\sigma^{n-1}[1 + a_1(n-1)\,\theta(n-1) + a_2(n-2)\,\theta(n-2)], \qquad n = 1, 2, 3 \tag{9}$$

$$a_1 = 0, \qquad a_2 = f(\sigma^{-1} - \sigma^{-2}) \tag{9a}$$

where $\theta(x)$ is the Heaviside function and is required to combine Eqs. (4a) to (4c) in a single compact equation. Similarly, using Eqs. (2), (5), and Table II makes it possible to reexpress $C_n(\eta)$ for $n \leqslant 11$ as

$$C_n(f) = q\sigma^{n-1}\left[1 + \sum_{i=1}^{\infty} (n-i)\,\theta(n-i)\,a_i(f)\right] \tag{10}$$

It should be possible to prove by induction that Eq. (10) holds for any n. The functions $a_i(f)$ are polynomials in f of degree $i_{\max}$, i.e.,

$$a_i = \sum_{l=0}^{i_{\max}} a_{i,l} f^l \tag{11}$$

where $i_{\max}$ is the maximum possible number of contacts of a $(i+1)$-bond chain in dimension $d = (i+1)/2 \ [(i+2)/2)]$ for i odd [even]. The $\{a_{i,l}\}$ are functions of σ^{-1} and are presented in the Appendix. When $\sigma = 1$ $(d = 1)$, all coefficients $\{a_i\}$ with $i = 1, 2,...$ vanish. This is as expected since in $d = 1$, $C_n(f) = q = 2$ for all n and f. Thus, this condition serves as another useful check on the computed coefficients.

We stress that Eq. (10) summarizes an enormous amount of information: all the material contained in Table II and Eq. (5). Hence it produces the *exact partition functions for chains through 11 bonds in any dimension and for any interaction energy* ε. (This includes SAWs, NAWs, and theta chains as special limits.) Figure 4 exhibits C_n as function of n for a SAW, a NAW, a θ' chain, and an NRRW in $d = 3$ (a sc lattice) with $2 \leqslant n \leqslant 11$.
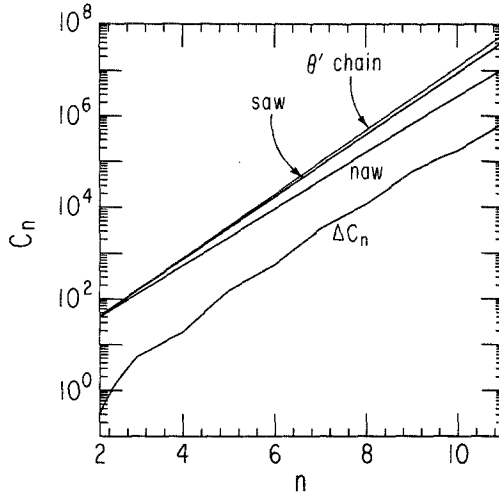
Fig. 4. The n dependence of the n-segment chain partition function C_n for SAWs, NAWs, and θ' chains on a sc lattice. We define $\Delta C_n = C_n(\theta') - C_n(\text{NRRW})$.

Clearly, since Eq. (10) contains the step function, the continuous function C_n vs. n has a small discontinuity in its first derivative at integer n. (However, the discontinuities are so small that they are imperceptible in Fig. 4.)

The large-n limit of (10) provides the necessary ingredients for a $1/d$ expansion of the chain free energy as discussed in the following section. To understand how the short-chain expression (10) may be extended to a form valid for large n, we now use Eqs. (A1)–(A10) to analyze the structure of individual contributions to the n-bond chain partition function C_n. Only a_1 and a_2 produce contributions of order σ^{-1}, and these are in the form

$$\text{contributions from } a_1 \text{ through } a_2 = (n-2)\,\sigma^{-1}f \qquad (12a)$$

Similarly, only a_2, a_3, and a_4 give contributions linear in f and of order σ^{-2} as follows:

$$\text{contributions from } a_2 \text{ through } a_4$$
$$= \{ -(n-3) + [-(n-2) - 2(n-3) + 4(n-4)]f \}\,\sigma^{-2}$$
$$= [-(n-3) + (n-8)f]\,\sigma^{-2} \qquad (12b)$$

Although contributions proportional to f^2 and of order σ^{-2} exist for all a_i $(i > 3)$, a very simple structure emerges upon inspection of Eqs. (A1)–(A10), namely, all a_i for $i \geqslant 5$ contain the term $(n-i)f^2\sigma^{-2}$.

