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Virial Coefficients for Lattice Polymers

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ABSTRACT: We outline the calculation of the second and third virial coefficients for polymers modeled as self-avoiding walks on the plane-square lattice by explicit enumeration of all chain conformations and arrangements on the lattice. The beginning terms in the activity series and the density dependence of the configurational statistics are constructed as a function of chain length for short chains.

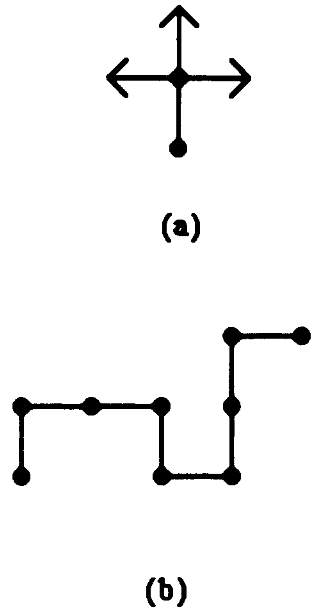

Figure 1. Lattice polymer modeled as a self-avoiding random walk on the plane-square lattice. (a) The three possible choices of orientation of a chain link; the valence angle is not held fixed. (b) A sample chain configuration derived from the generator in (a). The chain length is measured by the number of solid dots.

1. Introduction

In the present paper we explore the calculation of the second and third virial coefficients for short chains on a lattice by explicit computer enumeration of all chain conformations and arrangements on the lattice. Our motivation is the use of equilibrium virial coefficients to describe the cooperative kinetics of adsorption of polymers to a surface, as outlined in the following paper.[1] Because we are interested in the adsorption to a planar surface, we treat a 2-D lattice; the method we use can equally well be applied in the 3-D case.

Lattice models of polymer solutions have a long history, the most successful early theory being the Flory–Huggins mean-field model.[2,3] The approximate treatment of the second virial coefficient for random flight molecules was presented by Casassa and Markovitz.[4] A simple model of the second virial coefficient for polymer globules has been given by Rabin.[5] Huber and Stockmayer[6] have discussed the osmotic second virial coefficient and the accuracy of two-parameter theories. Recently Yato and Okamoto have studied the Θ-point condition (vanishing of the second virial coefficient) as a function of chain length for lattice polymers with three-body interactions.[7] Janssens and Bellemans have studied the second virial coefficient for lattice polymers in three dimensions for the cubic lattice.[8]

Our approach will be the straightforward enumeration of all chain conformations and lattice arrangements, thus giving the exact beginning terms for the density dependence of the thermodynamic functions and configurational statistics of a model polymer system. There is a very large literature on the explicit enumeration of all self-avoiding random walks; the work by Ishinabe[9] contains many references to the literature. As a concrete model we consider lattice polymers on the plane-square lattice where each unit of the chain has three possible orientations on the lattice relative to the previous unit as illustrated in Figure 1a. In this model the valence angle is not held fixed, a feature that gives a high degree of flexibility to short chains; a sample configuration is shown in Figure 1b.

In order to construct the partition function for this system one must first enumerate the irreducible set of conformations as a function of chain length. An irreducible conformation is one that is not obtainable by rotation, reflection, or translation from another in the set. Figure 2 shows the irreducible set of conformations for the present model for chain lengths (taken as the number of units, or solid dots, as in Figure 1b) $n = 2$–5; the set for $n = 6$ is given in Figure 3. Taking σ_n as the number of irreducible conformations for a given n, one has $\sigma_n = 1, 2, 4, 9, 22, 56,$ and 147 for $n = 2$–8, respectively. Another important quantity in constructing the partition function for this model is the number of orientations, designated ω_i, that each conformation can have at every site on the lattice. This number can be $\omega_i = 2$, 4, or 8 depending on the symmetry of the conformation. The three possible cases are illustrated in Figure 4. The ω's for the various conformations are assigned in Figures 2 and 3. One notes that the fraction of conformations having $\omega = 8$ (indicating the least symmetry) increases with chain length (for long chains most of the conformations do not have any special symmetry); the fractions of the conformations having the various ω factors, f_ω, are shown in Table I. Having enumerated the possible conformations and their symmetries, the next task is to count all possible ways of placing one, two, etc. molecules on a lattice of M sites.

2. Grand Partition Function

We will treat the solvent as a constant background and hence it will not appear explicitly in our treatment. In a later section we will include the solvent in a more explicit fashion. Thus at this stage of our treatment the grand partition function for our model appears as a partition function for a single-component lattice gas. In general the grand partition function for such a lattice gas is

$$\Xi = e^{M\Gamma} \tag{2.1}$$

where M is the total number of lattice sites (the analogue of the volume in continuous space models). For a lattice

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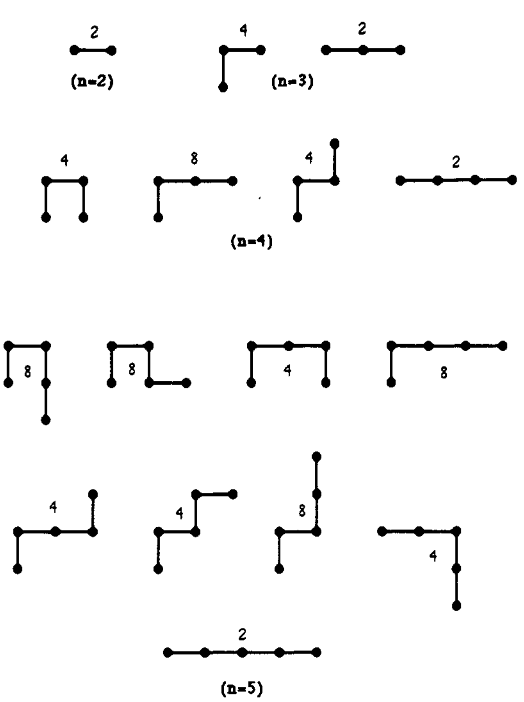


Figure 2. Irreducible sets of conformations for n = 2–5. All other conformations are obtained by rotation, reflection, and translation of the conformations shown. The number associated with each conformation is the ω, or degeneracy, factor illustrated in Figure 4.

