Second Osmotic Virial Coefficient for Linear Excluded Volume Polymers in the Domb-Joyce Model†

A. J. Barrett

Department of Mathematics and Computer Science, Royal Military College of Canada, Kingston, Ontario K7L 2W3, Canada. *Received April 19, 1984*

ABSTRACT: Monte Carlo techniques have been used to estimate the second osmotic virial coefficient A_2 for a polydisperse system of linear polymers with excluded volume. The results have been combined with rigorous perturbation coefficients to obtain an approximate two-parameter expression for A_2. Previously obtained expressions for the radius of gyration and the intrinsic viscosity are then combined with the approximation to obtain new expressions for two universal ratios which may be compared with experiment and other theoretical predictions.

1. Introduction

For years, the two-parameter model has served as a theoretical description of excluded volume polymers. Even though exact only in the limit of long chains and small excluded volume, it has been applied with considerable success to a wide range of chain lengths and excluded volume regimes.[1] Some of the corrections to the two-parameter approximation have been discussed in some detail by Barrett and Domb;[2] another perspective has recently been published by Oono and Freed.[3] It is now clear that the two-parameter theory is not exact, except as stated above, but is rather a good approximation for many situations.

One of the most important features of two-parameter theory is the principle of *universality*. It states in essence that, within a factor of scale, certain configurational properties depend not on the details of particular polymer structure but only on chain length and the strength of the excluded volume interaction (which accounts for solvent condition as well). The Domb-Joyce model[4] provides a description of linear polymers which successfully exploits this aspect. A polymer is represented by an interacting random walk, on or off lattice, where the interaction can be continuously adjusted from zero (for random walks) to full strength (for self-avoiding walks). It is thus possible to model chains with varying degrees of excluded volume. If a universal description is valid, then the results obtained should be independent of detailed lattice structure (or indeed of the presence or not of lattice structure). This is found to be the case, at least to a good approximation for sufficiently long polymers. For small excluded volume, a generalization of the Fixman expansion is possible which clearly displays the desired universality. For large excluded volume, it is possible to interpret available numerical results for self-avoiding walks within the framework of universality. Between these two limiting situations, it is necessary to interpolate to obtain a description valid for all solvent conditions.[5]

This philosophy has been applied with some success by Domb and Barrett to propose approximate closed expressions for the mean dimensions of linear chains,[2] as well as the radius of gyration, the probability of ring closure,[6] and the intrinsic viscosity in the Kirkwood-Riseman approximation.[7] Recent experiments show very good agreement with the formula for the radius of gyration;[8,9] the other formulas also seem to agree reasonably well.

We propose in this article to complete the series of formulas based on the Domb-Joyce model by devising a similar expression for the second osmotic virial coefficient A_2. This is a quantity of interest in its own right; however, it may be combined with the radius of gyration to define the penetration factor Ψ, which is also of importance. Another universal ratio may be obtained by combining A_2 with the intrinsic viscosity $[\eta]$. Much of the value of these ratios lies in the fact that they are more easily determined experimentally than the quantities which form them.

The theoretical study of the second virial coefficient of the osmotic pressure of a polymer solution goes back almost 40 years. Early work by Flory,[10] Zimm,[11] and other workers established A_2 as a decreasing function of the polymer molecular weight, but it is only very recently that quantitative agreement with experiment has been obtained for a broad range of solvent conditions. The situation is still not entirely satisfactory. The only rigorous results yet available are the coefficients of the perturbation series for A_2 in powers of the two-parameter excluded volume variable z. Of these, only two have been evaluated to date, and the expression for the second has been corrected and recalculated a number of times since it was first proposed by Albrecht[12] in 1957. The latest version, the fifth, has just been published by Tanaka and Šolc.[13]

The extremely limited range of validity of the perturbation expansion stimulated the development of a number of approximate closed-form expressions, notably the Flory-Krigbaum-Orofino[14,15] function, its modification as proposed by Stockmayer,[16] and the Kurata-Yamakawa[17,18] function, valid for moderately concentrated solutions. A review of this work may be found in Yamakawa's book.[1]