Hence, assuming this holds for all i, the full $\sigma^{-2} f^2$ dependence of C_n for all n is obtained by summing all these contributions to a_i,

$$\text{contributions from all } \{a_i\}, i > 3$$

$$= [4(n-4) + (n-5) + (n-6) + (n-7) + \cdots] \sigma^{-2} f^2$$

$$= [(n+3)(n-4)/2] \sigma^{-2} f^2 \tag{12c}$$

Equations (10) and (12) generate C_n through second order in σ^{-1} as

$$C_n = q\sigma^{n-1} \{ 1 + (n-2) f\sigma^{-1} + [(3-n) + (n-8)f$$

$$+ (n+3)(n-4) f^2/2] \sigma^{-2} + \cdots \} \tag{13}$$

a form which is valid for $n > 4$. Thus, Eq. (13) is expected to apply for the large-n limit. After inspecting Eqs. (A1)–(A10), it appears that similar arguments may be used to obtain all contributions to C_n through order σ^{-5}. These assumptions are supported in the next section by using results from the lattice cluster theory, which permits the direct determination of a d^{-1} expansion for the chain free energy.

4. THE d^{-1} EXPANSION OF THE PARTITION FUNCTION

The lattice cluster theory[13–16] (LCT) has been developed extensively by Freed and co-workers to study a variety of thermodynamic properties of dense polymer solutions, melts, and blends. This theory also considers the standard lattice model of polymers on a d-dimensional hypercubic lattice, and produces $1/d$ expansions for thermodynamic properties. The LCT begins with an exact representation of the chain partition function and then expands it about a zeroth-order Flory approximation (which is exact for $d = \infty$). Most of the LCT work focuses on the many-chain thermodynamic limit of n finite and $N \to \infty$, $p \to \infty$, $0 < \Phi = p(n+1)/N \leqslant 1$, with N the number of lattice sites, p the number of chains, and Φ the polymer volume fraction.[13,14] Nemirovsky and Coutinho-Filho[15] have extended the method to athermal chains in the infinite dilution limit (i.e., a single dense self-avoiding walk), and recently Nemirovsky et al.[16] have generalized these single-chain results to macromolecules with nearest-neighbor contact interactions and to self-avoiding, self-interacting trees of any specified topology. Although the previous applications of the LCT[13–16] focus only on the thermodynamic limit of large p and N (n and N) for dense (dilute) polymers, the general formulation applies to finite systems and thereby provides exact information for small systems such as short chains at infinite dilution.

The lattice cluster theory suggests that the partition function $C_n(f)$ has the exact structure

$$C_n = q\sigma^{n-1} \left[1 + \sum_{j=1}^{n-1} A_j(f)\,\sigma^{-j} \right] \tag{14}$$

where the n-dependent coefficients $A_j(f)$ are polynomials in f of degree j_{max},

$$A_j = \sum_{k=0}^{j_{max}} A_{j,k}\,f^k \tag{14a}$$

and where j_{max} is the maximum power of f in the coefficient of σ^{-j} in the polynomials $\{a_i\}$, $i = 1, 2,..., 2j+1$ of the Appendix. For example, $j_{max} = 1$, 2, 3, 5, 6, 7, 9,..., for $j = 1$, 2, 3, 4, 5, 6, 7,..., respectively. Configurations with $j = j_{max}$ are the only ones that are relevant in the large-f limit (the collapsed chain). The A_j are conveniently grouped in cumulant clusters,

$$(A_j)_c = \sum_{k=0}^{j_{max}} (A_{j,k})_c\,f^k$$

that naturally appear when expanding $\log C_n(f)$, which is (minus) the system's free energy,

$$\log C_n(f) = \log q + (n-1)\log\sigma + \sum_{j=1}^{n-1} [A_j(f)]_c\,\sigma^{-j} \tag{15}$$

where, for example,

$$(A_{3,3})_c = A_{3,3} - A_{1,1}A_{2,2} + (1/3)(A_{1,1})^3 \tag{16a}$$

$$(A_{4,2})_c = A_{4,2} - (1/2)(A_{2,1})^2 - A_{1,0}A_{3,2} - A_{1,1}A_{3,1}$$
$$+ (A_{1,0})^2 A_{2,2} + (A_{1,1})^2 A_{2,0} \tag{16b}$$