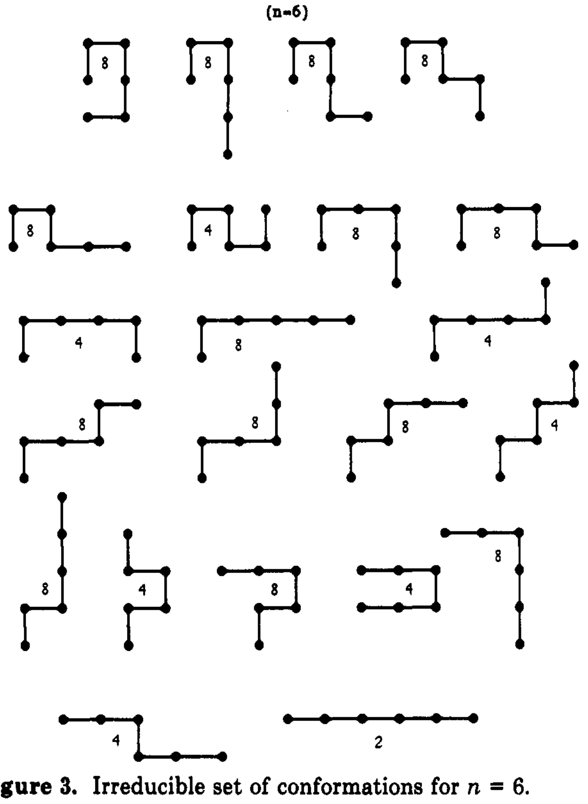


Figure 3. Irreducible set of conformations for n = 6.

gas $\Gamma = p/kT$, the symbols having their usual meanings; in our polymer model we understand that there is a background solvent and hence we will simply treat Γ as the grand potential, a quantity that can be manipulated in the usual manner to obtain average quantities of interest.

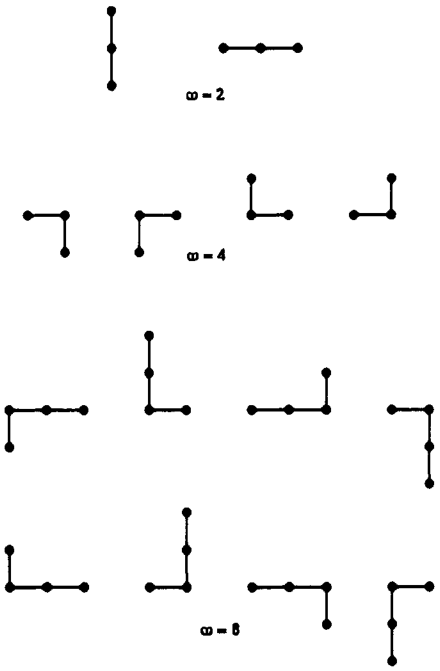


Figure 4. Sample conformations illustrating the three symmetry types, ω = 2, 4, and 8, for polymer conformations on the plane-square lattice.

Table I
Fraction of Symmetry Types as a Function of Chain Length

n	f_2	f_4	f_8	n	f_2	f_4	f_8
2	1	0	0	5	1/9	4/9	4/9
3	1/2	1/2	0	6	1/22	7/22	14/22
4	1/4	1/2	1/4	7	1/56	12/56	43/56

Our treatment follows the standard calculation of virial coefficients from the grand partition function[3] for a simple gas, the only difference being the explicit summations over the internal conformational states of the molecule. The grand partition function is a sum over the number of polymer molecules on the lattice

$$e^{M\Gamma} = 1 + Z_1 z + Z_2 z^2 + Z_3 z^3 + \dots \tag{2.2}$$

where Z_l is the configurational partition function (Boltzmann weighted number of ways of placing l molecules with an irreducible set, σ_n, of internal states on a lattice of M sites) and z is the configurational part of the activity. The activity is defined such that (see the Appendix of the following paper[1])

$$\left(\sum_{i=1}^{\sigma}\omega_i\right)z = \rho \quad \text{as} \quad \rho \to 0 \tag{2.3}$$

Introducing specific configurational partition functions $Q_{ij...}$ for conformations i, j, etc., one has

$$Z_1 = \sum_{i=1}^{\sigma} Q_i \qquad Z_2 = \frac{1}{2!}\sum_{i=1}^{\sigma}\sum_{j=1}^{\sigma} Q_{ij} \qquad Z_3 = \frac{1}{3!}\sum_{i=1}^{\sigma}\sum_{j=1}^{\sigma}\sum_{k=1}^{\sigma} Q_{ijk} \tag{2.4}$$

The sums for Z_2 and Z_3 can also be written in the form

$$Z_2 = \sum_{i,j}{}' Q_{ij} \qquad Z_3 = \sum_{i,j,k}{}' Q_{ijk} \tag{2.5}$$

where the prime indicates that each ij or ijk combination is taken one time once.

To proceed we write the grand potential as a Mayer activity series

$$\Gamma = \sum_{l=1}^{\infty} b_l z^l \tag{2.6}$$

Using (2.6) in (2.2) one has the standard result

$$e^{MT} = 1 + [Mb_1]z + [Mb_2 + (1/2)M^2b_1^{\,2}]z^2 + [Mb_3 + M^2b_1b_2 + (1/6)M^3b_1^{\,3}]z^3 + \ldots = 1 + Z_1z + Z_2z^2 + Z_3z^3 + \ldots \quad (2.7)$$

so that

$$Z_1 = Mb_1$$

$$Z_2 = Mb_2 + (1/2)M^2b_1^{\,2}$$

$$Z_3 = Mb_3 + M^2b_1b_2 + (1/6)M^3b_1^{\,3} \quad (2.8)$$

or

$$Mb_1 = Z_1$$

$$Mb_2 = Z_2 - (1/2)Z_1^{\,2}$$

$$Mb_3 = Z_3 - Z_1Z_2 + (1/3)Z_1^{\,3} \quad (2.9)$$

One notes in (2.8) that the Z's are polynomials in M, the number of sites in the lattice, and one sees that b_l is simply the part of Z_l linear in M. This fact has been used by Springgate and Poland[10] to give a general method for calculating the b_l for lattice gases. Here, due to the complexity of the set of irreducible conformations, we will use a brute force method and calculate the Z's explicitly simply by moving all the different combinations of conformations about on the lattice. If one makes the size of the lattice large enough,[10] so that the finite size of the lattice does not introduce any artificial intermolecular interactions (e.g., by interacting "around the torus" when one uses a finite lattice with periodic boundary conditions), then one can obtain the b_l exact for the infinite lattice by taking the combinations of Z's indicated in (2.9) calculated for a finite lattice.