More recently, Tanaka and Šolc[13] have proposed an approximate formula based on a simple Padé analysis of the perturbation series. Their result is noteworthy since it attempts to account for the effects of polydispersity. The Tanaka-Šolc expression is a remarkably simple one which is guaranteed to be correct for very long chains near the Θ temperature. While the arguments are less convincing for shorter chains with "fully developed" excluded volume, the Padé approach has had considerable success in describing, for example, the mean dimension and the radius of gyration.[19]

Another method of studying the behavior of excluded volume chains is suggested by the analogy which may be drawn between an excluded volume polymer and a self-avoiding walk on a lattice.[20] The first such study of A_2, a Monte Carlo experiment by Bellemans and Janssens,[21] was followed by a more extensive one, based on the exact enumeration of short chains, by McKenzie and Domb.[22] This latter work also attempted to deal with the problems posed by polydispersity. The main results of these "enumerative" studies can be summarized in the form of simple power laws which describe the asymptotic behavior of A_2.

Most recent research has applied the renormalization group and modern scaling theory to the large excluded volume regime.[23] This approach has done much to increase

† This work has been supported, in part, by CRAD, Grant 3610-656.

0024-9297/85/2218-0196$01.50/0

our understanding; however, it has yet to provide a complete detailed mathematical description of polymers in solution. Recent work by Oono and Freed,[3] Oono and Kohmoto,[24] and Oono[40] appears to be in good agreement with experimental data.

Our aim in this paper is (1) to extend the Monte Carlo results of Bellemans and Janssens to polydisperse systems, (2) to apply the results within the Domb–Joyce model to obtain an approximate closed formula, (3) to combine the approximate formula with others previously obtained for the radius of gyration and the intrinsic viscosity to yield approximate formulas for the penetration factor Ψ and the ratio $A_2M/[\eta]$, and (4) to test these approximate expressions against other theoretical predictions and experiment.

The greatest stumbling block to this plan is the question of how to treat polydispersity. It is by now well accepted that for a monodisperse system, the order parameter may be taken as the chain length. In the case of a polydisperse system we shall take the order parameter to be the length of the *longer* chain present; we shall further assume that the exponent is unaffected by polydispersity. This suggestion was also made earlier by Witten and Schafer.[25]

For a polydisperse system of polymers in solution, the second osmotic virial coefficient is defined by

$$A_2 = \sum_{i,j} w_i w_j A_{ij}$$

where w_i and w_j are the weight fractions of species i and j, respectively. In two-parameter theory,[1,13]

$$A_{ij} = \frac{N_A \beta}{2m^2} h(\chi,z)$$

where N_A is Avogadro's number, β is the binary cluster integral for a pair of polymer segments, and m is the molecular weight of a segment. We define χ to be the ratio

$$\chi = M/N$$

where M is the molecular weight of species i and N the molecular weight of species j. Without loss of generality we take $M \leq N$ and $\chi \leq 1$. It can be seen that the choice of N as the order parameter is somewhat arbitrary; M would serve equally well since for fixed χ, $N \to \infty$ implies $M \to \infty$. The excluded volume parameter z is that associated with the longer chain, in keeping with our basic assumption, and is defined for continuum chains by

$$z = \left(\frac{3}{2\pi}\right)^{3/2} N^{1/2} \beta \tag{1}$$

The function $h(\chi,z)$ represents the fraction of pairs of chains, one chain of length N and the other of length M steps, which intersect once or more. Expanding formally, we have for small z

$$h(\chi,z) = 1 - C_1 z + C_2 z^2 - \ldots \tag{2}$$

On the basis of the work of McKenzie and Domb[22] and Bellemans and Janssens,[21] and more recently on the basis of scaling arguments (see e.g., de Gennes),[23] the function $h(1,z)$ is widely supposed to have the asymptotic (large z) behavior

$$h(1,z) \sim bz^{-0.4} \tag{3}$$

(We have taken the exponent to be −0.4 for convenience. The actual value is expected to be slightly different, but the differences will not be apparent insofar as this present work is concerned.) The asymptotic behavior for general χ is less obvious. The argument of Tanaka and Šolc is essentially that if the Padé method works for $\chi = 1$, then it should also be valid for $\chi \neq 1$. Our approach is different in that we suppose that the exponent in the above asymptotic result is unchanged if the chains are not of the same length. We do suggest that the amplitude b is a function of χ. The Monte Carlo experiments are designed to test this hypothesis.

