

# THERMODYNAMIC INTERACTIONS IN DILUTE POLYMER SOLUTIONS: THE VIRIAL COEFFICIENTS

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## ABSTRACT

The statistical thermodynamics of dilute polymer solutions is reviewed from the point of view of the continuum theory based on molecular distribution functions. The comparatively rigorous perturbation treatment of the second and third virial coefficients, and various approximate theories derived from it to give closed-form expressions useful for good-solvent systems, are outlined. Indications from theory and representative experimental data are discussed for linear chains, branched chains, and binary solutes comprising polymers alike chemically but different in molecular weight and/or branched structure. It is suggested that apparently anomalous thermodynamic and conformational behaviour observed with branched chains reveals a basic inadequacy in the so called 'two-parameter' class of statistical theories.

## INTRODUCTION: HISTORICAL

One of the most striking properties of long-chain polymers is the extreme departure of their solutions from Raoult's law. This behaviour attracted early attention in physicochemical studies of polymers and conceptual understanding of the basis for it was one of the important milestones in the progressive application of physical principles to macromolecular systems.

Two rather distinct formalisms, one based on lattice models and the other on molecular distribution functions, have been applied in studying the thermodynamics of polymer solutions. First, the development of lattice or cell theories for simple liquid mixtures<sup>1</sup> and, in particular, efforts to extend them to mixtures of molecules of disparate size<sup>2</sup> inspired application of similar ideas to polymer solutions. The result was the celebrated theory presented independently by Huggins<sup>3</sup> and by Flory<sup>4,5</sup> in 1942. Despite innumerable variations and extensions of the lattice treatment—and a glance at the program of this Microsymposium indicates clearly enough that after thirty years the lattice method is still far from a dead issue—the essence of it can be expressed very simply. One imagines the solution volume to be divided into cells in each of which one can place either a segment of a polymer chain or a solvent molecule. The numbers of distinguishable configurations

available to the system are counted as the polymer chains are added one by one to the lattice, and thence the entropy of mixing is derived. With parameters for specific interactions between solvent molecules and chain segments the total free energy of mixing is obtained. Approximations are of course unavoidable. The most important one from our point of view is that while the connected nature of each polymer chain is respected in counting the conformations available to it when it is placed on the lattice, this chain 'sees' those previously placed on the lattice only as a random distribution of unconnected chain segments<sup>5</sup>. Intuitively this approximation is acceptable in concentrated solutions where the segment distribution does approach randomness on a microscopic scale; and despite difficulties that have been the source of much discussion, the lattice approach has certainly been successful for such solutions<sup>5</sup>.

By comparison, the model should be inadequate for dilute solutions, in which the polymer chains form discrete dilute 'clouds' of polymer segments (containing say 1% polymer by volume) separated on the average from one another by regions containing only solvent. Curiously, this difficulty was apparently ignored for years, even though it manifests itself by an important discrepancy between theoretical prediction and experiment. In the simplest form of the Flory-Huggins theory<sup>5</sup> the activity  $a_1$  of solvent referred to the usual standard state of pure solvent is given by

$$a_1 = (1 - v_2) \exp \{ (1 - V_1/\bar{v}M) v_2 + \chi_1 v_2^2 \} \quad (1)$$

where  $v_2$  is the volume fraction of polymer in the solution;  $M$  is the molecular weight of the polymer and  $\bar{v}$  its partial specific volume;  $V_1$  is the molar volume of solvent; and  $\chi_1$  is a parameter characterizing the energy of interaction between solvent molecules and chain segments. Introducing the weight concentration  $c = v_2/\bar{v}$  (grams of polymer per ml of solution) and the relation

$$RT\Pi V_1 = - \ln a_1 \quad (2)$$

for the osmotic pressure  $\Pi$ , we can combine equations 1 and 2 and expand the function  $\Pi/c$  in powers of concentration to obtain<sup>5</sup>

$$\Pi/RTc = M^{-1} + (\bar{v}^2/V_1)(\frac{1}{2} - \chi_1)c + (\bar{v}^3/3V_1)c^2 + O(c^3) \quad (3)$$

which is the Flory-Huggins expression for the general osmotic virial expansion

$$\Pi/RTc = M^{-1} + \sum_{i=2,3,\dots} A_i c^{i-1} \quad (4)$$

Perhaps the most notable aspect of equation 3 is that the second virial coefficient  $A_2$  exhibits no molecular weight dependence (if  $\chi_1$ , as the simple model demands, is independent of molecular weight). Although some experimental studies appeared to substantiate this invariance, we now know that  $A_2$  is indeed a function of molecular weight. *Figure 1*, a compilation of data of Berry<sup>6</sup> on polystyrene in *cis*-decalin (decahydronaphthalene), serves as an illustration. The product  $A_2 M^{\frac{1}{2}}$  plotted against a quantity proportional to  $M^{\frac{1}{2}}$  obviously does not give a straight line. Virial coefficient data on

polymers can usually be represented quite well over wide ranges of molecular weight by the form<sup>7</sup>

$$A_2 \propto M^{-\nu} \quad (5)$$

with  $\nu$  about 0.25 for very good solvents, and smaller for poorer solvents. However, no theoretical basis for equation 5 has been suggested.

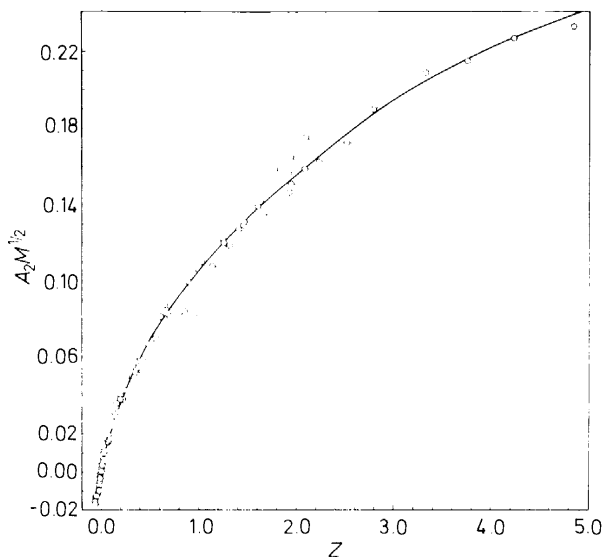


Figure 1. Plot of  $A_2M^{1/2}$  versus  $z$  (determined by  $\langle s^2 \rangle_0$  and temperature dependence of  $A_2$  at  $T = \Theta$ ) for polystyrene in *cis*-decalin (from data of Berry<sup>6</sup>). The points are marked to differentiate data for the various samples.

We remark here, anticipating the subsequent discussion, that the particular separation of entropy and heat effects in the idealized lattice theory is not essential. The parameter  $\chi_1$  can be regarded more generally as a free-energy quantity and  $-RT(\frac{1}{2} - \chi_1)v_2^2$  represents, to terms of order  $v_2^2$ , the partial molar free energy of dilution (or excess chemical potential of solvent). Then, it is useful to let

$$\frac{1}{2} - \chi_1 = \psi_1(1 - \Theta/T) \quad (6)$$

where  $\psi_1$  is Flory's entropy-of-mixing parameter and  $\Theta$  is a characteristic temperature at which polymer-solvent interactions vanish<sup>5</sup>. In this form, the second virial coefficient of equation 3 is given by

$$A_2 = (\bar{v}^2/V_1)\psi_1(1 - \Theta/T) \quad (7)$$

The coefficients of terms of order  $c^2$  and higher on the right hand side of equation 3 are notable for their lack of quantities characterizing thermodynamic interactions. In view of the formal identification of virial coefficients

with such interactions, it appears that these terms are not physically meaningful in the form generated by the Flory-Huggins method.