We then have explicitly

$$Mb_1 = \sum_{i=1}^{\sigma} Q_i$$

$$Mb_2 = \sum_{i=1}^{\sigma}\sum_{j=1}^{\sigma}((1/2)Q_{ij} - (1/2)Q_iQ_j)$$

$$Mb_3 = \sum_{i=1}^{\sigma}\sum_{j=1}^{\sigma}\sum_{k=1}^{\sigma}((1/6)Q_{ijk} - (1/2)[(1/3)\{Q_iQ_{jk} + Q_jQ_{ik} + Q_kQ_{ij}\}] + (1/3)Q_iQ_jQ_k) \quad (2.10)$$

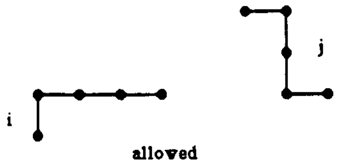
In the equation for b_3 we have written the middle term in a symmetric fashion; if one has only a single conformation then this term would have the simple form $(1/2)Q_1Q_2$, where the subscripts refer to the number of particles. Equations 2.10 can be used to define the following quantities, which we will use in section 4 to treat configurational statistics

$$b_1 = \sum_{i=1}^{\sigma}\gamma_i \qquad b_2 = \sum_{i=1}^{\sigma}\sum_{j=1}^{\sigma}\gamma_{ij} \qquad b_3 = \sum_{i=1}^{\sigma}\sum_{j=1}^{\sigma}\sum_{k=1}^{\sigma}\gamma_{ijk} \quad (2.11)$$

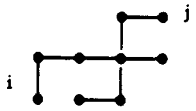
Table II
Polymer Mayer Coefficients as a Function of Chain Length for the Case Where the Only Cooperative Effect Is Excluded Volume[a]

n	b_1	b_2	b_3
2	2	−7	38 (2/3)
3	6	−124	4144
4	18	−1 723	269 586
5	50	−18 884	$(11.62 \pm 0.43) \times 10^6$
6	142	−199 923	$(47.07 \pm 1.16) \times 10^7$
7	390	−1 913 552	$(15.98 \pm 0.92) \times 10^9$
8	1086	−18 084 811	

[a] The values of b_3 for n = 5–7 are Monte Carlo estimates.



allowed



forbidden

Figure 5. Sample configurations of two conformations in an allowed and a forbidden arrangement.

For the case of excluded volume only (we will introduce inter- and intramolecular interactions later) the Q's are simply the number of allowed arrangements. For $l = 1$ we have explicitly

$$Z_1 = \sum_{i=1}^{\sigma} Q_i = \sum_{i=1}^{\sigma} M\omega_i = M\Omega \qquad b_1 = \Omega = \sum_{i=1}^{\sigma}\omega_i \quad (2.12)$$

The quantities $b_1 = \Omega$ are listed in Table II for n = 2–8.

For $l = 2$ (treating the case of excluded volume only) the Q_{ij}'s have the following structure

$$Q_{ij} = M\omega_i(\omega_jM - \omega_{ij}) \quad (2.13)$$

which simply says that there are M ways to place the first molecule on the lattice and $(\omega_jM - \omega_{ij})$ ways to place the second, the term ω_{ij} giving the number of configurations that are excluded. Figure 5 illustrates this construction, showing an allowed and a forbidden (due to excluded volume) configuration for a given set of conformations. One then has

$$b_2 = -(1/2)\sum_{i=1}^{\sigma}\omega_i\sum_{j=1}^{\sigma}\omega_{ij} \quad (2.14)$$

For the case of excluded volume only, the b_2 are given for n = 2–8 in Table II. The b_3 for n = 2–4 are also given in Table II, as are Monte Carlo estimates of b_3 for n = 5–7.

3. Interpretation of the b_l

The b_l's measure how much space is occupied by the molecules on the lattice and hence is excluded from occupancy by other molecules as illustrated schematically in Figure 6. Some configurations can interpenetrate, as shown in Figure 6a, but in general there is an area surrounding each molecule, indicated schematically in Figure 6b, that is forbidden from occupancy by other molecules. If $\langle m \rangle$ is the average number of lattice sites occupied by a molecule, we can define higher moments, $\langle m^k \rangle$, in terms of the b_l. Our definition is inspired by the qualitative forms of the Z's for various numbers of polymers in the system:

$$Z_1 \approx M\langle\omega\rangle$$

$$Z_2 \approx \frac{1}{2!}\langle\omega\rangle^2 M(M - \langle m\rangle)$$

$$Z_3 \approx \frac{1}{6!}\langle\omega\rangle^3 M(M - \langle m\rangle)(M - 2\langle m\rangle) \qquad (3.1)$$

The above relations suggest the definition (with $b_1 = \Omega$)

$$b_l = (-1)^{l+1}\left(\frac{1}{l}\right)\Omega^l\langle m^{l-1}\rangle \qquad (3.2)$$

giving

$$\langle m\rangle = -\frac{2b_2}{b_1^{\,2}} \qquad \langle m^2\rangle = \frac{3b_3}{b_1^{\,3}} \qquad (3.3)$$

The above quantities are tabulated in Table III.

To explore the form of $\langle m\rangle$ we assume an asymptotic relation of the form

$$\langle m\rangle \sim an^{\varphi} \qquad (3.4)$$

Using two values of n one has the estimate

$$\varphi \sim \ln\,[m(n_2)/m(n_1)]/\ln\,[n_2/n_1] \qquad (3.5)$$

The values of φ obtained from the data of Table III (taking $n_2 = n$ and $n_1 = n - 1$) are shown in Table IV. These same estimates of φ are plotted versus $1/n$ in Figure 7. One gets two sets of points (one for odd and one for even values of the chain length), both of which extrapolate to φ = 1.45 ● 0.02.

