perceptibly either by intramolecular or by intermolecular interactions therefore hold also for short sequences of units.

Acknowledgment. This work was supported by the National Science Foundation, Grant No. DMR-73-07655 A02.

References and Notes

(1) D. Y. Yoon and P. J. Flory, *Polymer*, **16**, 645 (1975).
(2) D. Y. Yoon and P. J. Flory, *Macromolecules*, preceding paper in this issue.
(3) P. R. Sundararajan and P. J. Flory, *J. Am. Chem. Soc.*, **96**, 5025 (1974).
(4) R. G. Kirste, W. A. Kruse, and K. Ibel, *Polymer*, **16**, 120 (1975).
(5) R. G. Kirste, *Makromol. Chem.*, **101**, 91 (1967).
(6) R. G. Kirste and O. Kratky, *Z. Phys. Chem. (Frankfurt am Main)*, **31**, 363 (1962).
(7) G. Allegra, E. Benedetti, and C. Pedone, *Macromolecules*, **3**, 727 (1970).
(8) T. Tanaka, Y. Chatani, and H. Tadokoro, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 515 (1974).
(9) P. J. Flory, P. R. Sundararajan, and L. C. DeBolt, *J. Am. Chem. Soc.*, **96**, 5015 (1974).
(10) P. J. Flory, "Statistical Mechanics of Chain Molecules", Interscience, New York, NY., 1969.
(11) P. J. Flory, *Macromolecules*, **7**, 381 (1974).
(12) Y. Fujiwara and P. J. Flory, *Macromolecules*, **3**, 288 (1970).
(13) R. G. Kirste, W. A. Kruse and J. Schelten, *Makromol. Chem.*, **162**, 299 (1972).
(14) H. Benoit et al., *Nature (London), Phys. Sci.*, **245**, 13 (1973).
(15) D. G. Wignall, J. Schelten, and D. G. H. Ballard, *J. Appl. Crystallogr.*, **7**, 190 (1974); *Eur. Polym. J.*, **9**, 965 (1973); **10**, 861 (1974).
(16) G. Leiser, E. W. Fischer, and K. Ibel, *J. Polym. Sci., Polym. Lett.*, **13**, 39 (1975).
(17) The scattering function $I\mu^2$ employed by Kriste, Kruse, and Ibel[4] (see their Figure 6) is the equivalent of $[\bar{M}_w/(X + 1)]F_x(\mu) \approx M_0F_x(\mu)$, where $\bar{M}_w$ is the weight of a monomer unit. Their data have been divided by M_0 = 100 g/mol in order to establish correspondence with our $F_x(\mu)$.

On the Osmotic Second Virial Coefficient of Polymer Solutions

M. Janssens[1] and A. Bellemans*

Université Libre de Bruxelles, Brussels, Belgium. *Received May 27, 1975*

ABSTRACT: The osmotic second virial coefficient A_2 of nonathermal polymer solutions is discussed for a simple lattice model. Each molecule (n-mer) corresponds to a self-avoiding walk of $n - 1$ steps on the simple cubic lattice and each intrachain or interchain contact contributes a quantity $-\epsilon$ to the energy of the system. The function $A_2(n,f)$ where $f = \exp(\epsilon/kT)$ is obtained exactly by direct counting for $n \leq 6$ and is evaluated approximately by a Monte Carlo technique for higher n values up to $n = 40$. In the asymptotic limit $n \to \infty$, it appears that the theta temperature (defined by $A_2 = 0$) is given by $k\Theta/\epsilon \simeq 3.71$ ($f_\Theta \simeq 1.309$) while the quantity $(dA_2/d \ln f)_\Theta$ seems to remain different from zero. Two different theories of polymer solutions are briefly compared to these results.

I. Introduction

The aim of this paper is to investigate the asymptotic form of the second virial coefficient for nonathermal polymer solutions, within the frame of the conventional lattice model. In this sense this paper is the natural continuation of the preceding one,[2a] which was confined to athermal solutions.

Each polymer molecule (n-mer) is represented by a self-avoiding walk occupying n sites of a regular lattice (walk of $n - 1$ steps) and overlap of two such n-mers is forbidden. Empty sites are considered as occupied by solvent molecules (monomers). These n-mers are fully flexible and can assume any configuration on the lattice (provided that overlaps do not occur). An interaction energy $-\epsilon$ is associated to each pair of n-mer segments occupying neighboring sites (provided these segments are not consecutive ones in the same chain).