Obviously, the $(A_{j,k})_c$ are functions of n. An important feature suggested by the lattice cluster theory is that long enough chains (as defined below) yield the *clusters* $(A_{j,k})_c$ *as linear functions of n for all n,*

$$(A_{j,k})_c = \alpha_{j,k}^{(1)} n + \alpha_{j,k}^{(0)} \tag{17}$$

with $\alpha_{j,k}^{(1)}$ and $\alpha_{j,k}^{(0)}$ real numbers that are determined here from the enumeration data. For example, taking the logarithm of (13) and expanding in powers of σ^{-1} yields

$$\log C_n = \log q\sigma^{n-1} + (n-2)f\sigma^{-1}$$
$$+ [(3-n) + (n-8)f + (3n-16)f^2/2]\,\sigma^{-2} \tag{18}$$

Notice that Eq. (18) has an exact cancelation of the n^2 contribution to the partition function (13). In fact, the lineality in n of (17) for n large is just a consequence of the extensively of the free energy in the thermodynamic

limit of infinitely long chains. However, the LCT suggests that this lineality already holds for chains of $n > 2j - 1$ for $k > 0$ (or $n > 2j - 2$ for $k = 0$). These conclusions are also strongly supported by the direct enumeration data. Similar inferences are suggested by Fisher and Gaunt[17] in their SAW work. This interesting result enables us to construct a $1/d$ expansion for the free energy.

The determination of the asymptotic form of the coefficients $\alpha_{j,k}$ for all $k > 0$ requires chains of at least $2j$ bonds. Since for given j there are two numbers $\alpha_{j,k}^{(1)}$ and $\alpha_{j,k}^{(0)}$ to be determined in order to produce two equations for these two unknowns, it suffices to have information for walks of $2j$ and $2j + 1$ steps. (Of course, longer chains could also be used.) The coefficient $\alpha_{j,0}$ (for athermal SAWs) may be obtained from data of only $2j - 1$ and $2j$ segments. For example, we evaluate $(A_{1,0})_c$ using the $C_1(f = 0)$ and $C_2(f = 0)$ given in the previous section together with Eqs. (14), (16), and (17). Similarly, to determine $(A_{1,1})_c$, we employ information from C_2 and C_3. Of course the form in Eq. (17) is valid for any n larger than $2j$ for $k > 0$ or larger than $2j - 1$ for $k = 0$. For example, the values of $\alpha_{1,k}$ ($k = 0$ and 1) obtained using data for chains with $n = 1$–3 suffice to predict $A_1(f)$ for all n larger than 3. This provides a very useful check for the results given in Section 3 and on the consistency of the calculational scheme presented in this work. This procedure enables the computation of the cumulants in Table III.

The free energy of the n-bond self-avoiding walk with nearest-neighbor interactions is expressed by (15) and Table III as a $1/d$ expansion by using information gathered for short walks. However, the important point here is that this expansion is now also valid in the limit of large n. Therefore, Eq. (15) may be used to extract information concerning the asymptotic $n \to \infty$ behavior of these walks.

The above discussion should already clarify the minimum enumeration data that is required to produce the d^{-1} expansion for any polymer property. Equation (14) implies that the specification of the n-bond parti-