From the data of Table III one observes that the following approximate relation holds

$$\langle m^2\rangle^{1/2} \approx 1.11\langle m\rangle \qquad (3.6)$$

Since the $\langle m\rangle$ data are fit well by the relation

$$\langle m\rangle \sim (1.58)n^{1.45} \qquad (3.7)$$

the combination of (3.6) and (3.7) gives

$$\langle m^2\rangle \sim (1.95)n^{2.90} \qquad (3.8)$$

If we speculate that the relation of (3.6) can be extended to higher moments

$$\langle m^l\rangle = c_{l+1}(n^{\varphi})^l \qquad (3.9)$$

where the c_l are appropriate constants (like the 1.11 in (3.6)), then one would have

$$b_l = (n^{-\varphi})(-1)^{l+1}\left(\frac{1}{l}\right)c_l(\Omega n^{\varphi})^l \qquad (3.10)$$

Introducing the following scaled activity and density

$$r = n^{\varphi}\rho \qquad s = (\Omega n^{\varphi})z \qquad (3.11)$$

and using the standard relation between the density and the activity

$$\rho = \partial\Gamma/\partial \ln z = \sum_{l=1}^{\infty} l b_l z^l \qquad (3.12)$$

one has the beginning terms of the relation between the activity and the density in a general form for all chain lengths

$$r = s - (1.58)s^2 + (1.95)s^3 + \ldots$$

$$s = r + (1.58)r^2 + (3.04)r^3 + \ldots \qquad (3.13)$$

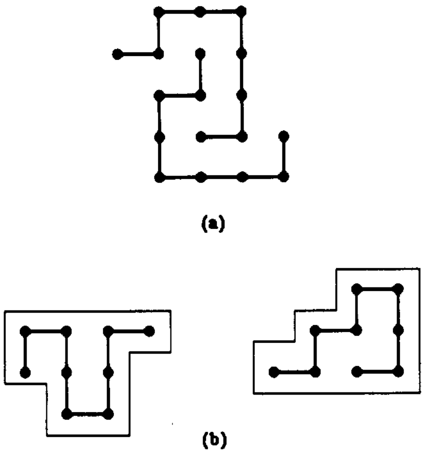


Figure 6. Schematic illustration of the effect of excluded volume. (a) Illustration of two chain conformations that interpenetrate. (b) Schematic illustration of the region around two chains that cannot be occupied by another molecule.

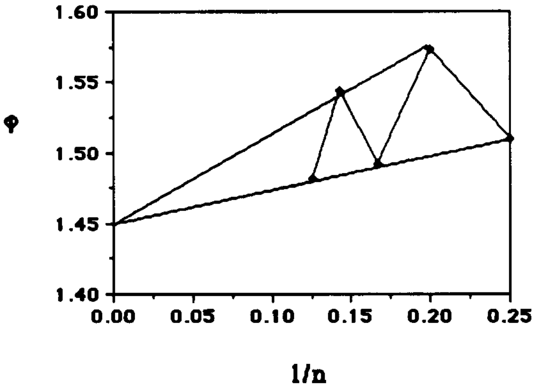


Figure 7. Estimate of the exponent φ in equation 3.4, plotting the data of Table IV. The two sets of points (for odd and even values of the chain length) extrapolate to the same limit.

Table III
The Quantites $\langle m^k\rangle$ Defined in Equation 3.3 as a Function of Chain Length

n	$\langle m\rangle$	$\langle m^2\rangle$	$\langle m^2\rangle$	$\langle m^2\rangle^{1/2}/\langle m\rangle$
3	6.889	57.556	7.587	1.101
4	10.636	138.676	11.776	1.107
5	15.107	278.9	16.70	1.105 ● 0.018
6	19.830	493.2	22.21	1.120 ● 0.012
7	25.162	808.2	28.43	1.130 ● 0.029
8	30.668			

Table IV
Estimates of Exponents Using Equation 3.5 or an Analogue Thereof[a]

n	φ(3.4) ($x = 1$)	φ(3.4) ($x = 0$)	γ_1(4.20) (for D_1)	γ_2(4.20) (for D_2/D_1)
4	1.510	1.207	1.86	7.17
5	1.573	1.232	1.95	1.77
6	1.492	1.255	1.68	2.98
7	1.544	1.263	1.76	1.68
8	1.482			

[a] $n_2 = n$ and $n_1 = n - 1$. The numbers in parentheses are the appropriate equation numbers defining the particular exponents.

4. Configurational Statistics

In order to calculate average configurational properties of the system we must known the probability of a particular conformation. To this end we put labels, ζ_i, in the b_l's to keep track of the various conformations

$$b_1 = \sum_{i=1}^{\sigma} \gamma_i \zeta_i \qquad b_2 = \sum_{i=1}^{\sigma}\sum_{j=1}^{\sigma} \gamma_{ij}\zeta_i\zeta_j$$

$$b_3 = \sum_{i=1}^{\sigma}\sum_{j=1}^{\sigma}\sum_{k=1}^{\sigma} \gamma_{ijk}\zeta_i\zeta_j\zeta_k \qquad (4.1)$$

The analogue of (3.12) then gives the density of species α

$$\rho_\alpha = (\partial\Gamma/\partial\zeta_\alpha)_{\zeta_\alpha=1} \qquad (4.2)$$

Note that we set $\zeta_\alpha = 1$ since we do not want the value of the ζ's to alter the statistics; the ζ's simply work as labels to allow us to count states via the use of (4.2). One then has

$$\rho_\alpha = \rho_\alpha{}^{(1)}z + \rho_\alpha{}^{(2)}z^2 + \rho_\alpha{}^{(3)}z^3 + ... \qquad (4.3)$$

where

$$\rho_\alpha{}^{(1)} = \gamma_\alpha$$

$$\rho_\alpha{}^{(2)} = \gamma_{\alpha\alpha} + \sum_{i=1}^{\sigma} \gamma_{i\alpha}$$

$$\rho_\alpha{}^{(3)} = \gamma_{\alpha\alpha\alpha} + \sum_{i=1}^{\sigma} \gamma_{i\alpha\alpha} + \sum_{i=1}^{\sigma}\sum_{j=1}^{\sigma} \gamma_{ij\alpha} \qquad (4.4)$$

We can introduce normalized probabilities of the various conformations as follows

$$p_\alpha = \rho_\alpha/\rho \qquad \rho = \sum_{i=1}^{\sigma} \rho_i \qquad (4.5)$$

We note that the density has the limiting value

$$\rho_{\max} = 1/n \qquad (4.6)$$

that is, since a chain has n units, the maximum density is $1/n$.