Putting ϵ equal to zero brings us back to the athermal case, studied previously by McKenzie and Domb[2b] and subsequently by us,[2a] by means of exact enumeration and Monte Carlo sampling, respectively.

We shall limit our considerations to the simple cubic lattice as exemplifying three-dimensional systems. The less relevant two-dimensional case will be studied in a separate paper devoted to the square lattice.

II. Basic Formulas

The second virial coefficient A_2 is related as follows to the osmotic pressure π

$$\pi/kT = \varphi/n + A_2\varphi^2 + \ldots \tag{1}$$

where φ is the fraction of sites occupied by n-mer segments (the volume fraction of n-mers). In terms of the partition functions Z_1, Z_2 relative to one and two n-mers respectively, one has[3]

$$A_2(n,f) = -V(Z_2 - Z_1^2)/2n^2Z_1^2 \tag{2}$$

with

$$Z_s(n,f) = \sum_\nu g_n(V,s;\nu)f^\nu \tag{3}$$

$$f = e^{\epsilon/kT} \tag{4}$$

Here $g_n(V,s;\nu)$ denotes the total number of ways of placing s *distinguishable* nonoverlapping n-mers on a lattice of V sites, such that ν pairs of n-mers segments are in contact.

For a pair of chains ($s = 2$), called respectively 1 and 2, it is convenient to split the total number of contacts ν into ν_i intrachain and ν_e interchain contacts, i.e.,

$$\begin{aligned} \nu &= \nu_i + \nu_e \\ \nu_i &= \nu_{11} + \nu_{22} \\ \nu_e &= \nu_{12} \end{aligned} \tag{5}$$

We then have on account of eq 3

$$Z_2 - Z_1^2 = \sum_{\nu_{11},\nu_{22}} \left[\sum_{\nu_e} g_n(V,2;\nu_{11},\nu_{22},\nu_e)f^{\nu_e} - g_n(V,1;\nu_{11})g_n(V,1;\nu_{22}) \right] f^{\nu_i}$$

which may be rewritten as

Table I
Exact Values of $c_n(1;\nu)$ for $n \leq 13$

	n												
ν	1	2	3	4	5	6	7	8	9	10	11	12	13
0	1	3	15	63	267	1 107	4 623	19 071	78 987	324 543	1 337 511	5 483 235	22 527 315
1				12	96	516	2 688	13 344	64 440	302 832	1 401 288	6 377 568	28 762 776
2						144	1 056	5 964	33 096	176 772	908 604	4 546 296	22 273 956
3							96	2 244	14 712	84 252	478 416	2 634 960	13 926 504
4								0	2 316	32 736	206 208	1 217 628	7 084 656
5								72	432	3 840	58 464	529 560	3 220 728
6										1 968	12 144	128 940	1 209 132
7											2 304	47 136	325 824
8												0	80 928
9												1 752	9 552

Table II
Exact Values of $c_n^*(2;\nu_i)$ for $n \leq 6$

	n					
ν_i	1	2	3	4	5	6
0	1	33	1 713	50 733	1 360 221	32 506 881
1				18 144	921 600	28 699 368
2				1 584	154 848	13 906 824
3						3 320 064
4						433 152

$$Z_2 - Z_1^2 = \sum_{\nu_i,\nu_e} g_n(V,2;\nu_i,\nu_e) f^{\nu_i}(f^{\nu_e} - 1) - \sum_{\nu_{11},\nu_{22}} \left[g_n(V,1;\nu_{11}) g_n(V,1;\nu_{22}) - \sum_{\nu_e} g_n(V,2;\nu_{11},\nu_{22},\nu_e) \right] f^{\nu_i} \quad (6)$$

The first term of the rhs of eq 6 counts such configurations that n-mers 1 and 2 have one contact at least ($\nu_e > 0$), while the second term actually counts configurations where these two n-mers overlap. Both terms are exactly proportional to V, provided that (i) periodic boundaries are assumed and (ii) the lattice is sufficiently large compared to n. Under such conditions we have

$$g_n(V,s;\nu) = V c_n(s;\nu) \quad (7)$$

where $c_n(s;\nu)$ represents the number of ways of placing s n-mers on the lattice with the first segment of the first n-mer fixed on an arbitrary site, and