Table III.   Cluster Coefficients $(A_{j,k})_c$ of (17) for All k with j up to 5

j \ k	0	1	2	3	4	5	6
1	0	$n-2$					
2	$3-n$	$n-8$	$(3n-16)/2$				
3	$13-2n$	$7n-64$	$11n-91$	$(16n-128)/3$			
4	$(205-23n)/2$	$35n-538$	$117n/2-827$	$56n-686$	$103n/4-263$	$3n-18$	
5	$856-64n$	$250n-5308$	$251n-6477$	$532n-8636$	$379n-5559$	$(626n-8582)/5$	$14n-148$

tion function requires determination of $n-1$ polynomials in f, $\{A_j(f)$ for $j=1$ to $n-1\}$, each of degree j_{max}. For example, to obtain $C_2(f)$ for all dimensions d we only need $A_1(f)$, which, in turn, is determined from direct enumeration of a two-bond chain in only $d=1$. Calculation of $C_3(f)$ for all d requires $A_1(f)$ and $A_2(f)$, so it is only necessary to perform the enumeration of three-bond chains in $d=1$ and $d=2$. Similarly, $C_4(\eta)$ $[C_5(\eta)]$ for all d may be evaluated from $A_1(f)$ to $A_3(f)$ $[A_1(f)$ to $A_4(f)]$, which in turn are obtained from enumeration of four-bond (five-bond) chains in $d=1$ through $d=3$ ($d=1$ to $d=4$) to determine the three (four) unknown α's of (17). However, the above discussion indicates that the $n=2$ and 3 results already provide the full σ^{-1} contribution to the partition function for longer chains. This, in turn, reduces the number of unknowns for $C_4(\eta)$ $[C_5(\eta)]$ to two (three). Hence $C_4(\eta)$ $[C_5(\eta)]$ requires enumeration in $d=1$ and $d=2$ ($d=1$ to $d=3$). Similarly, the calculation of $C_6(\eta)$ $[C_7(\eta)]$ involves only $\{A_j(f)\}$ for $j=1$–5 ($j=1$–6) to deduce the five (six) unknowns. Again, shorter-chain information provides the full σ^{-1} and σ^{-2} dependence, reducing the number of unknowns by two and then only requiring enumeration data in $d=1$ to $d=3$ ($d=1$ to $d=4$).

In general, in order to calculate the exact value of some polymer property for chains of $2j$ or $2j-1$ bonds for all d, it is necessary to perform enumeration for chains with the same number of bonds in dimensions $d=1$ through j. Furthermore, the calculation of the jth order within the d^{-1} expansion can be accomplished with only enumeration data for chains with n up to $2j+1$ in dimensions up to $d=j+1$. [For athermal walks (SAWs), chains with n up to $2j$ suffice.] These general results considerably reduce the number of enumerations required to generate $C_n(f)$ as simultaneous functions of n, d, and f, as well as to produce the d^{-1} expansions. Furthermore, because a large amount of enumeration data in higher d may be predicted from that in lower d, there are a large number of internal consistency checks.

5. EXPANSION IN d^{-1} FOR μ AND AS FUNCTIONS OF f

Using Eqs. (15) and Table III together with the asymptotic form of the partition function (3), we obtain the connectivity constant μ through fifth order in σ^{-1} as

$$\begin{aligned}
\log \mu = \log \sigma + f\sigma^{-1} &+ (-1 + f + 3/2\,f^2)\,\sigma^{-2} + (-2 + 7f \\
&+ 11f^2 + 16/3\,f^3)\,\sigma^{-3} + (-23/2 + 35f + 117/2\,f^2 \\
&+ 56f^3 + 103/4\,f^4 + 3f^5)\,\sigma^{-4} + (-64 + 250f + 251f^2 \\
&+ 532f^3 + 379f^4 + 626/5\,f^5 + 14f^6)\,\sigma^{-5} + \cdots
\end{aligned} \qquad (19)$$

where the coefficients of each σ^{-j} contain terms to all order in f. It is well known that the critical indices assume their classical (mean field) values above the critical dimension d_c. The critical dimension is believed to be $d = 4$ for SAWs, and numerical evidence for this is indicated in another work devoted to the exponent v. Combining (3) and the results of Section 4 produces the d^{-1} expansion of the free energy amplitude A,

$$
\begin{aligned}
\log A = \log(1 + \sigma^{-1}) &- 2f\sigma^{-1} + (3 - 8f - 8f^2)\,\sigma^{-2} \\
&+ (13 - 64f - 91f^2 - 128/3\,f^3)\,\sigma^{-3} + (205/2 - 538f \\
&- 827f^2 - 686f^3 - 263f^4 - 18f^5)\,\sigma^{-4} + (856 - 5308f \\
&- 6477f^2 - 8636f^3 - 5559f^4 - 8582/5\,f^5 - 148f^6)\,\sigma^{-5} + \cdots \quad (20)
\end{aligned}
$$

again with coefficients of each σ^{-j} evaluated to all orders in f.