Using (3.12) we can give the net density dependence of the p_α as follows

$$p_\alpha = \frac{\rho_\alpha{}^{(1)}z + \rho_\alpha{}^{(2)}z^2 + \rho_\alpha{}^{(3)}z^3 + ...}{b_1 z + 2b_2 z^2 + 3b_3 z^3 + ...} \qquad (4.7)$$

which can be expanded to give

$$p_\alpha = (\rho_\alpha{}^{(1)}/b_1) + (-2[b_2/b_1{}^2]\rho_\alpha{}^{(1)} + \rho_\alpha{}^{(2)}/b_1)z + (\rho_\alpha{}^{(1)}\{4(b_2/b_1)^2 - 3b_3/b_1\}/b_1 - 2\rho_\alpha{}^{(2)}b_2/b_1{}^2 + \rho_\alpha{}^{(3)}/b_1)z^2 + ... \qquad (4.8)$$

One can invert (3.12) to give z as a function of ρ

$$z = a_1\rho + a_2\rho^2 + a_3\rho^3 + ...$$

$$a_1 = 1/b_1 \qquad a_2 = -2b_2/b_1{}^3 \qquad a_3 = 8b_2{}^2/b_1{}^5 - 3b_3/b_1{}^4 \qquad (4.9)$$

and hence express p_α as a series in the net density

$$p_\alpha = p_\alpha{}^{(0)} + p_\alpha{}^{(1)}\rho + p_\alpha{}^{(2)}\rho^2 + ... \qquad (4.10)$$

where

$$p_\alpha{}^{(0)} = \rho_\alpha{}^{(1)}/b_1$$

$$p_\alpha{}^{(1)} = \rho_\alpha{}^{(2)}/b_1{}^{(2)} - 2(b_2/b_1{}^3)\rho_\alpha{}^{(1)}$$

$$p_\alpha{}^{(2)} = \rho_\alpha{}^{(1)}(8b_2{}^2/b_1{}^5 - 3b_3/b_1{}^4) - 4(b_2/b_1{}^4)\rho_\alpha{}^{(2)} + \rho_\alpha{}^{(3)}/b_1{}^3 \qquad (4.11)$$

Any average property depending on conformation is then given by

$$\langle f\rangle = f^{(0)} + f^{(1)}\rho + f^{(2)}\rho^2 + ... \qquad (4.12)$$

where

$$f^{(j)} = \sum_{\alpha=1}^{\sigma} f_\alpha p_\alpha{}^{(j)} \qquad (4.13)$$

As as example of the use of the above formalism, we calculate the beginning terms in the activity and density series for the moments of the end-to-end distance distribution for our model polymer system. We define the series

$$\langle R^k\rangle = \sum_{l=0}^{\infty} C_l(k)z^l \qquad \langle R^k\rangle = \sum_{l=0}^{\infty} D_l(k)\rho^l \qquad (4.14)$$

The coefficients C_0 and C_1 and Monte Carlo estimates of C_2 are given in Table V for n = 3–7.

The beginnings of the density expansions for the first three moments are

$$\langle R(n=3)\rangle = 1.776(1 + 0.634\rho + ...)$$

$$\langle R(n=4)\rangle = 2.102(1 + 0.147\rho + ...)$$

$$\langle R(n=5)\rangle = 2.577(1 - 0.062\rho + ...)$$

$$\langle R(n=6)\rangle = 2.958(1 - 0.280\rho + ...)$$

$$\langle R(n=7)\rangle = 3.393(1 - 0.387\rho + ...)$$

$$\langle R^2(n=3)\rangle = 2.667(1 - 0.0278\rho + ...)$$

$$\langle R^2(n=4)\rangle = 4.556(1 - 0.0219\rho + ...)$$

$$\langle R^2(n=5)\rangle = 7.040(1 - 0.0325\rho + ...)$$

$$\langle R^2(n=6)\rangle = 9.563(1 - 0.560\rho + ...)$$

$$\langle R^2(n=7)\rangle = 12.574(1 - 0.726\rho + ...)$$

$$\langle R^3(n=3)\rangle = 4.552(1 - 0.0422\rho + ...)$$

$$\langle R^3(n=4)\rangle = 10.676(1 - 0.269\rho + ...)$$

$$\langle R^3(n=5)\rangle = 20.48(1 - 0.433\rho + ...)$$

$$\langle R^3(n=6)\rangle = 32.95(1 - 0.735\rho + ...)$$

$$\langle R^3(n=7)\rangle = 49.69(1 - 0.978\rho + ...) \qquad (4.15)$$

We have determined three terms in the density expansion of $\langle R^2\rangle$ for n = 3 and n = 4

$$\langle R^2(n=3)\rangle = 2.667 - 0.0741\rho + 0.0535\rho^2 + ...$$

$$\langle R^2(n=4)\rangle = 4.556 - 0.999\rho - 2.669\rho^2 + ... \qquad (4.16)$$

Table V
Activity Series for Moments of the End-to-End Distance Distribution Definined in (4.14)[a]

n		C_0	C_1	C_2
3	$\langle R\rangle$	10.7	−400	$(200 \pm 6) \times 10^2$
	$\langle R^2\rangle$	16	−664	$(332 \pm 18) \times 10^2$
	$\langle R^3\rangle$	27.3	−1 136	$(569 \pm 44) \times 10^2$
4	$\langle R\rangle$	37.8	−7 142	$(168 \pm 8) \times 10^4$
	$\langle R^2\rangle$	82.0	−16 022	$(377 \pm 27) \times 10^4$
	$\langle R^3\rangle$	192.2	−37 720	$(891 \pm 83) \times 10^4$
5	$\langle R\rangle$	129	−97 732	$(90.3 \pm 4.4) \times 10^6$
	$\langle R^2\rangle$	352	−271 600	$(253 \pm 15) \times 10^6$
	$\langle R^3\rangle$	1024	−795 774	$(747 \pm 48) \times 10^6$
6	$\langle R\rangle$	420	−1 199 543	$(433 \pm 25) \times 10^7$
	$\langle R^2\rangle$	1358	−3 931 878	$(145 \pm 13) \times 10^8$
	$\langle R^3\rangle$	4679	−13 662 379	$(514 \pm 62) \times 10^8$
7	$\langle R\rangle$	1323	−13 185 595	$(170 \pm 17) \times 10^9$
	$\langle R^2\rangle$	4904	−49 511 000	$(653 \pm 90) \times 10^9$
	$\langle R^3\rangle$	19380	−197 570 573	$(265 \pm 46) \times 10^{10}$

[a] The coefficients C_2 were estimated by Monte Carlo sampling.