The remainder of this paper is organized as follows: Section 2 develops the perturbation series for A_2 in the Domb–Joyce model, section 3 describes the Monte Carlo experiment, the approximate expression is developed in section 4, and section 5 contains some discussion.

2. Perturbation Series

We first recall the formalism for a single chain. A random walk, on a lattice or in the continuum, may be characterized by the generating function

$$P(\mathbf{R},x) = \sum_n p_n(\mathbf{R}) x^n$$

where $p_n(\mathbf{R})$ is the fraction of n-step random walks whose nth step is located at a distance $\mathbf{R}$ from the walk origin. (For continuum walks, $p_n(\mathbf{R})\, d\mathbf{R}$ is the probability that the walk terminates in the volume element $d\mathbf{R}$ at $\mathbf{R}$ after n steps.) We may further define

$$P(x) = \sum_{\mathbf{R}} P(\mathbf{R},x) = (1-x)^{-1}$$

where for continuum walks the sum is to be replaced by an integral. Asymptotically, $P(\mathbf{R},x)$ has the form[26,27]

$$P(\mathbf{R},x) \sim \frac{2\pi^{1/2}}{a} h_0 \frac{e^{-6^{1/2}(1-x)^{1/2}R}}{R}$$

where h_0 contains all details of the walk structure and may be written

$$h_0 = \left(\frac{3}{2\pi}\right)^{3/2} \frac{g}{a^3}$$

Here a is the step length (or a^2 is the mean square length) and g is the volume per lattice site. For Gaussian continuum walks $g = 1$.

An interaction is now introduced into the walk by assigning a statistical weight $1 - w$ to each self-intersection of the chain. If $w = 1$, then all self-intersections have a weight of 0 and the statistics are those of self-avoiding walks. If $w = 0$, the statistics are those of random walks. It is clear that w is analogous to the binary cluster integral and is related to the two-parameter variable z by

$$z = h_0 n^{1/2} w$$

This generalized definition of z contains the earlier definition (1) as a special case. For further details, the reader may consult Domb and Joyce[4] or Barrett and Domb.[2]

In the presence of the interaction, the function $P(x)$ is generalized to

$$P(x,w) = \sum_n p_n(w) x^n$$

which defines $p_n(w)$. Two limits are of interest: $p_n(0) = 1$, and $p_n(1)$ is the fraction of all random walks which are self-avoiding. $P(x,w)$ may be formally expanded in powers of w:

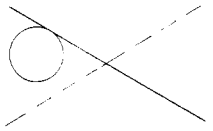
$$P(x,w) = T_0(x) - T_1(x) w + \ldots$$

The coefficient of x^n in T_0 is 1; the coefficient of x^n in $T_1(x)$ gives the fraction of walks which self-intersect at least once, and so on.

In order to generalize the formalism to the intersection of two chains, we let $P(x)$ be the generating function for the first chain and $P(y)$ be the generating function for the second. The generating, or partition, function for the intersecting pair is $\Xi(x,y,w)$, and it too may be formally expanded in powers of w:

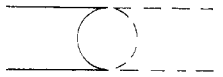
$$\Xi(x,y,w) = U_0(x,y) - U_1(x,y) w + \ldots$$

Table I
Graphs and Generating Functions[a]



(2) $-2\pi^{1/2}h_0(1-x)^{5/2}(1-y)^{-2}$

(1) $\pi^{1/2}h_0(1-x)^{-5/2}(1-y)^{-2}$



(2) $\dfrac{2\pi^{1/2}h_0(1-x)^{-2}(1-y)^{-2}}{(1-x)^{1/2}+(1-y)^{1/2}}$

[a] It is also necessary to take into consideration the "dual" graphs, obtained by interchanging the "x" and "y" chains. The appropriate generating functions are obtained by interchanging x and y in the functions given above. The numbers in parentheses are the graph weights.

The function h defined in (2) is essentially the coefficient of $x^N y^M$ in Ξ.