It is interesting to consider limiting cases of our general formulas (19) and (20) after exponentiation and expansion in σ^{-1}. The $f = 0$ limit reproduces the results of Fisher and Gaunt[17] and of Gaunt[27] for μ_{SAW} and A_{SAW}, respectively,

$$
\mu_{SAW} = \sigma(1 - \sigma^{-2} - 2\sigma^{-3} - 11\sigma^{-4} - 62\sigma^{-5} + \cdots) \tag{21a}
$$

$$
A_{SAW} = (1 + \sigma^{-1})(1 + 3\sigma^{-2} + 13\sigma^{-3} + 107\sigma^{-4} + 895\sigma^{-5} + \cdots) \tag{21b}
$$

Hara and Slade[28] study SAWs in five or more dimensions. In particular, at $d = 5$ they derive the bounds $1 \leqslant A_{SAW} \leqslant 1.493$ and $\mu_{SAW} > 8.82128$ which are satisfied by (21) (see Tables IV and V).

Table IV.   Connectivity Constants of SAWs, NAWs, and θ' Chains on d-Dimensional Hypercubic Lattices

	μ_{SAW}		μ_{NAW}		$\mu_{\theta'}$	
d	Extrap	Series	Extrap	Series	Extrap	Series
2	2.638	2.556	2.314	1.833	2.797	2.944
3	4.683	4.676	4.065	3.808	4.899	4.948
4	6.775	6.771	5.92	5.822	6.96	6.967
5	8.835	8.840	7.94	7.891	8.98	8.981
6	10.880	10.880	9.94	9.941	10.986	10.988
7	12.900	12.904	11.96	11.963	12.991	12.992
8	14.920	14.920	13.97	13.975	14.994	14.994

Table V.   Free Energy Amplitudes of SAWs, NAWs, and θ' Chains on
d-Dimensional Hypercubic Lattices

d	A_{SAW}		A_{NAW}		$A_{\theta'}$	
	Extrap	Series	Extrap	Series	Extrap	Series
4	1.268	1.282	1.643	1.783	1.187	1.190
5	1.180	1.199	1.471	1.583	1.134	1.140
6	1.133	1.143	1.363	1.422	1.105	1.108
7	1.105	1.109	1.293	1.319	1.086	1.088
8	1.087	1.089	1.245	1.258	1.073	1.074

The NAW $(f = -1)$ limit produces

$$\mu_{NAW} = \sigma(1 - \sigma^{-1} - 3\sigma^{-3} - 18\sigma^{-4} - 306\sigma^{-5} + \cdots) \tag{22a}$$

$$A_{NAW} = (1 + \sigma^{-1})(1 + 2\sigma^{-1} + 5\sigma^{-2} + 36\sigma^{-3} + 323\sigma^{-4}$$
$$+ 4998\sigma^{-5} + \cdots) \tag{22b}$$

Gaunt et al.[21] obtain the first three terms of (22a). The first correction to the NAW connectivity constant could have been guessed as $\sigma(1 - \sigma^{-1}) = q - 2$, which is the number of choices per segment of a NAW for high d. Finally, a θ' chain with $f = \sigma^{-1}$ yields

$$\mu_{\theta'} = \sigma(1 - \sigma^{-3} - 3\sigma^{-4} - 18\sigma^{-5} + \cdots) \tag{23a}$$

$$A_{\theta'} = (1 + \sigma^{-1})(1 + \sigma^{-2} + 5\sigma^{-3} + 31\sigma^{-4} + 232\sigma^{-5} + \cdots) \tag{23b}$$