Table VI
Limiting Forms of $b_2(x)$ of Equation 5.4 for $x = 0$ and $x \to \infty$

n	$b_1(x{=}0)$	$b_2(x{=}0)$	$\langle m\rangle$	$b_2(x{\to}\infty)$	$(S_n/k)/n$
2	2	−23	11.5	$2x^2$	0.347
3	6	−316	17.56	$6x^3$	0.597
4	14	−2 435	24.85	$78x^4$	1.089
5	34	−18 908	32.71	$274x^5$	1.123
6	82	−138 243	41.12	$224x^6$	0.902
7	198	−979 260	49.96	$1080x^8$	0.998

Table VII
The Values x_0 Giving $b_2(n,x_0) = 0$ for the b_2 of (5.4)

n	x_0	$\ln x_0$	n	x_0	$\ln x_0$
2	1.373	0.317	5	1.515	0.415
3	1.439	0.364	6	1.535	0.429
4	1.482	0.393	7	1.557	0.443

We noted in (4.6) that the maximum density was $1/n$. If we define a density relative to close packing

$$\rho^* = \rho/\rho_{\max} = n\rho \qquad (4.17)$$

(which varies from zero to one), then the series in (4.16) become

$$\langle R^2(n{=}3)\rangle = 2.667[1 - 0.0834\rho^* + 0.1805\rho^{*2} + ...]$$

$$\langle R^2(n{=}4)\rangle = 4.556[1 - 0.8771\rho^* - 9.373\rho^{*2} + ...] \qquad (4.18)$$

From (4.14) one can write the density expansions for $\langle R^2\rangle$ as follows

$$\langle R^2\rangle = D_1[1 + (D_2/D_1)\rho + ...] \qquad (4.19)$$

and then explore asymptotic relations of the form

$$D_1 \sim (n)^{\gamma_1} \qquad -D_2/D_1 \sim (n)^{\gamma_2} \qquad (4.20)$$

Using analogues of (3.4) and (3.5) one can estimate the exponents γ_1 and γ_2; the appropriate data are given in Table IV. It is known[11] that the value of $\gamma_1 = {}^3/_2$ for two-dimensional systems; the extrapolation of the data in Table IV versus $(1/n)$ is consistent with this value. Thus using a few beginning terms in the appropriate series, one can get a reasonable estimate of an exponent. Clearly the values for γ_2 have not settled down yet, although they seem to be heading toward a value not very different from that for γ_1.

5. Inter- and Intrapolymer Interactions

Up to this point in our discussion the only interaction between the polymer molecules that we have been treating is that of excluded volume; that is, a configuration of molecules is either allowed (conformations do not overlap) or forbidden (conformations do overlap), as illustrated in Figure 5. We now include energies of interaction between polymer units, both inter- and intramolecular. The kind of interactions that we are considering are shown in Figure 8a where x and y are respectively the intramolecular and intermolecular Boltzmann factors. The factors x and y have the form

$$\text{(intramolecular)} \qquad x = \exp(-\epsilon_x/kT)$$

$$\text{(intermolecular)} \qquad y = \exp(-\epsilon_y/kT) \qquad (5.1)$$

where ϵ_x and ϵ_y are the appropriate interaction energies; if the ϵ's are negative the interactions are attractive, while in the limit of $\epsilon = +\infty$ ($x = y = 0$) the interactions are hard-core repulsions (reflecting excluded volume, i.e., the conformation with the interaction is forbidden).

Figure 8b shows the conformations with the maximum number of intramolecular interactions (x factors) for n = 2–7 for a single molecule, while Figure 8c shows the two-molecule clusters with the maximum number of intermolecular interactions (y factors) for n = 2–6. The quantities $b_1(x)$ and $b_2(x,y)$ are then polynomials in powers of x and y; the maximum power of x and y attainable for given n is determined by the conformations shown in Figure 8b,c. The $b_1(x)$'s for n = 2–7 are given below

$$b_1(n{=}2) = 2$$

$$b_1(n{=}3) = 6$$

$$b_1(n{=}4) = 14 + 4x$$

$$b_1(n{=}5) = 34 + 16x$$

$$b_1(n{=}6) = 82 + 44x + 16x^2$$

$$b_1(n{=}7) = 198 + 128x + 64x^2 \qquad (5.2)$$

while the $b_2(x,y)$'s for n=2–6 are

$$b_2(n{=}2) = -23 + 14y + 2y^2$$

$$b_2(n{=}3) = -316 + 138y + 48y^2 + 6y^3$$

$$b_2(n{=}4) = (-2435 + 906y + 320y^2 + 104y^3 + 14y^4) + x(-1280 + 480y + 208y^2 + 32y^3) + x^2(-168 + 64y + 32y^2)$$

$$b_2(n{=}5) = (-18908 + 6182y + 2386y^2 + 806y^3 + 232y^4 + 34y^5) + x(-16256 + 5152y + 2448y^2 + 592y^3 + 144y^4) + x^2(-3488 + 1056y + 640y^2 + 96y^3)$$

$$b_2(n{=}6) = (-138243 + 40130y + 16926y^2 + 6136y^3) + x(-136844 + 39264y + 18204y^2 + 5736y^3 + 1688y^4 + 376y^5 + 12y^6) + x^2(-81276 + 23348y + 11782y^2 + 3424y^3 + 854y^4 + 80y^5) + x^3(-23488 + 6720y + 3776y^2 + 1024y^3) + x^4(-4032 + 1024y + 896y^2 + 128y^3) \qquad (5.3)$$