In the face of the difficulty of accounting for the thermodynamic properties of dilute solutions by the lattice method, a different approach was called for; and the statistical mechanical methods of the theory of real gases, focusing on the evaluation of the configuration integral for a dilute system of interacting particles<sup>8</sup>, provided an appropriate conceptual framework.† Using the Montroll-Mayer molecular distribution functions,<sup>10</sup> McMillan and Mayer<sup>11</sup> demonstrated the precise formal equivalence between pressure of a gas and the osmotic pressure of a solution; but it remained for Zimm<sup>12</sup> to marshal the techniques that made it possible to cope with the enormous number of internal degrees of freedom possessed by a flexible polymer chain. Since most of the discussion to follow centres about this theory, we describe it in some detail.

### PERTURBATION THEORY FOR DILUTE POLYMER SOLUTIONS: THE SECOND VIRIAL COEFFICIENT FOR HOMOGENEOUS POLYMERS

In the general theory of solutions formulated by McMillan and Mayer, the second virial coefficient is given by

$$A_2 = - \frac{N_A}{2VM^2} \int g_2(1, 2) d(1) d(2) \quad (8)$$

$$g_2(1, 2) = F_2(1, 2) - F_1(1) F_1(2) \quad (9)$$

in which  $N_A$  is Avogadro's number.

The distribution functions  $F_1(1)$ ,  $F_1(2)$ ,  $F_2(1, 2)$  are defined by probabilities

$$F_1(1) d(1)/V, \quad F_1(2) d(2)/V$$

that molecule 1 in the macroscopic system of volume  $V$  has its coordinates in the differential 'volume' of configuration space symbolized by  $d(1)$ , that molecule 2 is similarly in  $d(2)$ , and

$$F_2(1, 2) d(1) d(2)/V^2$$

that molecules 1 and 2 are simultaneously in the element  $d(1) d(2)$ . Obviously, if there is no correlation between the two molecules (if they exert no forces on each other)  $F_2(1, 2)$  equals  $F_1(1) F_1(2)$ , the  $g_2$  function vanishes, and  $A_2$  must vanish.

To obtain results from these general relations, Zimm<sup>12</sup> pictures the polymer molecule as a linear sequence of  $n$  identical segments of length  $b_0$  connected by flexible joints (or as beads on a string). The interaction between any two chain segments not directly connected in a chain contour is described by a potential of average force  $u(r_{ij})$  that depends only on the scalar distance  $r$  between the segments (e.g.,  $r_{i,j_2}$  separating segment  $i$  in

† We remark, however, that complicated lattice treatments can give a molecular-weight dependent  $A_2$ , and that any lattice formalism can be regarded as a special case of the more general theory described here<sup>8,9</sup>.

molecule 1 and segment  $j$  in molecule 2). It is assumed, by an approximation that is standard but of uncertain effect, that the  $u(r)$  are additive. Then  $F_2(1, 2)$  can be factored to give

$$F_2(1, 2) = F_1(1)F_1(2) \exp \left\{ - \sum_{i_1, i_2} \sum u(r_{i_1 i_2})/kT \right\} \quad (10)$$

where the sums run over all  $n$  segments of each of the two chains in any specified configuration to give the total energy of interaction of molecules 1 and 2. Although the only energies appearing in this formulation are for interactions between chain segments, it must be understood that these are averaged quantities containing implicitly the effects of polymer-solvent and solvent-solvent interactions.

By analogy with the procedure in the theory of a real gas<sup>8, 13</sup> each Boltzmann factor for a segment pair is expressed by a function

$$\chi(r_{i_1 j_2}) \equiv 1 - \exp \left\{ - u(r_{i_1 i_2})/kT \right\} \quad (11)$$

Substitution of this into equation 10 permits  $g_2$  to be expanded in a series of products of  $\chi$  functions:

$$\begin{aligned} -g_2(1, 2) = F_1(1)F_1(2) & \left[ \sum_{i_1, i_2} \sum \chi(r_{i_1 i_2}) - \sum_{(i_1, i_2, j_1, j_2)} \dots \sum \chi(r_{i_1 i_2})\chi(r_{j_1 j_2}) \right. \\ & \left. + \sum_{(i_1, i_2, j_1, j_2, k_1, k_2)} \dots \sum \chi(r_{i_1 i_2})\chi(r_{j_1 j_2})\chi(r_{k_1 k_2}) + \dots \right] \quad (12) \end{aligned}$$

the parentheses about the indices indicating that the sums are limited to avoid redundant counting.

At this point, the crucial assumption is made that the  $\chi$  functions, and hence the potentials  $u(r)$ , are of such short-range character that a delta-function formulation<sup>14</sup> is adequate: i.e., the excluded volume integral for interaction of a pair of segments can be written

$$\beta_{i_1 i_2} = \int \chi(r_{i_1 i_2}) d\mathbf{r}_{i_1 i_2} = \int \beta_{i_1 i_2} \delta(\mathbf{r}_{i_1 i_2}) d\mathbf{r}_{i_1 i_2} \quad (13)$$

where  $\delta(\mathbf{r}_{i_1 i_2})$  is a three-dimensional Dirac delta function peaked when  $r_{i_1 i_2} = 0$ . This means that the  $\chi$  function vanishes unless the two segments in question are 'in contact'. Thus, any product of  $\chi$  functions in equation 12 contributes to the integral of  $g_2(1, 2)$  only for configurations in which all the segment pairs designated in the product are simultaneously in contact<sup>12</sup>. The short-range nature of the  $\chi$ s makes it possible to begin the evaluation of  $A_2$  by integrating successive terms on the right of equation 12 over all  $6n$  spatial coordinates of two molecules of the same polymer species. Since all the chain segments are assumed to be identical, the integral of every  $\chi$  function will be the same and we can eliminate subscripts on the  $\beta$ s.

The result of the integration over coordinates can be expressed formally as

$$\begin{aligned} - \int g_2(1, 2) d(1) d(2) = \beta V \sum_{i_1, i_2} \sum \{ 1 - \beta \sum_{(j_1, j_2)} P(O_{j_1 j_2} | O_{i_1 i_2}) \\ + \beta^2 \sum_{(j_1, j_2, k_1, k_2)} \dots \sum P(O_{j_1 j_2}, O_{k_1 k_2} | O_{i_1 i_2}) + O(\beta^3) \} \quad (14) \end{aligned}$$

where the  $P$ s are conditional probability densities: e.g.,  $P(O_{j_1 j_2}, O_{k_1 k_2} | O_{i_1 i_2})$  for contacts between pairs  $j_1, j_2$  and  $k_1, k_2$ , given that segments  $i_1, i_2$  are in contact. Zimm assumes that the distribution functions  $F_1(1), F_1(2)$  are given

by random-flight statistics (as multivariate Gaussian forms). A theorem due to Wang and Uhlenbeck<sup>15</sup> and Fixman<sup>14</sup>, allows the probability functions to be written down immediately: e.g., for the simplest one:

$$P(O_{j_1 j_2} | O_{i_1 i_2}) = (3/2\pi b_0^2)^{\frac{3}{2}} (|j_1 - i_1| + |j_2 - i_2|)^{-\frac{3}{2}} \quad (15)$$

The remaining task is to perform the summations over the segments. These can be written as integrals since  $n$  is large. For  $P(O_{j_1 j_2} | O_{i_1 i_2})$ , the highest-order term evaluated by Zimm, the quadruple integration is straightforward. But for the terms of order  $\beta^2$  inside the brackets in equation 14, carrying out the integrations with the prescribed limits is difficult<sup>16,17</sup> and apparently cannot be accomplished entirely analytically. Quantitative evaluation of still higher terms does not so far appear feasible<sup>16</sup>, even by machine methods. The result for the second virial coefficient of a homogeneous polymer can be written:

$$A_2 = AF(z) \quad (16)$$

$$A = N_A \beta n^2 / 2M^2 \quad (17)$$

$$F(z) = 1 - Bz + C_2 z^2 + \dots \quad (18)$$

$$z = \left( \frac{3}{2\pi b_0^2} \right)^{\frac{1}{2}} \beta n^{\frac{1}{2}} = \left( \frac{3}{2\pi n b_0^2} \right)^{\frac{1}{2}} \beta n^2 \quad (19)$$

The above forms are not limited to linear chains, but for that case

$$B = 2.8653, \quad C_2 = 9.201 \quad (20)$$

The factor  $A$ , the so-called 'single contact' term is independent of chain architecture (linear, branched, ring) and of molecular weight, but does depend on the chemical nature of the polymer-solvent combination and the temperature. It represents the second virial coefficient for a hypothetical solution of completely disconnected chain segments. Dependences on molecular weight and temperature are contained in the random-flight variable  $z$  and thus in  $F(z)$ .