The coefficient U_0 is simply the generating function for the fraction of all chains which intersect each other, as shown in Figure 1. We may think of this as two "x" chains and two "y" chains rooted to the point of intersection. The generating function for this this configuration is then seen to be

$$P^2(x)P^2(y) = (1-x)^{-2}(1-y)^{-2}$$

Extracting the coefficient of $x^N y^M$, we obtain the obvious result $(N+1)(M+1)$. The computations for U_1 proceed in an exactly similar fashion. The contributing graphs and the corresponding generating functions are listed in Table I. The extraction of the coefficient of $x^N y^M$ proceeds as described by Barrett.[28] The result, which duplicates that found by other authors for the continuum model only, is

$$C_1 = \frac{16}{3}(1+\chi^{1/2}) + \frac{32}{15\chi}[1+\chi^{5/2}-(1+\chi)^{5/2}]$$

Note that here we have made use of the definition of χ and defined z as the excluded volume variable of the longer chain:

$$z = h_0 N^{1/2} w$$

3. Monte Carlo Algorithm

A more appropriate definition of $h(\chi,z)$ for numerical work may be given in terms of N, M, and w instead of χ and z. Let C_N be the number of N-step self-avoiding walks, and let C_{NM} be the number of distinct, intersecting, configurations of an N-step with an M-step self-avoiding walk. For self-avoiding walks, $w = 1$, and we may define h to be the ratio

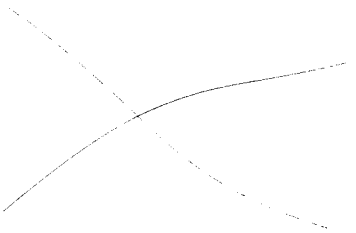


Figure 1. Two intersecting chains: (—) "x" chain; (– – –) "y" chain.

$$h = \frac{C_{NM}}{(N+1)(M+1)C_N C_M}$$

A convenient, unbiased, estimator of h is the reciprocal of the number of intersections of the N-step chain with the M-step chain. It is the average of this quantity that we estimate by Monte Carlo sampling.

For a series of values of χ, samples of pairs of self-avoiding walks were generated by the method of Rosenbluth and Rosenbluth.[30] The first walk of each pair has N steps and the second χN steps, for N up to 100 steps. Both walks were "grown" from the same origin, and the number of interchain contacts was recorded. Next, the walks were translated on the lattice so that the step i of the first walk intersected step j of the second walk, for all possible values of i and j, and again the number of interchain contacts was recorded.

A separate sample of size 10000 pairs was generated for each value of χ, and where possible the results were compared with the exact values computed by McKenzie and Domb.[22] Some results are quoted in Table II.

4. Asymptotic Form of $h(\xi,z)$

The results of McKenzie and Domb and Bellemans and Janssens indicate that for large values of $N = M$

$$h \sim BN^{-\gamma}$$

where γ is widely believed to be approximately 0.2. We generalize this expression for $\chi \neq 1$ as follows:

$$h \sim B(\chi)N^{-0.2}$$

and attempt to interpret the Monte Carlo results to determine the behavior of $B(\chi)$. First of all we convert the above result to an asymptotic expression in z:

$$h(\chi,z) \sim b(\chi)z^{-0.4}; \qquad b = h_0^{0.4}B$$

Figure 2 shows the values of b determined by fitting the Monte Carlo data to the expression

$$hN^{0.2} = B + \frac{C}{N^{1/2}} + \frac{D}{N} + \ldots$$

Table II
Monte Carlo Results[a] for $C_{NM}/[(N+1)(M+1)C_N C_M]$

	χ = 1 (sc)		χ = 0.7 (fcc)		χ = 0.6 (sc)		χ = 0.4 (sc)		χ = 0.1 (bcc)	
5	0.7013	0.7016[22]			0.7474	0.7463[22]	0.7873	0.7913[22]		
10	0.5931	0.5921[21]	0.6869		0.6371		0.6786		0.8629	
20	0.4957	0.4997[21]	0.5822		0.5337		0.5717		0.7794	
30	0.4461	0.4451[21]	0.5274		0.4812		0.5156		0.7184	
40	0.4146		0.4904		0.4417		0.4782		0.6753	
50	0.3915	0.3105	0.4640	0.3715	0.4214	0.3339	0.4513	0.3543	0.6407	0.4768
60	0.3742		0.4429		0.4007		0.4307		0.6131	
80	0.3478	0.2839	0.4098	0.3405	0.3746	0.3056	0.3997	0.3247	0.5716	0.4405
100	0.3248	0.2720	0.3376	0.3266	0.3553	0.2930	0.3769	0.3434	0.5400	0.4239