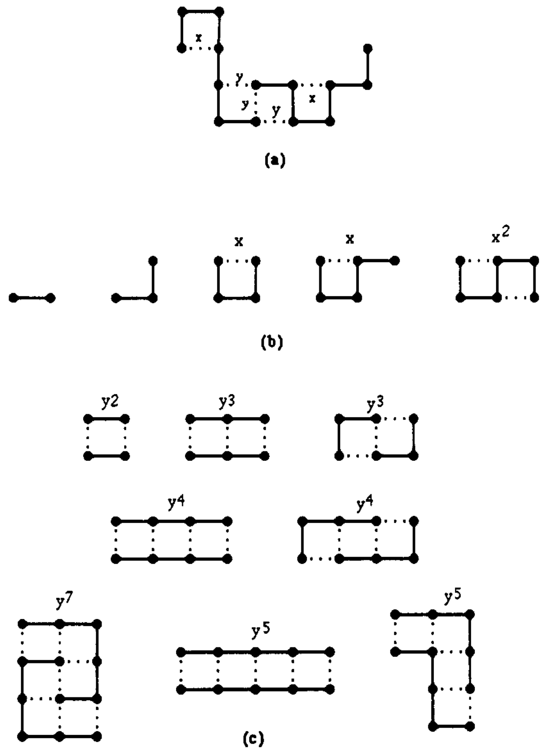


Figure 8. Illustration of intra- and intermolecular polymer interactions. (a) Illustration of the assignment of intrapolymer interactions (x factors) and interpolymer interactions (y factors). (b) Chain conformations giving the maximum number of intrapolymer interactions. (c) Two-chain clusters giving the maximum number of interpolymer interactions.

For the special case of $x = y$ (intra- and intermolecular interactions the same) the relations of (5.3) give (plus the case for $n = 7$ determined separately)

$$b_2(n{=}2) = -23 + 14x + 2x^2$$

$$b_2(n{=}3) = -316 + 138x + 48x^2 + 6x^2$$

$$b_2(n{=}4) = -2435 - 374x + 632x^2 + 376x^3 + 78x^4$$

$$b_2(n{=}5) = -18908 - 10074x + 4050x^2 + 4310x^3 + 1464x^4 + 274x^5$$

$$b_2(n{=}6) = -138243 - 96714x - 25086x^2 + 24200x^3 + 21948x^4 + 10516x^5 + 3232x^6 + 224x^7$$

$$b_2(n{=}7) = -979260 - 922614x - 486116x^2 + 98844x^3 + 189962x^4 + 129614x^5 + 42644x^6 + 12294x^7 + 1080x^8 \tag{5.4}$$

It is interesting to look at two limiting forms of $b_2(x)$, namely, the limit in which the interaction is infinitely repulsive ($x \to 0$) and the limit of infinitely attractive ($x \to \infty$) interactions. The $x = 0$ case simply extends the range of the excluded volume effect, while the $x = \infty$ case makes the compact clusters, as shown in Figure 8c, the most important configurations. The limiting cases are shown in Table VI. In the limit $x \to \infty$, where $b_2(x)$ is dominated by the influence of the most compact clusters, one can write

$$b_2(n,x) = \exp(S_n/k)x^{\eta} \tag{5.5}$$

where η is the maximum number of bonds that can be formed between two polymer molecules of length n (as shown in Figure 8c) and S_n is the entropy of such a cluster. The quantity $(S_n/k)/n$ is shown in Table VI. While this term should approach a constant value, reflecting the bulk entropy per chain unit, if the limiting value were known accurately one could then dissect S_n/k further to explore surface and more subtle combinatorial effects.[12]

The limit $x \to 0$ reduces the model again to excluded volume only, the range of exclusion being greater in this case than that considered before (e.g., all of the interactions shown in Figure 8 represent forbidden configurations). One can use relations 3.3, 3.4, and 3.5 to estimate the exponent φ for this case. The numbers so obtained are shown in Table IV; one expects the exponent to be the same as for the previous case ($\varphi \approx 1.45$) and these numbers do seem to be moving toward that value.

It is interesting to note that if the chains had only the rigid linear conformation, one would have (for $x = 1$)

$$Q_2 = \frac{1}{2!}(2M)[2M - (n^2 + 2n - 1)] \tag{5.6}$$

and one would have (the part of Q_2 linear in M)

$$b_2(n) = -(n^2 + 2n - 1) \tag{5.7}$$

i.e.

$$\langle m \rangle \sim n^2 \tag{5.8}$$

Examining the numbers in Table VI, one sees that in the excluded volume limit ($x \to 0$) the b_2's are negative while in the ($x \to \infty$) limit they are positive. Thus there will be some value of x where one has $b_2(n,x_0) = 0$. This is the analogue of the Boyle temperature for a simple gas. By use of the $b_2(n,x)$ of (5.4) to obtain x_0, the values of x_0 and $\ln x_0$ so obtained are given in Table VII. The values of $\ln x_0$ extrapolate approximately linearly with $1/n$ to give a limiting value (as $n \to \infty$) of approximately $\ln x_0 = 0.50$ or $x_0(n{=}\infty) = 1.65$. Yato and Okamoto[7] have explored the vanishing of the second virial coefficient (Θ-point condition) for more complicated interactions that allow b_2 to vanish at the same temperature for all chain lengths.

Finally, we turn to the question of the role of the solvent, which we have been treating as background up until now. If we assume that all lattice sites not occupied by polymers are occupied by solvent, then one obtains the scheme shown in Figure 9a where the factors u and v are indicated

u = solvent–solvent Boltzmann factor

v = polymer–solvent Boltzmann factor (5.9)

We also introduce separate activities for the solvent and the polymer

z_s = solvent activity z_p = polymer activity (5.10)

To construct the grand partition function for the solvent–polymer mixture we first note that the grand partition function for the case of solvent only (no empty sites) is (M = the total number of lattice sites)

$$\Xi = (z_s u^2)^M \tag{5.11}$$

This simply says that each lattice site is occupied by a solvent molecule with activity z_s and has a net of two bonds (giving two u factors) per particle with its four nearest neighbors (there are four nearest neighbor bonds, but each is shared by two particles, hence there is a net of two bonds per particle).