The coefficient  $B$  has been obtained for some nonlinear geometries. For long-chain flexible rings<sup>18</sup>, it is  $\pi\sqrt{2} = 4.457$ . For 'star' branched molecules— $f$  identical linear chain elements, each attached to a common junction by one end— $B$  is given by<sup>19</sup>

$$\begin{aligned} (15/32)f^{\frac{1}{2}} B_{\text{star}} &= (f - 1)(17\sqrt{2} - 9\sqrt{3} - 8) \\ &+ (f - 1)^2(9\sqrt{3} - 6\sqrt{2} - 7) \end{aligned} \quad (21)$$

Equation 21 shows that  $B_{\text{star}}$  increases monotonically from the linear value ( $f = 1, 2$ ) with increasing  $f$  to approach  $0.2201 f^{\frac{1}{2}}$  asymptotically. Derivation of  $B$  has also been accomplished for 'regular-comb' branched chains with  $f$  identical branches spaced uniformly along a main chain<sup>20</sup>. The results are expressed in terms of complicated single and double sums running over branch indices (1 to  $f$ ). Computer calculation is essential in this case.

The calculations for branched chains were motivated by laboratory synthesis of approximations to the idealized star and comb molecules by

anionic polymerization methods. Actually, a better representation of the real comb-chains is provided by a model with the branches spaced at random along the main chain (but still with the same number of branches in each chain). It turns out that this randomization of branch positions materially simplifies calculations and yields an analytical expression for  $B$ , one that remains cumbersome but is without the troublesome sums<sup>21</sup>. The behaviour

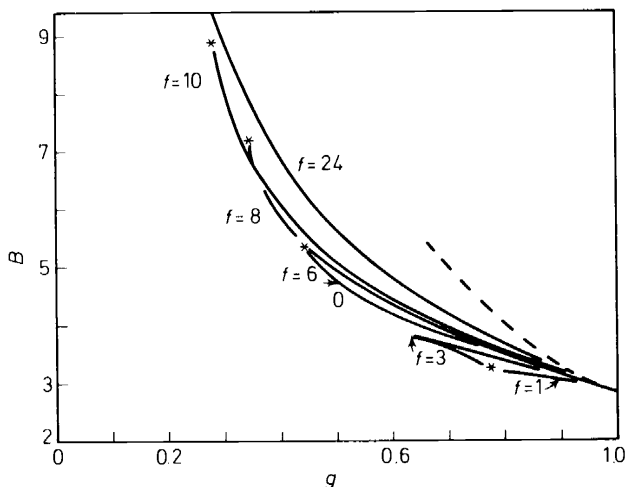


Figure 2. Double-contact interaction coefficient  $B$  as a function of the ratio of mean-square radii of nonlinear and linear chains of the same mass. The curves are for combs with  $f$  branches spaced so as to divide the main chain into  $f + 1$  identical elements. As  $g$  decreases, with  $f > 3$ , main segments between branches become shorter in relation to branch length and each curve terminates at the corresponding regular  $f$ -functional star. The degenerate case with  $f = 1$  designates a 3-functional star with two arms of equal length. Curves for  $f = 1, 2$  must be closed, beginning and ending at the linear-chain limit. The dashed line is the limiting relation for  $f = \infty$ . The circle at  $g = \frac{1}{2}$  is for the ring model.

of  $B$  with comb branching parallels that observed for stars and the ring;  $B$  increases as the structure is made more compact for a given number of segments per chain. The degree of correlation between  $B$  and the ratio  $g$  of mean-square radii of branched and linear chains of the same mass is indicated in Figure 2.

The derivation of  $F(z)$  can be improved in a way that affects only the quadratic and higher terms. The assumption that  $F_1(1)$  always pertains to a random-flight chain ignores the fact that interactions between segments within a single chain must be governed by the same potential of average force  $u(r)$  as interactions between segments in different chains<sup>16, 22</sup>. As a consequence of intramolecular interaction,  $F_1(1)$  must represent a perturbed distribution. Consistently with the treatment of intermolecular interactions,  $F_1(1)$  can be developed by an expansion about the unperturbed state, denoted

by the distribution function  $F^0(1)$ , in terms of  $\chi$  functions for intramolecular segment pairs:

$$F_1(1) = QF_1^0(1) \left[ 1 - \beta \sum_{(i,j)} \delta(r_{ij}) + O(\beta^2) \right] \quad (22)$$

where  $Q$  is the normalizing factor.

Using this and the analogous expansion for  $F_1(2)$ , we obtain new terms, containing  $P$ s for various combinations of intermolecular and intramolecular interactions, that must be added to equation 14 if it is to be strictly correct to use random-flight expressions for the  $P$ s. The new contributions are denoted by  $C_{12}$  in the relation

$$F'(z) = 1 - Bz + (C_2 + C_{12})z^2 + \dots \quad (23)$$

which replaces equation 18. Considerable effort has been put into calculating  $C_{12}$  for linear chains<sup>23, 24</sup>, the only case so far studied. It appears that the best value<sup>17</sup> of  $C_{12}$  for identical chains is 5.077, which yields

$$C_2 + C_{12} = 14.278 \quad (24)$$

The development described in the preceding paragraphs represents a perturbation theory with the sum in powers of  $\beta$  giving orders of correction to the unperturbed state, in which the second virial coefficient vanishes (as  $\beta$  vanishes) and random-flight statistics describes chain configurations—i.e., at the temperature  $\Theta$ . Formally, the theory is complete; but in fact, the unavailability of coefficients for terms beyond the third (at best) in the series means that any direct quantitative application of the results must be limited to systems for which the quadratic approximation of  $F'(z)$  is adequate. Since the series for  $F'(z)$  converges slowly, the range of  $z$  for which this is useful is very narrow.

So far, the development has been rather abstract. The number of chain segments  $n$  and the segment length  $h_0$  refer not to a real chain defined by chemical bonds and bond angles, but only to an imaginary statistical chain that does, however, reproduce the gross averaged properties of chain configurations. To establish a connection with reality, we observe that the mean-square radius of gyration  $\langle s^2 \rangle_0$  of the random flight characterized by parameters  $n$  and  $h_0$  is  $nh_0^2/6$ . A direct measurement of this dimension for the real chain at  $T = \Theta$  (by a diffraction measurement) thereby establishes the value of  $nh_0^2$ . Then from equations 16 to 19, we find

$$\left( \frac{dA_2}{dT^{-1}} \right)_{T=\Theta} = \left( \frac{N_A}{2M^2} \right) \left( \frac{d(\beta n^2)}{dT^{-1}} \right) \quad (25)$$

so that determination of the temperature variation of  $A_2$  permits  $\beta n^2$  to be determined unambiguously at temperatures near  $\Theta$ . Thus, we find that  $z$  contains two operationally meaningful parameters,  $nh_0^2$  and  $\beta n^2$ . For this reason, the general class of statistical mechanical theories that express  $A_2$ , or some other property, in terms of these or an equivalent pair of parameters are commonly termed 'two-parameter' theories<sup>25, 26</sup> in the sense first suggested by Stockmayer.<sup>25</sup>

