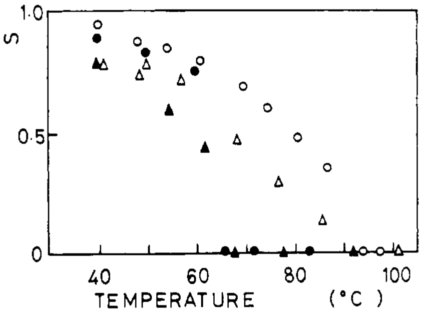

Figure 7. The degree of stacking S as a function of temperature for PBLG + PBDG (1:1) and PBLG + PBDG (3:1): ○, PBLG + PBDG (1:1), heating; ●, PBLG + PBDG (1:1), cooling; △, PBLG + PBDG (3:1), heating; ▲, PBLG + PBDG (3:1), cooling.

responds to the maximum degree of stacking and $S = 0$ to the absence of stacks.

Elliott, *et al.*,[12] have noted that a random siting of D and L molecules in the crystal seems more likely. It is, therefore, assumed that the mixing of L and D is random. Furthermore, we make assumptions that regular stacks of at most 31 benzyl groups out of 43 in the repeat length occur within an L–D pair of neighboring molecules and that only side chains of which benzyl groups do not form stacks contribute to the dielectric dispersion to the same degree as PBLG. Then, the relaxation strength $\Delta\epsilon$ for mixtures is written as

$$\Delta\epsilon = [1 - 2(31/43)Sf_{\mathrm{D}}(1 - f_{\mathrm{D}})]\Delta\epsilon_{\mathrm{PBLG}}$$

where f_{D} is the mole fraction of D molecules and $\Delta\epsilon_{\mathrm{PBLG}}$ is the relaxation strength for PBLG.

Figure 7 shows the degree of stacking S as a function of temperature for PBLG + PBDG (1:1) and PBLG + PBDG (3:1). At low temperatures, for both mixtures S tends to unity. S gradually decreases with increasing temperature until the transition temperature where S vanishes, showing a familiar behavior of the order–disorder transition. This probably indicates that the phase transition is the one from the ordered stacked state to the disordered unstacked one of the benzyl groups. It is necessary to examine theoretically the variation of S with temperature to understand the detailed mechanism of the transition.

Conclusion

All of these dielectric results are consistent with the suggestion that regular stacks of benzyl groups occur in mixtures of L and D molecules and that the phase transition is caused by the breakdown of the stacks. We believe that the mixing of L and D molecules is random. It is probably true that only the side-chains of the benzyl groups which do not form stacks contribute to the dielectric dispersion observed above room temperature. It is likely that the regular stacks of benzyl groups affect motions of side chains of the benzyl groups which do not form stacks, as evidenced by shifts to higher temperatures of the dispersion for mixtures.

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On the Osmotic Second Virial Coefficient of Athermal Polymer Solutions

A. Bellemans* and M. Janssens†

Université Libre de Bruxelles, Brussels, Belgium. *Received June 19, 1974*

ABSTRACT: The osmotic second virial coefficient $A_2(n)$ of athermal polymer solutions is discussed for a simple lattice model, each molecule (n-mer) corresponding to a self-avoiding walk of $n - 1$ steps on a simple cubic lattice. The exact evaluation of $A_2(n)$ by McKenzie and Domb (up to $n = 7$) is extended by a Monte-Carlo technique up to $n = 40$ and it is concluded that for n large $A_2(n) \simeq 0.58n^{-0.28}$.

The aim of this paper is to establish the asymptotic form of the osmotic second virial coefficient A_2 for athermal polymer solutions within the frame of the conventional lattice model. This problem was considered by McKenzie and Domb[1] who evaluated A_2 exactly for relatively short chains and made conjectures about its behavior for longer ones. By a Monte-Carlo technique we were able to extend the data on A_2 much further, so that somewhat more definite conclusions will be reached here. For the sake of clarity and definiteness, we will first rederive the expression for A_2.

Each polymer molecule is a linear chain occupying n sites (n-mer) of a regular lattice and no site may be occu-

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† Chercheur IRSIA.

Table I
Values of A_2 Obtained by the Monte-Carlo Method

n	Series a	Series b	Exact[1]
4	0.39231	0.39294	0.39145
5	0.37003	0.37200	0.36984
6	0.34995	0.35242	0.35082
7	0.33740	0.34032	0.33659
8	0.32254	0.32753	
9	0.31303	0.31560	
10	0.30339	0.30595	
11	0.29605	0.29749	
12	0.28845	0.29053	
13	0.28299	0.28228	
14	0.27488	0.27581	
15	0.27176	0.27087	
16	0.26888	0 26685	
17	0.26278	0.26390	
18	0.25830	0.25990	
19	0.25646	0.25599	
20	0.25050	0.25264	
21		0.24983	
22		0.24639	
23		0.24276	
24		0.23959	
25		0.23633	
26		0.23457	
27		0.23240	
28		0.23026	
29		0.22726	
30		0.22470	
31		0.22255	
32		0.22135	
33		0.22030	
34		0.21812	
35		0.21601	
36		0.21366	
37		0.21126	
38		0.20922	
39		0.20734	
40		0.20529	