We next begin to introduce polymer molecules, as illustrated in Figure 9b, where, for the conformations

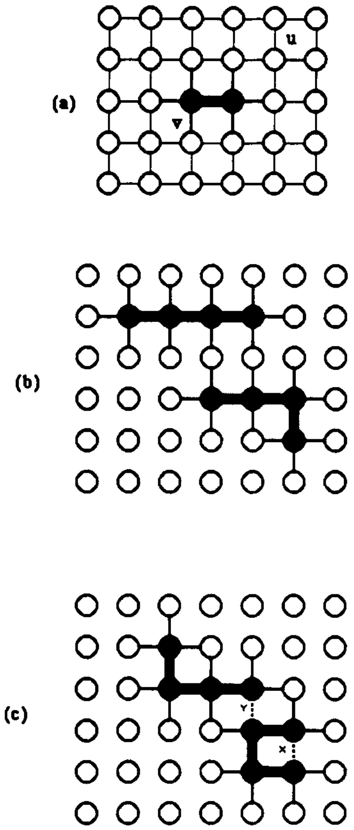


Figure 9. (a) Illustration of solvent–solvent interactions (u factors) and polymer–solvent interactions (v factors). (b) Illustration of the number of polymer–solvent interactions for two polymer molecules with no polymer–polymer interactions. (c) Illustration of the perturbation on the number of polymer–solvent interactions when polymer–polymer interactions are present.

shown, there are no intra- or intermolecular interactions. One notes that under this restriction the number of u factors lost per polymer molecule introduced is

$$(1/u)^{3n+1} \tag{5.12}$$

while the number of polymer–solvent interactions gained is

$$(v)^{2n+2} \tag{5.13}$$

Likewise for every polymer molecule introduced one gains a factor z_p and looses n factors z_s giving a net factor of

$$(z_p/z_s^{\,n}) \tag{5.14}$$

Thus every time one introduces a polymer molecule with no intra- or intermolecular interactions one makes the following perturbation of the grand partition function of (5.11)

$$z = \left(\frac{v^{2n+2}}{u^{3n+1}}\right)\frac{z_p}{z_s^{\,n}} \tag{5.15}$$

which is the activity we use previously, but here it is given a new interpretation.

When there are intra- and intermolecular interactions present between polymer molecules, one observes, e.g., as in Figure 9c, that every intra- and intermolecular interaction has the net effect, in addition to introducing the appropriate x or y factor, of giving back a u factor and deleting two v factors. Thus we can define new interactions parameters that reflect this

$$X = x(u/v^2) \qquad Y = y(u/v^2) \tag{5.16}$$

Our general grand partition function incorporating solvent–solvent (u), solvent–polymer (v), and polymer–polymer (x and y) interactions is now

$$\Xi' = \Xi/(z_s u^2)^M$$

$$\Xi' = 1 + Z_1(X,Y)z + Z_2(X,Y)z^2 + \ldots \tag{5.17}$$

which has exactly the same form as before except that X and Y are now the relative interaction parameters as given in (5.16) (reflecting a balance of polymer–polymer, polymer–solvent, and solvent–solvent interactions) and the activity z, through (5.15), has a more complex interpretation. However, all of the previous relations hold; the parameters simply have a more complicated (and physically realistic) interpretation. The fact that one needs only two interaction parameters if each lattice site is occupied by either solvent or polymer has been pointed out by Madden.[13]

We note that we have not allowed any unoccupied sites in the lattice (holes). We could do this, but at the cost of considerable complexity, since then the solvent would be the lattice gas version of the 2-D Ising model. By assuming no holes we are really taking the limits $z_p \to \infty$ and $z_s \to \infty$ with the ratio $z_p/z_s^{\,n}$ finite.

6. Discussion

In this paper we have shown that exact series expansions for lattice polymers can be obtained in a straightforward manner by simply counting (on the computer) the number of arrangements on the lattice of a given number of polymer molecules. This can be done with or without polymer–polymer attractions; for the case without attractions the only cooperative effect is excluded volume. From the limited data obtained here we find that the chain-length dependence is smoothly varying, indicating that the characteristic exponents can be determined from a moderate number of terms in the appropriate series.

The most interesting feature concerning the virial coefficients of polymers is, of course, the convoluted nature of the chains and their ability to interpenetrate and entangle with one another. The exact enumeration of the virial coefficients gives a quantitative measure of this effect.

Table VIII
Virial Coefficients Calculated from Equations 6.2 and the Data of Table II

n	B_2	B_3	$B_3/(nB_2^2)$
2	1.75	2.58	0.421
3	3.44	9.09	0.256
4	5.32	20.67	0.183
5	7.55	42.31	0.148
6	9.91	64.43	0.109
7	12.58	94.33	0.085
8	15.33		

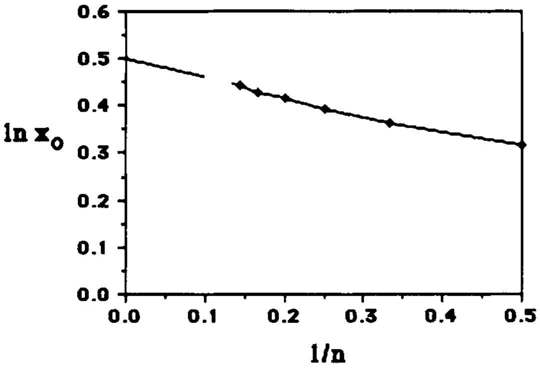


Figure 10. Plot of $\ln x_0$ versus $1/n$ using the data of Table VIII.

Finally we note that although we have discussed several kinds of series expansions here, we have not yet given the proper virial coefficients. To do this we take the activity series for the grand potential (related to the osmotic pressure of the system) given in (2.6) and use (4.9) to convert this to a density series. One then has the standard virial series

$$\Gamma = B_1\rho + B_2\rho^2 + B_3\rho^3 + \dots \qquad (6.1)$$

where

$$B_1 = 1 \qquad B_2 = -b_2/b_1^2 \qquad B_3 = 4b_2^2/b_1^4 - 2b_3/b_1^3 \qquad (6.2)$$

The B_i's, constructed from the data of Table II, are given in Table VIII for the case of excluded volume only. One notes that the quantity B_1 always equals one while b_1 does not (see (2.12)). For a polymer in a good solvent the ratio $B_3(nB_2^2)$ should be universal.[14] This quantity is given in Table VIII, where one sees that this ratio, for the chain lengths used, has not reached a limiting value.

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