A thermodynamic argument shows that when  $T \approx \Theta$ , the temperature dependence of  $\beta$  is given by<sup>5, 26</sup>

$$\beta = \beta_0(1 - \Theta/T) \quad (26)$$



Then the derivative in equation 25 is  $-\beta_0 n^2 \Theta / 2M^2$ . This can be identified with  $-v^2 \psi_1 \Theta / V_1$  in the symbolism of equation 7. The single-contact contribution to the virial coefficient, equation 17, is therefore the Flory-Huggins virial coefficient, and  $z$  can be expressed in the forms

$$\begin{aligned} z &= \left(\frac{1}{4\pi}\right)^{\frac{3}{2}} \left(\frac{\langle s^2 \rangle_0}{M}\right)^{-\frac{3}{2}} \frac{\beta_0 n^2}{M^2} \left(1 - \frac{\Theta}{T}\right) M^{\frac{1}{2}} \\ &= \frac{2}{N_A} \left(\frac{1}{4\pi}\right)^{\frac{3}{2}} \left(\frac{\langle s^2 \rangle_0}{M}\right)^{-\frac{3}{2}} \frac{\bar{v}^2}{V_1 \psi_1} \left(1 - \frac{\Theta}{T}\right) M^{\frac{1}{2}} \end{aligned} \quad (27)$$

in which the characteristic unperturbed dimension  $\langle s^2 \rangle_0 / M$  for linear chains is isolated. Values of  $z$  for the experimental correlation shown in Figure 1 were obtained by this method of analysis<sup>6</sup>.

For typical polymer-solvent binary systems,  $\Theta$  represents an upper critical solution temperature (UCST): the critical point or temperature above which the system is one phase at every composition if the molecular weight of the polymer is very high<sup>5</sup>. In practice, positive values of  $z$  are of most interest because the polymer precipitates if  $T$  is appreciably smaller than  $\Theta$ . As  $T$  is raised above  $\Theta$ , the solvent becomes progressively better and, with usual values of  $\psi_1$ , the region of  $z$  for which the quadratic approximation to  $F(z)$  is sufficient is rapidly exceeded. These characteristics are exemplified by the data for polystyrene and *cis*-decalin ( $\Theta = 12.2^\circ\text{C}$ ) in Figure 1.

While the experimental behaviour of  $F(z)$  for  $z$  appreciably greater than zero cannot be obtained from the perturbation theory, the data in Figure 1 do exhibit conformity with one basic requirement of the theory: that  $A_2 M^{\frac{1}{2}}$  be a function of  $z$  alone for a series of homogeneous polymers of the same chemical and topological structure (all linear in the present case) in a given solvent. The agreement is impressive considering that the data cover wide ranges both in temperature ( $10^\circ$  to  $110^\circ\text{C}$ ) and in molecular weight ( $2 \times 10^4$  to  $4.4 \times 10^6$ ).

The mean-square molecular radii of gyration of these polymers measured directly by light scattering<sup>6</sup> for molecular weights above  $4 \times 10^5$  show that the fractional linear expansion  $\alpha$  beyond random flight dimensions due to intramolecular segment-segment repulsions at  $T > \Theta$  can similarly be represented by a single function of  $z$ . This, again, is in accord with the appropriate perturbation theory<sup>14, 27, 28</sup>, developed in completely consistent fashion with the theory for  $A_2$ . Specifically, the series expression for the mean square radius is

$$a \equiv \langle s^2 \rangle / \langle s^2 \rangle_0 = 1 + az + O(a^2) \quad (28)$$

where  $a = 134/105$  for linear chains. The series for  $\alpha$  displays the same kind of slow convergence as does  $F'(z)$ . However, as Zimm, Stockmayer and Fixman<sup>27</sup> noted, elimination of  $z$  among equations 16, 18, and 28 yields a series for  $A_2 M^{\frac{1}{2}}$  in powers of  $(\alpha^2 - 1)$  that converges more rapidly than either series alone; and Figure 3 shows that in fact the experimental data already cited conform very well to a linear dependence between  $A_2 M^{\frac{1}{2}}$  and  $\alpha^2$ .

The assertion, implicit in what has been above, that  $z$  for  $T > \Theta$  can be deduced from parameters measured near  $\Theta$  requires some qualification. In the first place, the temperature dependence of  $\langle s^2 \rangle_0$  may be difficult to assess unambiguously because measured dimensions in a series of solvents chosen to give the unperturbed state (defined by  $A_2 = 0$ ) at various temperature are sometimes influenced by specific solvent effects. However,  $\langle s^2 \rangle_0$

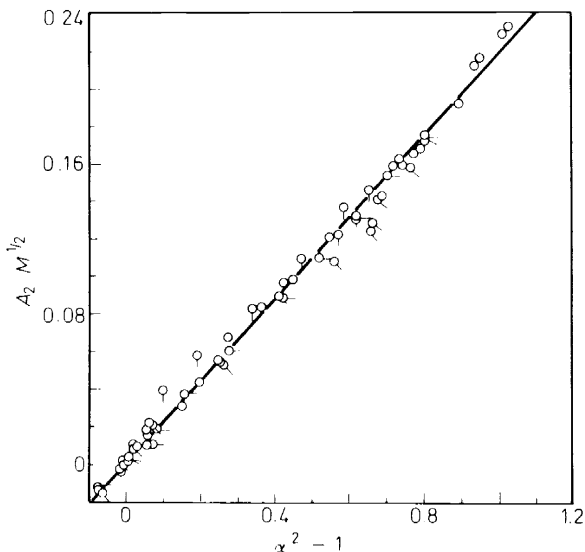


Figure 3. Polystyrene in decalin:<sup>6</sup> linear relation between  $A_2 M^{1/2}$  and  $(\alpha^2 - 1)$ .

clearly varies only slowly with temperature under ordinary circumstances<sup>5</sup>, and there is good reason to believe that the effect is in fact unimportant for the polystyrene-decalin system<sup>29</sup>. A more fundamental problem lies in the assumption that the temperature dependence of  $\beta$  is always given by equation 26 when  $z$  is large. If there is to exist a 'lower' critical solution temperature (LCST) somewhere between  $\Theta$  and the critical temperature of the solvent and if a vanishing  $A_2$  can be associated with the LCST, as well as with the UCST, the formulation of  $z$  given here cannot be adequate over an arbitrarily extended temperature range<sup>30</sup>. Flory's parameter  $\psi_1$ , therefore, has to be temperature dependent; or, what is the same thing, there exists an excess partial molal heat capacity of dilution. In a recent important contribution Eichinger<sup>31</sup> calls attention to this problem and develops a series expansion of  $\psi_1$  as a function of  $T - \Theta$ . The first-order correction is determined simply by the value of the LCST. From the nonappearance of the LCST for polystyrene in decalin below 300°C, Eichinger obtains an estimate of the correction to  $z$  in the temperature range of Berry's measurements and concludes that the change in  $z$  (which is downward, and considerable at the higher values of  $z$ ) does nothing to worsen the correlation exhibited in Figure 1.

In some treatments of the intrinsic viscosity  $[\eta]$ —notably in that of Fox and Flory<sup>5</sup>—the ratio  $[\eta]/[\eta]_0$ , the subscript indicating the unperturbed state, is a function of  $z$  alone. However, Berry<sup>32</sup> found that this simple dependence did not represent adequately his viscosity data on the polystyrene-decalin system, except at very high molecular weights. He suggested that the deviations could be attributed to draining effects. Reanalyzing Berry's data, Eichinger concludes that the corrected values of  $z$  show decidedly improved correlation with  $[\eta]/[\eta]_0$  except at quite low molecular weights (ca.  $2 \times 10^5$ ). Berry's method of obtaining  $z$  and the modification by Eichinger are thermodynamically straightforward and seem preferable to other proposals that have been advanced<sup>33, 34</sup>, primarily with a view to improving correlations of intrinsic viscosities with a universal dependence on  $z$ .