$$\sum_{\substack{\nu_{11},\nu_{22} \\ (\nu_{11}+\nu_{22}=\nu_i)}} \left[g_n(V,1;\nu_{11}) g_n(V,1;\nu_{22}) - \sum_{\nu_e} g_n(V,2;\nu_{11},\nu_{22},\nu_e) \right] = V c_n^*(2;\nu_i) \quad (8)$$

where $c_n^*(2;\nu_i)$ denotes the number of such configurations that n-mers 1 and 2 overlap and have ν_i intrachain contacts altogether, the first segment of n-mer 1 being kept fixed. Hence the final form of A_2, completely independent of V,

$$A_2(n,f) = -\frac{1}{2n^2} \left[\sum_{\nu_i,\nu_e} c_n(2;\nu_i,\nu_e) f^{\nu_i}(f^{\nu_e} - 1) - \sum_{\nu_i} c_n^*(2;\nu_i) f^{\nu_i} \right] \Big/ \left[\sum_{\nu} c_n(1;\nu) f^{\nu} \right]^2 \quad (9)$$

(Note that for $f = 1$, i.e., $\epsilon = 0$, the first term of eq 9 vanishes and we recover the athermal case.)

III. The Counting Problem and Numerical Work

Equation 9 for A_2 is especially convenient for numerical work. For $n \leq 6$ the quantities $c_n(2;\nu_i,\nu_e)$ and $c_n^*(2,\nu_i)$ were obtained exactly by counting the configurations. For larger n, up to 40, these two quantities were sampled by a Monte Carlo technique.

Basically the main part of the program works as follows. Given two particular configurations of n-mers 1 and 2 on the lattice, each of the n elements of chain 2 is successively seated on lattice sites which are either occupied by or first neighbors of a segment of chain 1. For the simple cubic lattice this corresponds in principle to $7n^2$ different positions of chain 2 relative to chain 1; actually many of these are identical and are eliminated by a redundancy check. Each such relative position of the two n-mers obviously contributes either to $c_n(2;\nu_i,\nu_e)$ or to $c_n^*(2;\nu_i)$.

Two different subroutines generate the pairs of chains subsequently used by the main program. The first one generates all possible configurations of the two chains for $n \leq 6$. The second one generates chains by the Monte Carlo technique of inversely restricted sampling.[4] The exact evaluation of $c_n(2;\nu_i,\nu_e)$ and $c_n^*(2;\nu_i)$ up to $n = 6$ took approximately 7 h on a CDC 6400 computer. On the other hand the Monte Carlo sampling of these same two quantities was achieved on the following basis: (i) 10^4 pairs of chains for $3 \leq n \leq 20$ and (ii) 10^3 pairs of chains for $21 \leq n \leq 40$ (approximately 35 h on the CDC 6400).

The values of $c_n(1;\nu)$ are relatively easier to obtain; they were evaluated exactly up to $n = 13$ and sampled by a similar Monte Carlo technique for larger n values, by means of two separate programs.

The exact values of $c_n(1;\nu)$, $c_n^*(2;\nu_i)$, and $c_n(2;\nu_i,\nu_e)$ are listed in Tables I, II, and III, respectively. Owing to space limitations the sampled values of these same quantities obtained for larger n by the Monte Carlo technique are not given. We find, as a check of the Monte Carlo method, that the sampled values of $c_6^*(2;\nu_i)$ and $c_6(2;\nu_i,\nu_e)$ differ from the exact values by approximately 1% and that the corresponding deviations of the derived quantities f_Θ and $(dA_2/d \ln f)_\Theta$ (defined in the next section) are even smaller.

IV. Analysis of the Results. Theta-Point Behavior

The general dependence of the second virial coefficient on temperature and chain length is illustrated on Figure 1 where $A_2(n,f)$ is plotted vs. f for $n = 1$, 6, 10, and 40. The asymtotic behavior of $A_2(n,1)$ (athermal case) has been discussed previously[2a] with the conclusion that

$$A_2(n,1) \simeq 0.58 n^{-0.28} \quad (10)$$

(n large). Our main interest here will therefore concentrate on the location of the so-called theta (or Boyle) point, defined by

$$A_2(n,f_\Theta) = 0$$
$$f_\Theta = e^{\epsilon/k\Theta} \quad (11)$$

In this point excluded volume effects are exactly compensated by attractive forces ($\epsilon > 0$).