The $(1 + \sigma^{-1})$ prefactor in Eqs. (21b), (22b), and (23b) corresponds to the Bethe approximation. All the above series appear to be asymptotic[23]; hence results for low dimensions should be treated with care. Either reasonable truncations or appropriate resummation techniques may be required for low d. Tables IV and V present, respectively, the connectivity constants $\{\mu\}$ in $d = 2-8$ and amplitudes $\{A\}$ in $4 \leqslant d \leqslant 8$ of SAWs, NAWs, and θ' chain as calculated from Eqs. (21)–(23) following Fisher by retaining terms through order σ^{-d} plus one-half of the following term, except for $d = 5-8$, where all terms are used.[17] Also, comparison is made with results[26] obtained by numerical extrapolation of the enumeration data. Figure 5 displays $\ln \mu$ as a function of the dimension for SAWs, NAWs, and θ' chains obtained by both d^{-1} expansions and series analysis. The agreement between the two methods is quite good above $d = 4$.
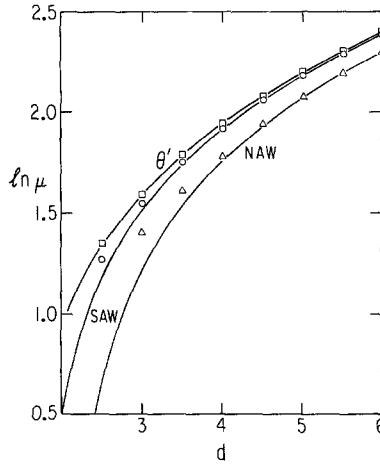
Fig. 5. The d dependence of the logarithm of the connectivity constant. The circles, triangles, and squares are from series analysis[26] for SAWs, NAWs, and θ' chains, respectively. The curves are from the fifth-order d^{-1} expansion.

6. CONCLUSIONS

This work combines several ingredients, given separately in the literature, to evaluate, for first time, the exact n-bond partition function C_n of a self-avoiding, self-interacting chain on a d-dimensional hypercubic lattice for any d with $n \leqslant 11$ segments. This is done using computer enumeration data in dimensions d only through 6, the theoretically predicted analytic structure for C_n, and some relations suggested by the lattice cluster theory and strongly supported by the numerical data. The exact partition function for short chains in any d and for any ε can be extrapolated numerically to the large-n limit using, for example, the ratio method to extract the asymptotic critical index γ, the connectivity constant μ, and the free energy amplitude A for all dimensions. All these quantities may be evaluated for any ε, including SAWs, NAWs, theta, and collapsed chains as particular cases. This analysis will be presented separately.

Alternatively, the exact short-chain n-bond partition function may be used to generate a d^{-1} expansion of the free energy that is *valid in the large-n limit*. This is illustrated in Section 5, where we derive a d^{-1} expansion for the ε-dependent chain connectivity constant μ through fifth order. A d^{-1} expansion for the ε-dependent free energy amplitude A is also derived to $O(d^{-5})$ for d larger than the critical dimension d_c. The general results for the ε-dependent μ and A are specialized to the SAW ($\varepsilon = 0$), NAW ($\varepsilon = \infty$), and θ' chain ($\varepsilon \approx -\sigma^{-1}$) limits. The self-avoiding walk

growth constant and amplitude agree, respectively, with those of Fisher and Gaunt[17] and of Gaunt.[27] Ref. 21 derives the d^{-1} expansion for μ_{NAW} through third order which is in agreement with ours evaluated through fifth. The remaining ε dependence is derived here for first time.

The method developed here is very useful to produce a long d^{-1} series in the large-n limit or to produce the exact partition function of short chains in any d by using only computer enumeration data for short chains in lower d. In fact, the computer data replace the time-consuming task of evaluating many-body diagrams. This technique may be extended to consider many lattice models and properties. For example, a future paper will consider the generalization to calculate the mean-square polymer end-to-end distance.[29] Further extensions should be possible to study models of semiflexible and rigid chains,[30] which are of great relevance to understanding liquid crystals, the glass transition, models of polymer chains terminally attached to an interface, confined polymers, and dense walks. We believe that future applications of the method may include the statistics of self-avoiding surfaces, critical phenomena, and disordered systems, such as spin glasses.[31]

APPENDIX. THE FUNCTIONS $a_i(f)$ OF EQ. (10)