### APPROXIMATE TREATMENTS FOR POLYMERS IN GOOD SOLVENTS

To account for the variation of the second virial coefficient with  $z$  that is found experimentally in good solvents, we have to calculate  $F'(z)$  from a model with  $z > 0$ . Since the manifestly intractable character of the coefficients of higher orders of  $z$  in equation 23 makes it impossible to sum the series, drastic approximations have to be made. In the various theories that have been proposed, the chain model described by random-flight statistics is in effect replaced by one in which the sequential connections of chain segments are to some degree destroyed. Mathematically, the procedure can be regarded as one of replacing the complicated simultaneous probabilities in equation 14 by combinations of simpler probabilities. Another approximation, presumably a relatively minor one, is to uncouple the intermolecular and intramolecular effects, approximating the latter simply by representing the real non-Gaussian chain as a random flight with segment length  $b = b_0\alpha$  adjusted to give the correct rms radius. The perturbation treatment applied to intermolecular interactions of two such uniformly expanded chains leads to a function  $F(\zeta)$  as in equation 18 with  $z$  replaced by  $\zeta = z/\alpha^2$ . Then the objective of the major approximation is to attain a useful closed form for  $F(\zeta)$ .

In one class of approximate theories, the connected chain is replaced by a cloud of disconnected segments constrained to some specified radial density distribution. The interaction of two such clouds can then be characterized by a configuration integral expressed in terms of a potential energy depending only on the distance between the centres of mass. The simplest model is one with a uniform segment density<sup>35</sup>. Flory and Krigbaum<sup>36</sup> used a single Gaussian density function and later Isihara and Koyama<sup>37</sup> improved on this by using the correct sum of  $n$  Gaussians for the density distribution of a random-flight chain of  $n$  segments about its centre of mass. The characteristic feature of these theories is the introduction of the approximation

$$\int P(O_{i_1 i_2}, O_{j_1 j_2}, \dots, O_{m_1 m_2}, S) dS = \int P(O_{i_1 i_2}, S) \dots P(O_{m_1 m_2}, S) dS \quad (29)$$

where  $P(O_{i_1 i_2}, \dots, S)$  is the probability density for the simultaneous occurrence of contacts between segments  $i_1$  and  $i_2$ ,  $j_1$  and  $j_2$ , etc., and of a separation  $S$  between centres of mass of two molecules 1 and 2. The details of the radial

segment-density function have been shown to have very little effect on the result<sup>38</sup>.

The Flory-Krigbaum  $F(\zeta)$  is expressed by a definite integral that is unmanageable analytically but can be evaluated numerically or graphically. A good quantitative approximation has been found by Orofino and Flory<sup>39</sup>:

$$F(\zeta) = [\ln(1 + 2.30\zeta)]/2.30\zeta \quad (30)$$

Markovitz and I<sup>40,41</sup> proposed a theory based on a different factorization of intersegmental contact probabilities†. The assumption

$$P(O_{j_1j_2}, O_{k_1k_2}, \dots, O_{m_1m_2} | O_{i_1i_2}) = P(O_{j_1j_2} | O_{i_1i_2}) \dots P(O_{m_1m_2} | O_{i_1i_2}), \quad (31)$$

which can be thought of as an averaging of the segment distributions of both chains about an 'initial' contact of segments  $i_1$  and  $i_2$ , makes it possible to do the summations (integrations) in equation 14 over all indices except  $i_1, i_2$  and to sum the series within the brackets. The remaining sums over  $i_1, i_2$  can be cast into the form:

$$F(\zeta) = \int_0^1 \int_0^1 \frac{1 - \exp[-4w(x, y)\zeta]}{4u(x, y)\zeta} dx dy \quad (32)$$

with

$$u(x, y) = 2x^{\frac{1}{2}} + 2y^{\frac{1}{2}} + 2(1-x)^{\frac{1}{2}} + 2(1-y)^{\frac{1}{2}} - (x+y)^{\frac{1}{2}} - (1-x+y)^{\frac{1}{2}} - (1-x-y)^{\frac{1}{2}} - (2-x-y)^{\frac{1}{2}} \quad (33)$$

and the double integral is very well approximated by

$$F(\zeta) = \frac{1 - \exp(-5.730\zeta)}{5.730\zeta} \quad (34)$$

with the appearance of the coefficient  $2B$  a logical consequence of the derivation.

In another approach, which is too involved to give in detail here, Kurata, *et al.*<sup>24</sup>, and Yamakawa<sup>43</sup> combine equations 8-10 and equation 13, and differentiate the result to obtain an expression for

$$\psi = (2M^2/N_A n^2) (\partial A_2 / \partial \beta) \quad (35)$$

Then, with approximations similar in part to those leading to equation 34, they obtain a differential equation for the quantity  $\psi$ . The remarkable final result is

$$F(\zeta) = \frac{1 - (1 + K\zeta)^{-(2B-K)/K}}{(2B-K)\zeta} \quad (36)$$

which by arbitrary variation of the constant  $K$  yields as special cases the form of equation 30 with the constant altered to 5.73, equation 34, and a semi-empirical relation proposed by Stockmayer (see Albrecht<sup>16</sup>):

$$F(\zeta) = (1 + 2.865\zeta)^{-1} \quad (37)$$

† We learned later that Fixman<sup>42</sup> had already obtained the same result in a somewhat different way.

In the original form of the theory of Kurata, *et al.*<sup>24</sup>,  $K$  is 0.683; but Yamakawa<sup>43</sup> has

$$K = (3C_2/B) - 2B \quad (38)$$

which makes the series expansion of  $F(\zeta)$  yield exactly the first three coefficients of the series in equation 18:

$$F(\zeta) = 1 - B\zeta + C_2\zeta^2 + O(\zeta^3) \quad (39)$$

Equation 34 reproduces the linear term of this series but equation 30 fails at the linear term unless the constant is arbitrarily changed to force agreement<sup>26</sup>.

Quantitative assessment of the approximate functions for  $F(\zeta)$  has been hampered by uncertainty over the precise nature of the expansion factor  $\alpha$  relating  $z$  and  $\zeta$ . Flory and Krigbaum took it to be the value for expansion of the mean dimensions of an isolated chain; and Markovitz and I did the same in deriving equation 34. Later I proposed that a better expansion factor to use would be a somewhat larger one for a cluster of two molecules<sup>22</sup>. The idea was prompted by marginal improvement in fitting of experimental data. But the main justification offered was apparent good agreement between the expansion calculated for a bimolecular cluster, represented as a cruciform branched molecule, and an apparent expansion  $\alpha_\zeta$  obtained by comparing equation 23 with equation 39 and bringing about agreement for three terms by requiring

$$\alpha_\zeta^3 \equiv z/\zeta = 1 + \frac{C_{12}}{B}z + \dots \quad (40)$$

The inaccurate value of  $C_{12}$  available in 1959 made the coefficient of the linear term in the expansion of  $\alpha_\zeta^2$  much larger than  $a$  in equation 28. However, with the correct  $C_{12}$ <sup>17,24</sup>, the value  $2C_{12}/3B = 1.181$  is in much better agreement with  $a$ , though slightly smaller. I believe, therefore, that the original definition of  $\zeta$  in terms of the expansion of a single chain was the more logical choice. Kurata, *et al.*<sup>24</sup>, discuss questions of mutual consistency that arise when a theory for  $\alpha(z)$  is combined with a theory for  $F(\zeta)$ .