Table III
Exact Values of $c_n(2;\nu_i,\nu_e)$ for $n \leq 6$ and $\nu_e > 0$

		ν_i				
n	ν_e	0	1	2	3	4
1	1	6				
2	1	126				
	2	12				
3	1	4 218				
	2	1 200				
	3	108				
4	1	97 398	35 328	3 072		
	2	32 376	12 384	1 344		
	3	8 208	2 496	0		
	4	1 308		96		
	5	0				
	6	24				
5	1	2 187 990	1 423 776	229 728		
	2	803 796	573 888	105 504		
	3	241 452	173 664	27 456		
	4	74 400	33 792	4 416		
	5	11 800	4 224	960		
	6	1 104	768			
	7	96				
6	1	45 506 982	38 674 080	18 337 224	4 257 792	533 760
	2	18 206 364	15 936 744	8 162 916	2 084 352	335 616
	3	5 938 656	5 726 256	2 665 008	608 640	37 632
	4	2 116 524	1 735 872	790 668	182 400	43 008
	5	620 856	458 192	150 144	45 312	0
	6	128 724	76 344	32 712	0	2 304
	7	19 560	15 456	0	768	
	8	3 504	0	140		
	9	0	288			
	10	72				

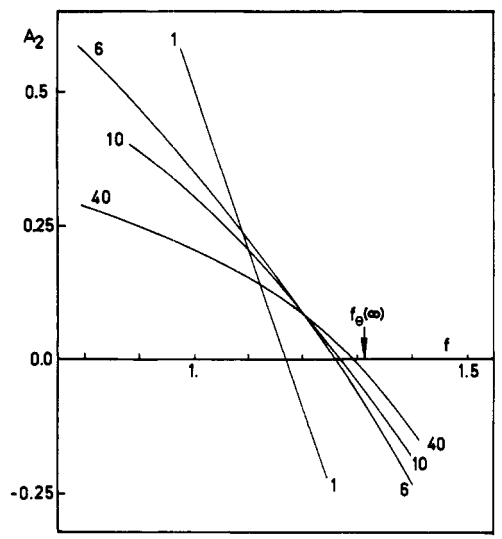

Figure 1. Plot of $A_2(n,f)$ for n = 1, 6, 10, and 40. Note that f = 1 corresponds to infinite temperature; values of f lower than one (i.e., $\epsilon < 0$) and higher than one (i.e., $\epsilon > 0$) correspond respectively to repulsion and attraction between n-mer segments.

Table IV
Values of f_Θ and $A_2{}^*$ as a Function of n (Note That for $n \leq 6$, These Values are Exact)

n	f_Θ	$A_2{}^*$	n	f_Θ	$A_2{}^*$
1	1.166 667	−3.500 000	21	1.282	−1.480
2	1.216 259	−2.621 548	22	1.282	−1.468
3	1.234 487	−2.339 287	23	1.283	−1.453
4	1.244 728	−2.140 419	24	1.284	−1.446
5	1.251 965	−2.027 748	25	1.284	−1.443
6	1.256 804	−1.911 747	26	1.284	−1.434
7	1.261 2	−1.864 4	27	1.285	−1.423
8	1.263 4	−1.807 8	28	1.287	−1.403
9	1.266 5	−1.756 7	29	1.285	−1.412
10	1.268 6	−1.714 6	30	1.287	−1.377
11	1.270 7	−1.682 6	31	1.287	−1.376
12	1.271 8	−1.655 1	32	1.286	−1.383
13	1.273 3	−1.630 1	33	1.287	−1.379
14	1.274 7	−1.601 5	34	1.287	−1.379
15	1.276 5	−1.578 8	35	1.287	−1.356
16	1.277 3	−1.561 8	36	1.288	−1.372
17	1.278 1	−1.541 6	37	1.288	−1.353
18	1.278 9	−1.527 0	38	1.289	−1.344
19	1.279 6	−1.515 2	39	1.289	−1.339
20	1.280 4	−1.498 6	40	1.289	−1.328