pied more than once. Vacant sites are considered as being occupied by solvent molecules (monomers). These n-mers are fully flexible and can assume any configuration provided there are no overlaps. For an assembly of such n-mers on a lattice of V sites (with periodic boundaries) the grand partition function may be expanded as

$$\Xi(z, V) = 1 + zVc_n + \frac{1}{2}z^2(V^2c_n^{\ 2} - Vc_{nn}) + \ldots$$

Here z denotes the n-mer activity and c_n is the number of internal configurations of one n-mer at infinite dilution; *i.e.*, actually the number of self-avoiding walks of $n - 1$ steps originated at a given site divided by a symmetry factor 2. The quantity c_{nn} cares for the (forbidden) overlapping configurations of two n-mers, *i.e.*, the total number of ways (divided by a symmetry factor 2^2) in which two *distinct* self-avoiding walks may intersect each other, one of them starting always from the same site. From standard statistical mechanics it follows that the osmotic pressure Π and average n-mer concentration ρ are given by

$$\Pi/kT = V^{-1}\ln\Xi = zc_n - \frac{1}{2}z^2c_{nn} + \ldots$$

$$\rho = V^{-1}(\mathrm{d}\ln\Xi/\mathrm{d}\ln z) = zc_n - z^2c_{nn} + \ldots$$

Eliminating z between these two equations and replacing ρ by the volume fraction of n-mers $\varphi = n\rho$, we get

$$\Pi/kT = \varphi/n + A_2(n)\varphi^2 + \ldots$$

with

$$A_2(n) = c_{nn}/2n^2c_n^{\ 2} \tag{1}$$

Table II
Estimated Values of β and C from the Data of Table I

Data	Range	β	C
Series a	$4 \leqslant n \leqslant 20$	1.723 ± 0.002	0.575 ± 0.003
	$8 \leqslant n \leqslant 20$	1.728 ± 0.003	0.568 ± 0.005
	$10 \leqslant n \leqslant 20$	1.730 ± 0.005	0.565 ± 0.008
Series b	$4 \leqslant n \leqslant 40$	1.720 ± 0.002	0.582 ± 0.003
	$8 \leqslant n \leqslant 40$	1.720 ± 0.002	0.582 ± 0.003
	$4 \leqslant n \leqslant 20$	1.719 ± 0.004	0.583 ± 0.006
	$8 \leqslant n \leqslant 20$	1.728 ± 0.008	0.578 ± 0.01
	$10 \leqslant n \leqslant 20$	1.730 ± 0.01	0.563 ± 0.01
	$21 \leqslant n \leqslant 40$	1.708 ± 0.01	0.608 ± 0.02

as second virial coefficient. Note here that the *general* expression of A_2 follows from the Ursell-Mayer expansion technique with

$$\Pi/kT = \rho - \frac{1}{2}\langle f_{12}\rangle\rho^2 + \ldots$$

$$\langle f_{12}\rangle = V\frac{\int f_{12}e^{-\beta[u(1)+u(2)]}\mathrm{d}\tau_1\,\mathrm{d}\tau_2}{(\int e^{-\beta u}\mathrm{d}\tau)^2}$$

$$f_{12} = e^{-\beta v(1,2)} - 1,\ \beta = 1/kT$$

where u and v represent the intra- and intermolecular energies, so that[2]

$$A_2(n) = -\langle f_{12}\rangle/2n^2 \tag{2}$$

The correspondence with our simple lattice model is obvious: u and v equal 0 for allowed configurations and $+\infty$ for forbidden ones, so that f_{12} is either 0 or -1, and

$$\begin{aligned} V^{-1}\int e^{-\beta u}\mathrm{d}\tau &\equiv c_n \\ -\langle f_{12}\rangle &\equiv c_{nn}/c_n^{\ 2} \end{aligned} \tag{3}$$

From the exact values of c_n and c_{nn} on several lattices for relatively low n values (*e.g.*, $n \leq 7$ for the simple cubic lattice), McKenzie and Domb arrived at the following asymptotic forms

$$-\langle f_{12}\rangle \sim n^{\beta},\ A_2(n) \simeq Cn^{\beta-2} \tag{4}$$

with β lying around 1.7–1.8 and suggested $\beta = 7/4$ as most probable value.

It seems at present quite impracticable to extend the exact enumeration of c_{nn} further. So in order to pursue the work of McKenzie and Domb we estimated the next terms on the simple cubic lattice by a Monte-Carlo method generating self-avoiding walks by the *inversely restricted sampling technique* described by Mazur and McCrackin.[3] Given a pair of such walks, we move them on the lattice in all possible ways relatively to each other in order to get their second virial coefficient. The average of this quantity over as many pairs of walks as possible gives an estimate of $A_2(n)$. Two series of computations were made. (a) Pairs of walks (1000) were generated *independently* for each value of n between 4 and 20; the corresponding $A_2(n)$ are listed in the second column of Table I. (b) Pairs of walks (1000) of length $n = 40$ were constructed, whereof $A_2(n)$ was estimated for n between 4 and 40 (third column of Table I). The essential difference between these two kinds of data is that in case (a) the $A_2(n)$ are not correlated to each other. The two series of values agree reasonably well within their overlapping region; as a check we also quote the exact data from McKenzie and Domb for $n \leq 7$.