All the relations for  $F(\zeta)$  are monotone decreasing functions of  $\zeta$  (or of  $z$ ) and therefore predict, as experiment requires, that  $A_2$  decreases with increasing  $M$ . The unmodified theories of the Flory-Krigbaum and Isihara-Koyama type give  $F(\zeta)$  decreasing much less rapidly than do the other forms. The quantity  $\zeta F(\zeta)$  is an increasing function of  $\zeta$  for all the theories. For equations 34, 36, and 37, it approaches a constant value at sufficiently large  $\zeta$ . For equation 34 in particular the asymptote is virtually attained when  $\zeta$  is unity. According to equation 30,  $\zeta F(\zeta)$  approaches proportionality with  $\ln \zeta$  at large  $\zeta$ .

Unambiguous experimental tests of the approximate expressions for  $A_2$  are difficult to achieve owing to at least three factors: (1) experimental data are sometimes of unknown reliability or may relate to materials of uncertain character; (2) quantitative differences among some of the theoretical relations are not large; (3) the estimation of  $z$  may be a controversial matter. In addition to the problems already discussed, use of intrinsic viscosity data and relations

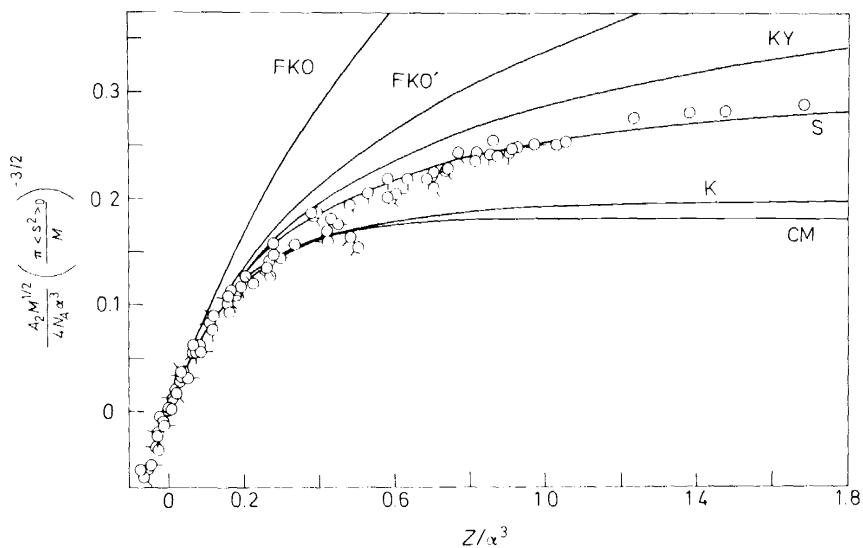


Figure 4. Plots of theoretical functions  $\zeta F(\zeta)$  versus  $\zeta$ : curves for equation 30 (FKO); equation 30 with constant changed to 5.73 (FKO'); equation 34 (CM); equation 36 with  $K = 0.683$  (K), and with  $K = 3.903$  (KY); equation 37 (S). The experimental points are for the polystyrene-decalin system with  $z$  as determined by Berry<sup>6</sup>.

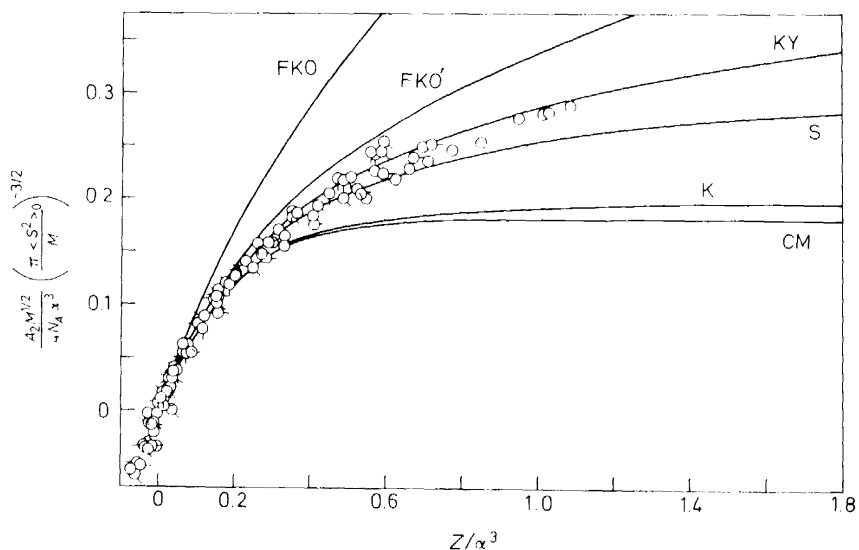


Figure 5. Plots as in Figure 4, but with  $z$  for experimental points corrected according to Eichinger<sup>31</sup>.

among  $[\eta]$ ,  $\alpha$ , and  $z$  to determine  $z$  in effect means that in the test of  $A_2$  data, other approximate theories are being simultaneously evaluated.

Despite uncertainties, it seems safe to assert that unmodified treatments of the Flory-Krigbaum type do not make  $A_2$  decrease sufficiently rapidly with molecular weight. One or more of the other theories usually provides a reasonable fit to experimental data depending on what data are being evaluated and how far one is willing to adjust parameters.

These statements are exemplified by *Figures 4 and 5* in which  $\zeta F(\zeta)$  is plotted against  $\zeta$  for the approximate theories and compared with Berry's experimental values of  $(A_2 M^{1/2} / \alpha^3) (\langle s^2 \rangle_0 / M)^{-1/2} / N_A 4\pi^2$  for polystyrene in decalin. The theoretical functions are the same in both plots, but the abscissas for the experimental points in *Figure 4* are determined by  $\zeta$  from Berry's calculation of  $z$ , and in *Figure 5* from Eichinger's modified  $z$  (see reference 31, p. 564). In *Figure 4*, the radically simple equation 37 (Curve S) is in excellent agreement with the data. Equation 34 (CM) makes  $\zeta F(\zeta)$  too small at large  $z$ . However, by using a  $\zeta$  calculated with a fictitious, unrealistically large, expansion factor  $\alpha_{II}$  obtained by assuming  $(\alpha_{II}^5 - \alpha_{II}^3)$  to be proportional to the actual  $(\alpha^5 - \alpha^3)$ , it is possible to bring equation 34 into agreement with the experimental points<sup>6</sup>. The expression of Kurata, *et al.*, equation 36 with  $K = 0$ , (Curve K) falls very close to Curve CM, but Yamakawa's modification (KY) gives a curve somewhat above the data. The only change in this picture brought about by use of the modified  $z$  in *Figure 5* is that Curve KY now appears to be preferable to Curve S. At large  $\zeta$ , where the correction to  $z$  becomes important,  $A_2 M^{1/2} / \alpha^3$  is nearly independent of  $z$ , and the considerable leftward translation of the points has only a minor effect on the shape of the curve delineated by them. With either choice of  $z$ , the Flory-Krigbaum-Orofino function, equation 30, makes  $\zeta F(\zeta)$  increase far too rapidly (Curve FKO). Changing the constant to 5.73 mitigates this behaviour but not sufficiently.

Application of approximate theories for  $F(\zeta)$  to nonlinear chain geometry has not been extensively explored. Models of the Flory-Krigbaum type can be used without basic change: it is only necessary to have a suitable smoothed radial density distribution for segments of the nonlinear chain. The mechanics of the derivation of equation 34 are the same for linear and nonlinear chains: the same form of  $F(\zeta)$  is obtained, with 5.730 replaced by the value of  $2B$  for the model in question.