[a] The numbers in the leftmost columns are the Monte Carlo results. Those in the rightmost columns are the predictions of eq 4, except as otherwise indicated.

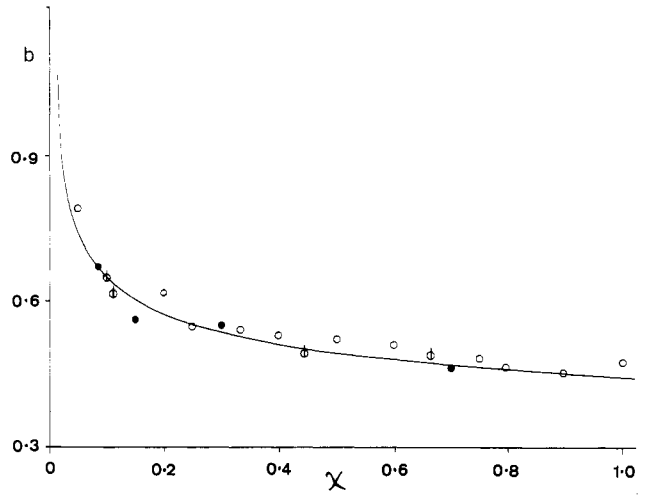


Figure 2. Extrapolated values of $b(\chi)$ vs. χ: (○) sc lattice; (●) bcc lattice; (⊙) fcc lattice. Solid curve: b as given by eq 4.

In other words the amplitudes shown are those *for infinite chains*. Note that results obtained on all three cubic lattices fall, at least to a good approximation, on the same curve.

Another way of analyzing the data is to plot log b vs. log χ. We find by doing this that a rough straight line is obtained, corresponding to

$$b(\chi) \sim \chi^{-0.2}$$

It is clear that the correct asymptotic exponent of for b is obtained, to a good approximation, by an expression of the form

$$h(\chi,z) = [1 + 5C_1z + D\chi z^2]^{-0.2}$$

which leads us to propose the closed-form expression below for $h(\chi,z)$. We have made use of the fact that $C_1 \sim \chi^{1/2}$, and so have taken $D\chi = 20C_1\chi^{1/2}$ as providing an acceptable fit to the Monte Carlo data. We note here that this is the only parameter in our model which may in any way be referred to as "adjustable". Once it has been determined, then insofar as comparison with experiment is concerned, there are no adjustable parameters.

$$h(\chi,z) = [1 + 5C_1z(1 + 4\chi^{1/2}z)]^{-0.2} \quad (4)$$

The graph of this function vs. χ for large z is also shown in Figure 2.

A quantity of some interest is the penetration factor Ψ, defined by

$$\Psi(z) = \frac{1}{4\pi^{3/2}} \frac{A_2M^2}{N_A\langle S^2\rangle^{3/2}}$$

Here, we take $\chi = 1$, so that $A_{ij} = A_2$. It is not hard to show that a more convenient expression of Ψ in terms of universal quantities is

$$\Psi(z) = z\frac{h(1,z)}{\alpha_S{}^3}$$

where $\alpha_S{}^2$ is the expansion factor for the radius of gyration:

$$\alpha_S{}^2 = \langle S^2\rangle/\langle S^2\rangle_0$$

If we substitute into this the approximate expression (4), and one[6] for $\alpha_S{}^3$, then we obtain the function

$$\Psi(z) = z\frac{(1 + 14.3z + 57.3z^2)^{-0.2}}{(1 + 6.4z + 8.4z^2)^{0.3}} \quad (5)$$

This equation is plotted in Figure 3, on the same axes as a number of experimental results.[8,31,33-35] As expected, eq