The calculated values of f_Θ are listed in Table IV as a function of n. It is immediately apparent that, starting ca. 1.167 for n = 1, these values converge fairly rapidly to ca. 1.30 as $n \to \infty$. It is observed empirically that the plot of f_Θ vs. $1/\sqrt{n}$ becomes almost linear for $n > 3$ as shown in Figure 2. On this basis two independent estimates of the limiting value $f_\Theta(\infty)$ were made. The first one, using the three exact values corresponding to n = 4, 5, and 6, leads to

$$f_\Theta(\infty) = 1.311 \pm 0.005$$

The second one, based on a least-squares analysis of the values deduced from Monte Carlo data ($7 \leq n \leq 40$), gives

$$f_\Theta(\infty) = 1.308 \pm 0.001$$

In view of the extremely good agreement of these values, we shall accept as best estimate

$$f_\Theta(\infty) = 1.309 \pm 0.001 \qquad (12)$$

leading in turn to

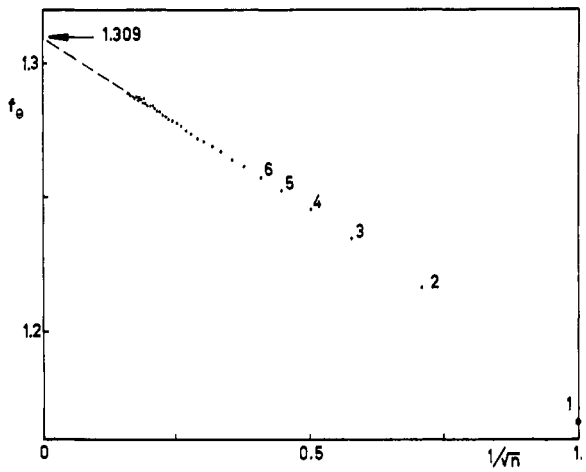

Figure 2. Plot of $f_\theta(n)$ vs. $1/\sqrt{n}$.

$$k\Theta(\infty)/\epsilon = 3.714 \pm 0.011 \tag{13}$$

Note that the asymptotic behavior of $f_\theta(n)$ can also be estimated from the slope of the plot of Figure 2; we find

$$f_\theta(n) \simeq (1.309 \pm 0.001)\left[1 - \frac{0.096 \pm 0.004}{\sqrt{n}}\right] \tag{14}$$

Another point of interest is the behavior of A_2 in the neighborhood of the theta-point, or more precisely the n dependence of the quantity

$$A_2^* = (\mathrm{d}A_2/\mathrm{d}\ln f)_\Theta \equiv [\mathrm{d}A_2/\mathrm{d}(\epsilon/kT)]_\Theta \tag{15}$$

which determines the partial heat of mixing of the system dilute in polymer. From the numerical values listed in Table IV, it appears that $|A_2^*|$ is a decreasing function of n but it is certainly not easy therefrom to guess its asymptotic behavior. Attempts were made to represent the data by means of the plausible expression

$$A_2^*(n) = -B - Cn^{-\eta}$$

involving three adjustable parameters. It turns out that almost equally good fits can be obtained for η ranging between 0.2 and 0.6, viz.,

$$A_2^*(n) \simeq -0.10 - 2.55n^{-0.2} \qquad (\sigma = 0.008)$$
$$A_2^*(n) \simeq -0.58 - 2.26n^{-0.3} \qquad (\sigma = 0.007)$$
$$A_2^*(n) \simeq -0.81 - 2.28n^{-0.4} \qquad (\sigma = 0.006)$$
$$A_2^*(n) \simeq -0.95 - 2.43n^{-0.5} \qquad (\sigma = 0.007)$$
$$A_2^*(n) \simeq -1.04 - 2.70n^{-0.6} \qquad (\sigma = 0.008)$$

(σ = standard deviation for $7 \leq n \leq 40$). It seems likely that A_2^* approaches a nonzero value as $n \to \infty$, which could reasonably be located as

$$0 < |A_2^*(\infty)| < 1 \tag{16}$$

V. Discussion and Conclusions

The results established in section IV are to be considered as *experimental* ones, relative to a well-definite *mathematical model* of polymers. They will now be compared to two widely used theories of polymer solutions.

We first consider the quasi-crystalline lattice model originally developed by Huggins[5] and Flory.[6] Starting from the so called zeroth approximation in the terminology used by Guggenheim,[7] we get after minor manipulations

$$A_2 = \frac{1}{2}\left\{1 - \frac{2}{q}(1 - n^{-1})^2 - \frac{q\epsilon}{kT}\left[1 - \frac{2}{q}(1 - n^{-1})\right]^2\right\} \tag{17}$$

where q denotes the lattice coordination number. In the limit of large n, the theta temperature is given by

$$k\Theta(\infty)/\epsilon = q - 2 \tag{18}$$

i.e., $k\Theta(\infty)/\epsilon = 4$ for the simple cubic lattice ($q = 6$), in fair agreement with eq 13. On the other hand, it follows from eq 17 that A_2^* approaches the finite limit

$$-(q - 2)^2/2q \tag{19}$$

This corresponds to $-4/3$ for the simple cubic lattice, which is not much outside the bounds defined by eq 16.