## THE SECOND VIRIAL COEFFICIENT FOR MIXED POLYMERS

In addition to its theoretical interest, the problem of interactions between dissimilar polymer chains has obvious practical importance because real polymer samples are to some degree heterodisperse. The measured virial coefficient (e.g.,  $A_{22}^{(II)}$  for the osmotic-pressure equation of state) is a weighted sum of virial coefficients for interactions of pairs of like and unlike species:

$$A_2^{(II)} = \sum_J \sum_K A_{JK} w_J w_K \quad (41)$$

where  $w_J$ ,  $w_K$  are weight fractions of species J and K in the solute. Thus, three coefficients  $A_{11}$ ,  $A_{12}$ ,  $A_{22}$  determine the variations of  $A_2^{(II)}$  with composition of a binary solute. For light scattering (provided species J and K do not

differ chemically) the weighting factors  $w_j w_k$  in equation 41 are replaced by  $M_j w_j M_k w_k / M_w^2$ .  $M_w$  denoting the weight-average molecular weight. Obviously, if a general relation can be obtained for J, K pairs, the virial coefficient can be calculated for any arbitrary distribution of species.

The perturbation treatment can be carried out for molecular pairs of unlike species. If they differ only in molecular weight and/or in architecture (branched chains, rings), there is but one excluded volume integral  $\beta$ ; and any cross-coefficient  $A_{JK}$  is determined by the same parameters that determine the virial coefficients  $A_{JJ}$  and  $A_{KK}$  for binary solutions. The following discussion is limited to such chemically homogeneous species.

It is convenient to generalize equation 18 in the following way<sup>44</sup>:

$$A_{11}/A = 1 - B_{11}z_1 + \dots \quad (42)$$

$$A_{22}/A = 1 - B_{22}z_2 + \dots = 1 - B_{22}z_1 \varepsilon^{\frac{1}{2}} \quad (43)$$

$$A_{12}/A = 1 - B_{12}z_1 + \dots \quad (44)$$

where

$$z_1 = \left( \frac{3}{2\pi b_0^2} \right) \beta n_1^{\frac{1}{2}}$$

refers to polymer 1 and

$$z_2 = z_1 \varepsilon^{\frac{1}{2}}$$

$\varepsilon$  denoting the molecular weight ratio  $M_2/M_1 = n_2/n_1$ . For definiteness we always set  $n_2 > n_1$ . For two linear polymers differing only in chain length,  $B_{12}$  is given by<sup>45,46</sup>

$$B_{12} = \frac{16}{3}(1 + \varepsilon^{\frac{1}{2}}) - \frac{32}{15\varepsilon}[(1 + \varepsilon)^{\frac{3}{2}} - \varepsilon^{\frac{3}{2}} - 1] \quad (45)$$

and  $B_{11} = B_{22} = 2.865$ . The cross-coefficient  $B_{12}$  has been calculated for other combinations<sup>46</sup>: two regular stars with different numbers of branches and/or molecular weights, two rings of different size, a star and a ring, a star and a linear chain, a ring and a linear chain, a comb and a linear chain. Certain generalizations are implied by the ensemble of results. (a) The coefficient  $B_{12}$  always approaches a value characteristic of the smaller member of an interacting pair as  $\varepsilon$  goes to infinity (or to zero). (b) For any two molecules that differ only by the scale factor  $\varepsilon$  (so that  $B_{11} = B_{22}$ ), the condition  $B_{11} < B_{12}$  holds. (c) For geometrically different pairs, there can be ranges of  $\varepsilon$  in which  $B_{12}$  is smaller than both  $B_{11}$  and  $B_{22} \varepsilon^{\frac{1}{2}}$ . It never happens that (d)  $B_{12}$  is larger than both  $B_{11}$  and  $B_{22} \varepsilon^{\frac{1}{2}}$ . Conditions (b), (c) and (d) require respectively that as the second virial coefficient for a binary solute approaches zero it changes monotonically with composition  $w$ , passes through a maximum, or passes through a minimum<sup>47</sup>. The three classes of behaviour of  $A_2$  versus  $w$  reflect completely general statements about the  $A_{JK}$ : a maximum in  $A_2$  means that  $A_{12}$  is the largest of the three  $A_{JK}$ ; a minimum, that  $A_{12}$  is the least; and no extremal point, that  $A_{12}$  is intermediate between  $A_{11}$  and  $A_{22}$ . These relations hold both for  $A_2^{(M)}$  and the virial coefficient  $A_2^{(R)}$  from light scattering.



Turning now to the approximate theories for polymers in good solvents, we note that the Flory-Krigbaum theory is cast in a form that lends itself to calculation of  $A_{12}$ . The Gaussian-sphere model leads to an averaging rule defining  $\zeta_{12}$  for linear chains<sup>36</sup>:

$$\left(\frac{\zeta_{12}}{M_1 M_2}\right)^{\frac{1}{2}} = \frac{2(\zeta_1/M_1^{\frac{1}{2}})^{\frac{1}{2}} (\zeta_2/M_2^{\frac{1}{2}})^{\frac{1}{2}}}{(\zeta_1/M_1^{\frac{1}{2}})^{\frac{1}{2}} + (\zeta_2/M_2^{\frac{1}{2}})^{\frac{1}{2}}} \quad (46)$$

Then  $F(\zeta_{12}) = A_{12}/A$  is obtained from the original Flory-Krigbaum function or from equation 30. A distinctive feature of this theory is the prediction that if  $\varepsilon > 4.24$ , the  $A_{JK}$  fall in the order  $A_{12} > A_{11} > A_{22}$  for any positive pair  $\zeta_1 \neq \zeta_2$ , if none of the parameters of the theory are regarded as adjustable. It follows that this is a sufficient condition for a maximum in  $A_2$  as a function of  $w$  for a binary solute. At first sight this result may seem peculiar; but it appears more ordinary when it is noted that  $\langle s^2 \rangle^{1/2}/n \propto n^{1/2}$  for a random-flight chain, and that hard spheres of unlike diameter and specific volume proportional to the square root of their mass can interact with  $A_{12} > A_{11} > A_{22}$ <sup>48</sup>—if the virial coefficients are expressed in the polymer chemist's units of volume/(weight)<sup>2</sup>.

This prediction of the Flory-Krigbaum theory has inspired a small amount of inconclusive experimentation in search of the maximum. Reference 48 includes a summary of the earlier work of this sort. More recently, Kato, *et al.*<sup>49</sup>, have reported a distinct maximum for mixtures of poly- $\alpha$ -methylstyrene fractions in cyclohexane.

A plot of light-scattering second virial coefficients for mixtures of two (almost) monodisperse polystyrenes (molecular weights  $5 \times 10^4$  and  $38 \times 10^4$ ) in *cis*-decalin at 80°C is shown as Figure 6.<sup>50</sup> The solid curve represents

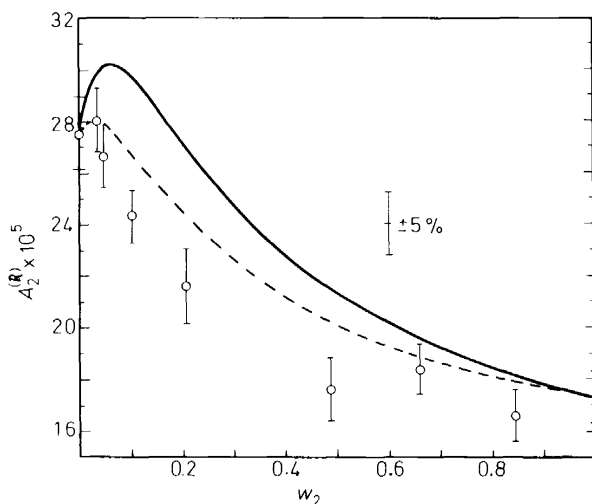


Figure 6. Second virial coefficient<sup>50</sup> (by light scattering) for mixtures of two polystyrenes ( $M_1 = 5.01 \times 10^4$ ,  $M_2 = 38.3 \times 10^4$ ) in *cis*-decalin at 80°C versus weight-fraction content  $w_2$  of the higher molecular weight component in the solute. Solid curve for hard-sphere relation; dashed curve derived from Flory-Krigbaum theory.