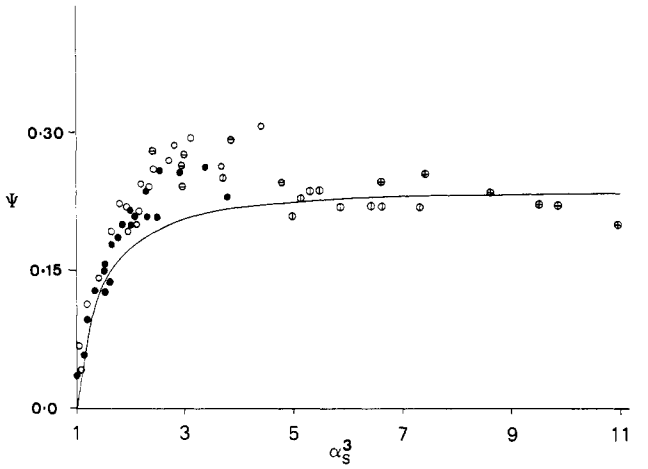


Figure 3. Plot of Ψ vs. $\alpha_S{}^3$. Experimental points: (●) ref 31; (○) ref 33; (⊖) ref 34; (⊙) ref 35; (⊕) ref 8. Solid curve: eq 5.

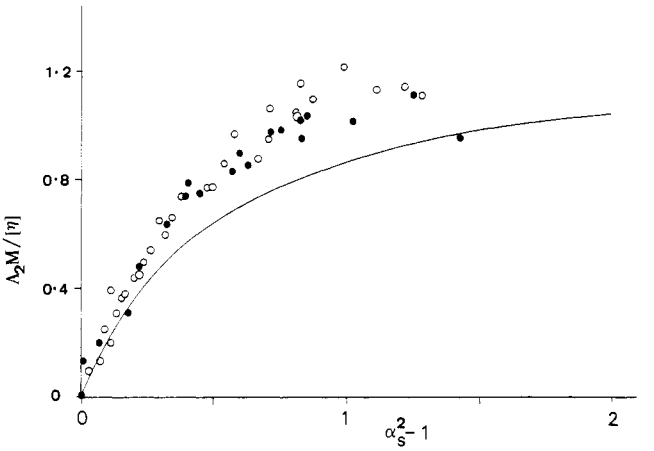


Figure 4. Plot of $A_2M/[\eta]$ vs. $\alpha_S{}^2 - 1$. Experimental points: (●) ref 31, ref 32; (○) ref 36. Solid curve: eq 6.

5 agrees very well for small z, and asymptotically. It is interesting to note that the limiting value of 0.24 agrees favorably with the Oono and Freed[3] estimate of 0.231 and the Oono[40] value of 0.219.

Another universal ratio is obtained by dividing A_2M by the intrinsic viscosity $[\eta]$, where M is the polymer molecular weight.

$$\frac{A_2M}{[\eta]} = \frac{4zh(1,z)}{\alpha_\eta{}^3XF(X)} \approx 3.18z\frac{(1 + 14.3z + 57.3z^2)^{-0.2}}{(1 + 3.8z + 1.9z^2)^{0.3}} \quad (6)$$

where $\alpha_\eta{}^3$ is the expansion factor for the intrinsic viscosity $[\eta]$:

$$\alpha_\eta{}^3 = [\eta]/[\eta]_0$$

and $XF(X)$ is a constant depending on the draining parameter X (see, e.g., Yamakawa,[1] p 269). In the nondraining limit, $XF(X) = 1.259$. The approximate function for $\alpha_\eta{}^3$ is that proposed by Barrett.[7] This equation, together with some experimental results,[31,32,36] is plotted in Figure 4. Again, it provides respectable agreement for very small and large values of z, but both curves seem somewhat low in the region of $z = 2$–4. In the limit of large z, nondraining limit, eq 6 predicts a value of 1.167, which may be compared with Oono's[40] calculation of 1.196. (Oono also cites further experimental work.)