Proceeding as indicated in Section 3, the $\{a_i\}$ for $i = 1\text{--}10$ are determined as

$$a_1 = 0 \tag{A1}$$

$$a_2 = (\sigma^{-1} - \sigma^{-2})f \tag{A2}$$

$$a_3 = (-\sigma^{-2} + \sigma^{-3})(1 + 2f) \tag{A3}$$

$$a_4 = (\sigma^{-3} - \sigma^{-4}) + (4\sigma^{-2} - 12\sigma^{-3} + 8\sigma^{-4})(f + f^2) \tag{A4}$$

$$a_5 = (-4\sigma^{-3} + 13\sigma^{-4} - 9\sigma^{-5}) + (-16\sigma^{-3} + 50\sigma^{-4} - 34\sigma^{-5})f$$
$$+ (\sigma^{-2} - 9\sigma^{-3} + 15\sigma^{-4} - 7\sigma^{-5})f^2$$
$$+ (4\sigma^{-3} - 16\sigma^{-4} + 12\sigma^{-5})f^3 \tag{A5}$$

$$a_6 = (7\sigma^{-4} - 22\sigma^{-5} + 15\sigma^{-6})$$
$$+ (25\sigma^{-3} - 170\sigma^{-4} + 377\sigma^{-5} - 232\sigma^{-6})f$$
$$+ (\sigma^{-2} + 35\sigma^{-3} - 244\sigma^{-4} + 521\sigma^{-5} - 313\sigma^{-6})f^2$$
$$+ (20\sigma^{-3} - 106\sigma^{-4} + 183\sigma^{-5} - 97\sigma^{-6})f^3$$
$$+ (15\sigma^{-4} - 60\sigma^{-5} + 45\sigma^{-6})f^4 + (3\sigma^{-4} - 12\sigma^{-5} + 9\sigma^{-6})f^5 \tag{A6}$$

$$a_7 = (-26\sigma^{-4} + 182\sigma^{-5} - 402\sigma^{-6} + 246\sigma^{-7})$$
$$+ (-2\sigma^{-3} - 118\sigma^{-4} + 798\sigma^{-5} - 1672\sigma^{-6} + 994\sigma^{-7})f$$
$$+ (\sigma^{-2} + 2\sigma^{-3} - 106\sigma^{-4} + 342\sigma^{-5} - 285\sigma^{-6} + 46\sigma^{-7})f^2$$
$$+ (8\sigma^{-3} + 4\sigma^{-4} - 442\sigma^{-5} + 1368\sigma^{-6} - 938\sigma^{-7})f^3$$
$$+ (47\sigma^{-4} - 389\sigma^{-5} + 950\sigma^{-6} - 608\sigma^{-7})f^4$$
$$+ (-12\sigma^{-5} + 48\sigma^{-6} - 36\sigma^{-7})f^5 \tag{A7}$$

$$a_8 = (\sigma^{-4} + 48\sigma^{-5} - 323\sigma^{-6} + 668\sigma^{-7} - 394\sigma^{-8})$$
$$+ (-2\sigma^{-3} + 242\sigma^{-4} - 2699\sigma^{-5} + 11622\sigma^{-6} - 20731\sigma^{-7}$$
$$+ 11568\sigma^{-8})f + (\sigma^{-2} + 2\sigma^{-3} + 357\sigma^{-4} - 3998\sigma^{-5}$$
$$+ 15831\sigma^{-6} - 25976\sigma^{-7} + 13783\sigma^{-8})f^2$$
$$+ (9\sigma^{-3} + 278\sigma^{-4} - 2637\sigma^{-5} + 8033\sigma^{-6} - 9840\sigma^{-7} + 4157\sigma^{-8})f^3$$
$$+ (117\sigma^{-4} - 434\sigma^{-5} - 1010\sigma^{-6} + 5070\sigma^{-7} - 3743\sigma^{-8})f^4$$
$$+ (309\sigma^{-5} - 2234\sigma^{-6} + 4919\sigma^{-7} - 2994\sigma^{-8})f^5$$
$$+ (41\sigma^{-5} - 287\sigma^{-6} + 615\sigma^{-7} - 369\sigma^{-8})f^6 \tag{A8}$$