We now turn to more modern theories, an excellent review of which is given in Yamakawa's book.[8] To relate his general expression (21.5) of the second virial coefficient to our own definition of A_2, we have to multiply it by $M^2/N_A n^2$ where M is the molar weight of the n-mer and N_A is Avogadro's number. We then get

$$A_2 = \tfrac{1}{2}\beta h(z) \tag{20}$$

with

$$z = (\tfrac{3}{2}\pi)^{3/2}\beta n^{1/2} \tag{21}$$

$$\beta = \int(1 - e^{-u_{ij}/kT})\,\mathrm{d}\mathbf{r}_{ij} \tag{22}$$

where u_{ij} is the potential of average force between two polymer segments. For sufficiently small values of z, one has the expansion[9]

$$h(z) = 1 - 2.865z + 14.278z^2 - \ldots \tag{23}$$

For the lattice model considered here, we have approximately

$$\beta = 1 - (q - 2)(f - 1) \tag{24}$$

The first term accounts for overlap of two segments and the second one for $q - 2$ possible contacts between them since, for large n, two neighboring sites of each segment are blocked by adjacent segments. Hence the theta temperature is given by

$$f_\theta(\infty) = (q - 1)/(q - 2)$$
$$k\Theta(\infty)/\epsilon = [\ln(q - 1)/(q - 2)]^{-1} \tag{25}$$

i.e., $k\Theta(\infty)/\epsilon = 4.48$ for the simple cubic lattice, in moderate agreement with eq 13. A slight improvement of β consists in replacing $q - 1$ by the effective coordination number μ relative to self-avoiding walks.[10] As $\mu \simeq 4.683$ for the simple cubic lattice, this gives $k\Theta(\infty)/\epsilon \simeq 4.16$, somewhat closer to eq 13.

Expansion 23 is expected to be especially useful near the theta temperature as β gets small in this region. We have from eq 20, 21, and 24

$$A_2^* = \frac{1}{2}\left[\frac{\mathrm{d}\beta}{\mathrm{d}\ln f}\left(h + z\frac{\mathrm{d}h}{\mathrm{d}z}\right)\right]_\Theta$$
$$= -\frac{1}{2}(q - 2)f_\Theta\left(h + z\frac{\mathrm{d}h}{\mathrm{d}z}\right)_\Theta$$

As z itself vanishes at the theta point we finally obtain, on account of eq 23 and 25

$$A_2^*(\infty) = -\tfrac{1}{2}(q - 1) \tag{26}$$

For the simple cubic lattice this gives $A_2^* = -2.5$, a value which deviates considerably from eq 16.

To sum up this discussion, the two theories examined here predict the location of the theta temperature reasonably well. The situation is less clear for $A_2^*(\infty)$, especially because our own value of this quantity is not very accurate. It seems nevertheless that the second theory largely overestimates $|A_2^*(\infty)|$. It may also be interesting to notice that

our theta temperature defined by the condition $A_2 = 0$, i.e., $k\Theta/\epsilon \simeq 3.71$, is not very different from the theta temperature reported for the same model by McCrackin, Mazur, and Guttman, which is based on dimensional analysis of a single chain ($k\Theta/\epsilon = 3.64$).

We are grateful to Dr. J. Orban for interesting discussions and to the referees (anonymous) for helping us to bring this paper into its final form.

References and Notes

(1) Chercheur IRSIA.
(2) (a) A. Bellemans and M. Janssens, *Macromolecules*, **7**, 809 (1974); (b) D. S. McKenzie and C. Domb, *Proc. Phys. Soc., London*, **92**, 632 (1967).
(3) See, e.g., T. L. Hill, "Statistical Mechanics", McGraw-Hill, New York, N.Y., 1956, p 277.
(4) See, e.g., J. Mazur and F. L. McCrackin, *J. Chem. Phys.*, **49**, 648 (1968).
(5) M. L. Huggins, *Ann. N.Y. Acad. Sci.*, **43**, 9 (1942).
(6) P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).
(7) E. A. Guggenheim, "Mixtures", Oxford University Press, London, 1952, Chapter 9.
(8) H. Yamakawa, "Modern Theory of Polymer Solutions", Harper and Row, New York, N.Y., 1971, Chapter 4.
(9) Y. Tagami and E. F. Casassa, *J. Chem. Phys.*, **50**, 2206 (1969).
(10) M. F. Sykes, *J. Chem. Phys.*, **39**, 410 (1963).
(11) F. L. McCrackin, J. Mazur, and C. M. Guttman, *Macromolecules*, **6**, 859 (1973).