5. Discussion

An approximate expression has been obtained for the second osmotic virial coefficient A_2. This is one of a series of such expressions based on the Domb–Joyce universal

Table III
Comparison with Tanaka and Šolc

A[a]			B[b]			C[c]		
z	TS	B	z	TS	B	z	TS	B
0.0	1.000	1.000	0.0	1.000	1.000	0.0	1.000	1.000
0.1	0.758	0.893	0.1	0.783	0.831	0.1	0.803	0.802
0.5	0.506	0.688	0.5	0.514	0.580	0.5	0.535	0.537
1.0	0.407	0.572	1.0	0.403	0.464	1.0	0.421	0.424
5.0	0.237	0.332	5.0	0.217	0.257	5.0	0.224	0.231
10.0	0.186	0.255	10.0	0.164	0.196	10.0	0.168	0.176
50.0	0.106	0.136	50.0	0.085	0.103	50.0	0.086	0.093

[a] A: $\chi = 0.1$; TS, $h = (1 + 12.04z)^{-0.35}$; B, $h = (1 + 6.7z + 8.5z^2)^{-0.2}$. [b] B: $\chi = 0.5$; TS, $h = (1 + 8.147z)^{-0.41}$; B, $h = (1 + 11.8z + 33.5z^2)^{-0.2}$. [c] C: $\chi = 1.0$; TS, $h = (1 + 6.86z)^{-0.42}$; B, $h = (1 + 14.3z + 57.3z^2)^{-0.2}$.

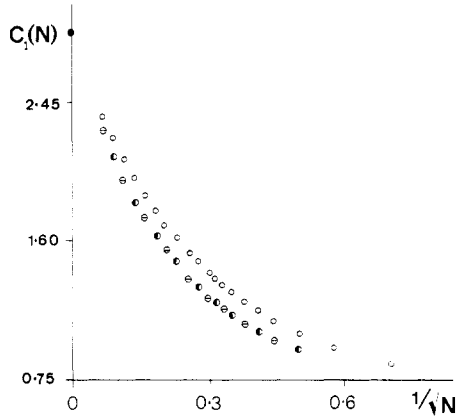


Figure 5. $C_1(N)$ vs. $N^{-1/2}$: (○) sc lattice; (◐) bcc lattice; (⊖) fcc lattice; (●) common two-parameter limit.

model of an excluded volume polymer, which provide a fairly complete description of polymer configurations within two-parameter theory. Moreover, since the expressions are designed to be correct in the limits of large and small excluded volume, they may be used to test other approximate theories. In particular, the approximate theory proposed by Tanaka and Šolc is found to be in close agreement with eq 4 for $\chi = 1$. However for $\chi < 1$, the agreement is less satisfactory, as can be seen in Table III. For large z, (4) also agrees well with the predictions of Freed, Oono, and co-workers. It is interesting to consider why the approximate function falls below the experimental values for both the universal ratios (5) and (6). One is tempted to suspect the function which is common to both, namely A_2. This approximate function may be refined to include the coefficient C_3 as computed by Tanaka and Šolc;[13] however, the improvement is not significant. In the case of (6) one could suspect the expression for α_η^3, since it has been obtained by using the preaveraged Oseen tensor in the Kirkwood–Riseman approximation. It should be noted, however, that the substitution of the approximate results of Tanaka[37] of Weill and des Cloizeaux[38] for α_η^3 into (6) leads to an even greater discrepancy. The curve obtained by Oono and Kohmoto[24] without preaveraging appears to be in closer agreement with the data.

The problem most likely lies within two-parameter theory itself. All the expressions considered here have been obtained for "very long", essentially infinite, chains, and one does expect that there will be discrepancies for chains of finite length. In order to assess the effect of finite length, consider first the perturbation coefficient C_1. It may be computed exactly for finite N as described by Barrett[39] and graphed as shown in Figure 5. Another means of assessing the effect of finite chains is to compare the values actually obtained by Monte Carlo with the predictions of eq 4. This is done in Table II; it is clear that the effect of finite length is far from negligible. Further discussions of the effects of finite lengths may be found in the articles by Barrett[39] and Bruns.[41]