$$a_9 = (\sigma^{-4} - 244\sigma^{-5} + 2793\sigma^{-6} - 11920\sigma^{-7} + 20977\sigma^{-8}$$
$$- 11507\sigma^{-9}) + (-2\sigma^{-3} - 6\sigma^{-4} - 1102\sigma^{-5} + 12144\sigma^{-6}$$
$$- 47760\sigma^{-7} + 78160\sigma^{-8} - 41434\sigma^{-9})f$$
$$+ (\sigma^{-2} + 2\sigma^{-3} - 8\sigma^{-4} - 1056\sigma^{-5} + 4986\sigma^{-6} + 101\sigma^{-7}$$
$$- 24544\sigma^{-8} + 20518\sigma^{-9})f^2$$
$$+ (10\sigma^{-3} + 40\sigma^{-4} - 220\sigma^{-5} - 8210\sigma^{-6}$$
$$+ 55476\sigma^{-7} - 115222\sigma^{-8} + 68126\sigma^{-9})f^3$$
$$+ (64\sigma^{-4} + 543\sigma^{-5} - 11113\sigma^{-6} + 49850\sigma^{-7} - 84400\sigma^{-8}$$
$$+ 45056\sigma^{-9})f^4$$
$$+ (440\sigma^{-5} - 3854\sigma^{-6} + 10560\sigma^{-7} - 9690\sigma^{-8} + 2544\sigma^{-9})f^5$$
$$+ (6\sigma^{-5} + 484\sigma^{-6} - 4346\sigma^{-7} + 10852\sigma^{-8} - 6996\sigma^{-9})f^6$$
$$+ (96\sigma^{-6} - 768\sigma^{-7} + 1824\sigma^{-8} - 1152\sigma^{-9})f^7 \tag{A9}$$

$$a_{10} = (\sigma^{-4} + 4\sigma^{-5} + 420\sigma^{-6} - 4659\sigma^{-7} + 18151\sigma^{-8}$$
$$- 29422\sigma^{-9} + 15505\sigma^{-10}) + (-2\sigma^{-3} - 6\sigma^{-4} + 2811\sigma^{-5} - 46349\sigma^{-6}$$

$$+ \, 317152\sigma^{-7} - 1056983\sigma^{-8} + 1623648\sigma^{-9} - 840271\sigma^{-10})f$$

$$+ \, (\sigma^{-2} + 2\sigma^{-3} - 11\sigma^{-4} + 4384\sigma^{-5} - 67171\sigma^{-6} + 401480\sigma^{-7}$$

$$- \, 1151683\sigma^{-8} + 1543849\sigma^{-9} - 730851\sigma^{-10})f^2$$

$$+ \, (11\sigma^{-3} + 43\sigma^{-4} + 3752\sigma^{-5} - 50483\sigma^{-6}$$

$$+ \, 222335\sigma^{-7} - 390187\sigma^{-8} + 209859\sigma^{-9} + 4670\sigma^{-10})f^3$$

$$+ \, (76\sigma^{-4} + 2164\sigma^{-5} - 17963\sigma^{-6} - 1564\sigma^{-7} + 293858\sigma^{-8}$$

$$- \, 724946\sigma^{-9} + 448375\sigma^{-10})f^4$$

$$+ \, (778\sigma^{-5} + 2374\sigma^{-6} - 78241\sigma^{-7} + 355728\sigma^{-8}$$

$$- \, 594535\sigma^{-9} + 313896\sigma^{-10})f^5$$

$$+ \, (6\sigma^{-5} + 3874\sigma^{-6} - 34490\sigma^{-7} + 99245\sigma^{-8}$$

$$- \, 104265\sigma^{-9} + 35630\sigma^{-10})f^6$$

$$+ \, (393\sigma^{-6} - 207\sigma^{-7} - 17299\sigma^{-8} + 56167\sigma^{-9} - 39054\sigma^{-10})f^7$$

$$+ \, (879\sigma^{-7} - 7254\sigma^{-8} + 17589\sigma^{-9} - 11214\sigma^{-10})f^8$$

$$+ \, (73\sigma^{-7} - 584\sigma^{-8} + 1387\sigma^{-9} - 876\sigma^{-10})f^9 \tag{A10}$$

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