Theory of Inhomogeneous Polymers. Lattice Model for Solution Interfaces

Eugene Helfand

Bell Laboratories, Murray Hill, New Jersey 07974. *Received September 22, 1975*

ABSTRACT: A lattice theory is developed to treat interfaces involving concentrated polymer solutions. The free energy is written in terms of the concentration profile and the anisotropy probabilities for polymer bond directions. Minimization of this free energy with appropriate constraints leads to formulas for the interfacial features. One of these constraints, unique to polymer systems, links the concentration profile to the bond anisotropy. Numerical results are presented in the following paper.

The Flory–Huggins theory[1] has contributed substantially to the understanding of concentrated polymer solutions. Besides providing quantitative formulas for thermodynamic predictions, it has given us insight into the statistical origins of the various free-energy terms. In the present work we employ a lattice model to provide an understanding of the molecular considerations which give rise to interfacial free energy and determine the average arrangement of polymer molecules at interfaces.

The model we shall adopt has its origins in the interfacial cell theories of Ono[2] and Ono and Kondo,[3] developed for the analysis of small molecule systems. Ash, Everett, and Findenegg[4] considered molecules which could occupy several cells. An extension to polymers presented by Roe[5] has been discussed elsewhere.[6]

This paper continues a series of contributions[6-8] aimed at developing and applying a general theory of inhomogeneous polymer systems. In some of the works the continuous Gaussian random walk model has been used for the statistics of polymer conformations. Applications have been made to block copolymers,[7] to the polymer–polymer[7] and polymer solution–solvent[8] interfaces. The Gaussian random walk statistics should be appropriate when the scale of the inhomogeneity is large compared with the length of a polymer segment. For the interface problem "scale of inhomogeneity" refers to some measure of the region of significant phase mixing. It is difficult to say a priori how useful the Gaussian model will be for narrower interfaces. An alternative approach is the use of lattice statistics. One application of the lattice model already reported[6] is to the polymer–polymer interface problem. In the present paper these ideas are extended to the description of interfaces involving concentrated solutions.[9]

Our exposition begins with a specification of the lattice model. The major theoretical development is the derivation of a formula for the system's entropy. The entropy is combined with a random contact heat of mixing expression, and the resulting free energy is minimized, subject to appropriate constraints, to produce formulas for the systems' features. One of these constraints, which we call the "flux constraint", is unfamiliar, so it is discussed extensively in section V.

Numerical solutions of the equations, together with a qualitative discussion of phenomena, are presented in the following paper.[10] There, too, one finds a brief summary of the major features of this paper.

There is a strong parallel between the present work and our earlier lattice theory of polymer–polymer interfaces. We have tried to make this report reasonably self-contained, but some material is presented in greater detail in ref 6, although minor adaptions are necessary.

I. The Model

We will consider that n_P polymer units and n_o solvent molecules fill a lattice of n sites:

$$n = n_o + n_P \tag{I.1}$$

The lattice is regarded as consisting of layers labeled with the index l. Each layer contains n_S cells.

There are two types of problems: either we have an interphase between a saturated polymer solution and solvent, in which case we allow l to run from $-\infty$ (solvent) to $+\infty$ (polymer solution); or we have in mind that there is an impenetrable wall, whereupon we let l go from 1 to ∞. The theories are so similar we present them simultaneously.

Each cell of the lattice has z nearest neighbors. If there is a polymer unit in a cell, the next unit along the chain can be in any of the z neighboring cells. (We will not take account of bond-angle restrictions or weighting of rotational states, although it could be done, as indicated in ref 6.)

For treatments of an inhomogeneity in the l direction it is necessary to specify that, of the z neighbors, a fraction m are in the layer above, a fraction m are below, and a fraction $(1 - 2m)$ are in the same layer.

The polymer molecules will be taken as being of extremely high molecular weight so that all units of the poly-