References and Notes

(1) Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971.
(2) Barrett, A. J.; Domb, C., *Proc. R. Soc. London, Ser. A* **1979**, *367*, 143.
(3) Oono, Y.; Freed, K. F. *J. Phys. A* **1982**, *15*, 1931.
(4) Domb, C.; Joyce, G. S. *J. Phys. C.* **1972**, *5*, 956.
(5) Domb, C.; Barrett, A. J. *Polymer* **1976**, *17*, 179.
(6) Barrett, A. J.; Domb, C. *Proc. R. Soc. London, Ser. A* **1981**, *376*, 361.
(7) Barrett, A. J. *Macromolecules* **1984**, *17*, 1566.
(8) Miyake, Y.; Einaga, Y.; Fujita, H. *Macromolecules* **1978**, *11*, 1180.
(9) Miyake, Y.; Fujita, H. *Macromolecules* **1981**, *14*, 742.
(10) Flory, P. J. *J. Chem. Phys.* **1945**, *13*, 453.
(11) Zimm, B. H. *J. Chem. Phys.* **1946**, *14*, 164.
(12) Albrecht, A. C. *J. Chem. Phys.* **1957**, *27*, 1002.
(13) Tanaka, G.; Šolc, K. *Macromolecules* **1982**, *15*, 791.
(14) Flory, P. J.; Krigbaum, W. R. *J. Chem. Phys.* **1950**, *18*, 1086.
(15) Orofino, T. A.; Flory, P. J. *J. Chem. Phys.* **1957**, *27*, 1067.
(16) Stockmayer, W. H. *Makromol. Chem.* **1960**, *35*, 54.
(17) Kurata, M.; Fukatsu, M.; Sotobayashi, H.; Yamakawa, H. *J. Chem. Phys.* **1964**, *41*, 139.
(18) Yamakawa, H. *J. Chem. Phys.* **1968**, *48*, 2103.
(19) Tanaka, G. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 305.
(20) Domb, C. *Adv. Chem. Phys.* **1969**, *15*, 229.
(21) Bellemans, A.; Janssens, M. *Macromolecules* **1974**, *7*, 809.
(22) McKenzie, D. S.; Domb, C. *Proc. Phys. Soc. London* **1967**, *92*, 632.
(23) de Gennes, P.-G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979.
(24) Oono, Y.; Kohmoto, M. *Phys. Rev. Lett.* **1982**, *49*, 1397.
(25) Witten, T. A.; Schafer, L. **1978**, *9*, 1843.
(26) Chandrasekhar, S. *Rev. Mod. Phys.* **1943**, *15*, 1.
(27) Joyce, G. S. In "Phase Transitions and Critical Phenomena"; Domb, C., Green, M. S., Eds.; Academic Press: London, 1971; Vol. 2.
(28) Barrett, A. J. *J. Phys. A* **1983**, *16*, 2321.
(29) Yamakawa, H.; Kurata, M. *J. Chem. Phys.* **1960**, *32*, 1852.
(30) Rosenbluth, M. N.; Rosenbluth, A. W. *J. Chem. Phys.* **1955**, *23*, 356.
(31) Norisuye, T.; Kawahara, K.; Teramoto, A.; Fujita, H. *J. Chem. Phys.* **1968**, *49*, 4330.
(32) Kawahara, K.; Norisuye, T.; Fujita, H. *J. Chem. Phys.* **1968**, *49*, 4339.
(33) Berry, J. C. *J. Chem. Phys.* **1966**, *44*, 4550.
(34) Yamamoto, A.; Fujii, M.; Tanaka, G.; Yamakawa, H. *Polym. J.* **1971**, *2*, 799.
(35) Fukuda, M.; Fukutomi, M.; Kato, Y.; Hashimoto, T. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 871.
(36) Tanaka, G.; Imai, S.; Yamakawa, H. *J. Chem. Phys.* **1970**, *52*, 2639.
(37) Tanaka, G. *Macromolecules* **1981**, *15*, 1028.
(38) Weill, G.; des Cloizeaux, J. *J. Phys. (Paris)* **1979**, *40*, 99.
(39) Barrett, A. J. *J. Phys. A* **1977**, *10*, 1977.
(40) Oono, Y. *J. Chem. Phys.* **1983**, *79*, 4629.
(41) Bruns, W. *J. Chem. Phys.* **1980**, *73*, 1970.