Our main objective is to determine the behavior of $A_2(n)$ for large n. Taking for granted the asymptotic forms (4) we obtain the estimates of Table II for β and C by a leastsquares analysis of the log–log plot of A_2 *vs* n. We conclude that $\beta \simeq 1.727$, $C \simeq 0.569$ for set (a) and $\beta \simeq 1.718$, $C \simeq 0.587$ for set (b) and adopt as final values $\beta = 1.722 \pm 0.005$, $C = 0.58 \pm 0.01$, to be compared to the earlier estimates of McKenzie and Domb: $\beta = 7/4$, $C = 0.52$. Hence the asymptotic forms

$$\begin{aligned} A_2(n) &= (0.58 \pm 0.01)n^{-0.278 \pm 0.005} \\ -\langle f_{12}\rangle &= (1.16 \pm 0.02)n^{1.722 \pm 0.005} \end{aligned} \qquad (5)$$

Discussion and Comparison to Other Works

The following formulas were established by Flory[4] and Huggins[5] respectively from the combinatorial entropy

$$A_2(n) = \frac{1}{2}$$

$$A_2(n) = \frac{1}{2}\left[1 - \frac{1}{3}(1 - n^{-1})^2\right]$$

their well-known failure at large n has been traced to the incorrect counting of configurations where the overlapping n-mers form rings on the lattice.[6]

A naive formulation of A_2 is to replace the actual n-mers by two hard spheres with radii proportional to their mean square end-to-end distances $\langle r^2\rangle$ or even better to their mean square radii of gyration $\langle s^2\rangle$. This gives, apart from a geometrical factor

$$-\langle f_{12}\rangle \sim \langle s^2\rangle^{3/2} \quad \text{and} \quad A_2(n) \sim \langle s^2\rangle^{3/2}/n^2$$

Exact enumerations of self-avoiding walks on the simple cubic lattice[7] suggest that $\langle s^2\rangle \sim n^{1.2}$, hence

$$A_2(n) \sim n^{-0.2} \qquad (6)$$

only in slight disagreement with (5).

An excellent survey of the various theories developed for A_2 had been given by Yamakawa.[8] To relate his general expression (eq 21.5) of the second virial coefficient to our own definition of A_2, we have to multiply it by M^2/N_An^2 where M is the molar weight of the n-mer and N_A is the Avogadro number; we get then, as β equals unity in the present case

$$A_2(n) = \frac{1}{2}h(z) \qquad (7)$$

with

$$z = (3/2\pi)^{3/2}n^{1/2} \qquad (8)$$

The function $h(z)$ has been extensively investigated for low z values, leading to the power expansion

$$h(z) = 1 - a_1z + a_2z^2 \ldots$$

(For the values of the coefficients, see, *e.g.*, ref 8.) However, exact series expansions of $h(z)$ are useless here so that we have to turn to approximate expressions devised for z large. A convenient way is to write (7) in terms of the mean-square radius of gyration so that

$$A_2(n) = 4\pi^{3/2}\frac{\langle s^2\rangle^{3/2}}{n^2}\psi(\bar{z}) \qquad (9)$$

where ψ is now a function of $\bar{z} = z/\alpha^3$, α being the expansion coefficient of the chain compared to a random walk

$$\alpha^2 = \langle s^2\rangle/\langle s^2\rangle_0$$

Exact enumerations of self-avoiding walks strongly suggest that, on the simple cubic lattice[7]

$$\langle s^2\rangle \sim 0.165n^{1.2}$$

so that

$$\alpha^2 \simeq 0.99n^{0.2} \quad \text{and} \quad \bar{z} \simeq 0.34n^{0.2}$$

and according to (9)

$$A_2(n) \simeq 1.49n^{-0.2}\psi(\bar{z})$$

Most theories[9–11] predict that $\psi(\bar{z})$ tends to a constant as $\bar{z}$ goes to infinity, *e.g.*, $\psi(\infty) = 0.547$[10] and 0.349;[11] this gives respectively

$$\begin{aligned} A_2(n) &\simeq 0.82n^{-0.2} \\ &\simeq 0.52n^{-0.2} \end{aligned}$$

in disagreement with (5).

Assuming the correctness of the asymptotic form (5) derived in the previous section for $A_2(n)$, we are tempted to conclude that the actual asymptotic behavior of $h(z)$ and $\psi(\bar{z})$ is such that

$$h(z) \sim z^{-0.56} \quad \text{and} \quad \psi(\bar{z}) \sim \bar{z}^{-0.39}$$

None of the presently existing theories does strictly agree with such predictions.

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