the behaviour of hard spheres of dimensions that would yield the measured values of  $A_{11}$  and  $A_{22}$  for the homogeneous polymers. The prominent maximum, far outside the bounds of experimental error, is not reproduced in the data on the mixtures. The Flory-Krigbaum function (the dotted curve) was constrained to fit the experimental data for the homogeneous solutes: specifically Berry's values of  $\psi_1$  and  $\Theta$  were assumed;  $F(\zeta_1)$  and  $F(\zeta_2)$  were then chosen to give the experimental  $A_{11}$  and  $A_{22}$ ;  $\zeta_1$  and  $\zeta_2$  thus fixed were used to get  $\zeta_{12}$  from equation 46; and thence  $F(\zeta_{12})$  and  $A_{12}$  were calculated. This curve is certainly a better representation than the hard-sphere relation although  $A_{12}$  may be marginally too large. The small maximum predicted by the Flory-Krigbaum curve, even if real, would obviously be completely obscured by experimental error. Data<sup>50</sup> (not shown) in the same system at lower temperatures are fitted quite well by this treatment of the Flory-Krigbaum theory; but it must be remembered that in artificially forcing the theory to fit at the ends of the curve, we have avoided a complete test of the theory. A calculation of  $A_{12}^{(R)}$  from the theory without this constraint would not fit the data and would produce a curve with a more prominent maximum.

The main interest attaching to the perturbation calculations of  $B_{12}$  for unlike chains perhaps lies in the extension to polymers in good solvents. In a discussion of this matter, I once proposed<sup>44</sup> that equation 34 could be extended to unlike species by writing

$$A_{12}/A \approx [1 - \exp \{-2B_{12}z_1/\bar{\alpha}^3\}]/(2B_{12}z_1/\bar{\alpha}^3) \quad (47)$$

with  $\bar{\alpha}$  representing an averaged expansion factor applying to *both* members of a binary cluster of unlike species. It can be easily verified that systematic application of the calculations leading to equation 34 to dissimilar chains does result in equation 47 if  $\bar{\alpha}$  is introduced as the common expansion factor. The difficulty is that it is not at all obvious how to obtain or even define  $\bar{\alpha}$ . The suggestion offered above, that  $\alpha$  for a molecule in a cluster can plausibly be taken as that for the isolated molecule, removes this difficulty (though of course it is arbitrary to assume that behaviour established for two like molecules must also hold for two that are very different). But, assuming that each chain is characterized by its expanded-random-flight parameter

$$\zeta_1 = z_1/\alpha_1^3, \quad \zeta_2 = z_2/\alpha_2^3$$

we can carry through the derivation of  $A_{12}$  in a way completely analogous to that for interaction of identical molecules. For two linear chains of different length the result is

$$A_{12}/A = [1 - \exp \{-2B'_{12}\zeta_1/\omega^3\}]/(2B'_{12}\zeta_1/\omega^3) \quad (48)$$

where  $\omega = \alpha_2/\alpha_1$  and

$$B'_{12} = \frac{16}{3} (1 + \epsilon^{\frac{1}{2}}\omega) - \frac{32}{15\epsilon\omega^2} [(1 + \epsilon\omega^2)^{\frac{3}{2}} - (\epsilon\omega^2)^{\frac{3}{2}} - 1] \quad (49)$$

Thus,  $B'_{12}$  is obtained from  $B_{12}$  simply by putting  $\epsilon\omega^2$  in place of  $\epsilon$ . The same transformation can be applied to  $B_{12}$  for any combination of structures for species 1 and 2.

Calculations<sup>51</sup> with equation 49 show that this relation will not predict a discernible maximum in  $A_2$  for ordinarily accessible ranges of  $\epsilon$  and  $\omega$ .

It seems plausible to correlate the appearance of the maximum in  $A_2$  with the degree of molecular interpenetration characteristic of the models: the rigid sphere precluding any overlapping, the soft spheres of the Flory-Krigbaum model allowing more, and the averaging of segment densities leading to equation 49 representing an extreme of penetration.

### THE THIRD VIRIAL COEFFICIENT

The third virial coefficient involves both binary and triple molecular clusters:

$$A_3 = -\frac{N_A^2}{3VM^3} \int g_3(1, 2, 3) d(1) d(2) d(3) + 4A_2^2 \quad (50)$$

where

$$g_3(1, 2, 3) = F_3(1, 2, 3) - F_1(1)F_2(2, 3) - F_1(2)F_2(1, 3) - F_1(3)F_2(1, 2) \\ + 2F_1(1)F_1(2)F_1(3) \quad (51)$$

$F_3(1, 2, 3)$  denoting the triplet distribution function for three molecules. The perturbation procedure<sup>12, 25, 52</sup> gives the first term:

$$A_3 = \frac{1}{3}N_A^2n^4\beta^2M^{-3}(1.664)z + O(z^2) \quad (52)$$

The important thing about this relation is the indication that the two-parameter formalism requires  $A_3$  and  $A_2$  to vanish simultaneously at  $T = \Theta$

Comparatively, the third coefficient has not been much studied either theoretically or experimentally. On the one hand, the mathematical difficulties are unattractive; and on the other, this coefficient can hardly be extracted from data with any great accuracy. The resolution of  $A_3$  from  $A_2$  and from effects of still higher terms is a considerable challenge to the capabilities of experiment.

The chief practical interest in  $A_3$  has been stimulated by the usefulness of a relation between  $A_3$  and  $A_2$ —and even a rather crude approximation may be adequate—to aid in extrapolation of data (say  $\Pi/RTc$  versus  $c$ ) to infinite dilution to obtain accurate values of molecular weight and  $A_2$ .

The simplest reasonable assumption is that  $A_2$  and  $A_3$  are related as for hard spheres

$$A_3/A_2^2M \equiv \gamma = \frac{5}{8} \quad (53)$$

However, this ratio depends on the 'hardness' of the molecules, with  $\frac{5}{8}$  the upper limit. Long ago, W. H. Stockmayer and I devised an approximation<sup>53</sup> based on the Flory-Krigbaum model for intermolecular interactions. Using a fictitious potential function, for which we could easily calculate both  $A_2$  and  $A_3$ , we made graphical comparisons to adjust the parameters in this potential until it best approximated the Flory-Krigbaum potential. We found  $g$  to increase from zero with increasing  $z$ , as expected, and to approach  $\frac{5}{8}$  asymptotically.

From experience, it appears that plots of  $\Pi/c$  versus  $c$  are not satisfactorily linear to as high concentrations as plots of  $(\Pi/c)^{1/2}$  versus  $c$ . Thus, it is interesting to note that with

$$\gamma = \frac{1}{4} \quad (54)$$

$(\Pi/c)^{1/2}$  is a linear function of  $c$ , provided terms of order  $c^2$  can validly be ignored. It has been suggested<sup>5</sup> that this value of  $\gamma$  be assumed routinely with square-root plots in analysis of data to obtain  $M$  and  $A_2$ . In our theory,  $\gamma$  is  $\frac{1}{4}$  for  $\alpha \approx 1.5$ . (The value of  $\gamma$  that linearizes the analogous square-root plot for light scattering is  $\frac{1}{3}$ .)

More elegant approximate theories of  $A_3$  have been worked out by Koyama<sup>54</sup> and by Yamakawa<sup>52</sup>. The first gives practically the same result as our theory and the second overestimates  $\gamma$  (at least it overestimates the upper limit by about twofold).

### BRANCHED POLYMERS: UNSOLVED PROBLEMS

The foregoing discussion has revolved almost entirely about the statistical mechanical 'two-parameter' concept. It has appeared as though a unified treatment of the virial coefficients, the intramolecular excluded volume effect, and (perhaps) the intrinsic viscosity of typical coiling polymers could be substantially achieved within this framework. The success of this general approach is no doubt impressive if we consider only linear chains. However, a confrontation with the extremely limited information so far available on dilute solution properties of branched chains with precisely known structure raises basic questions. The problems are illustrated by the data in *Table 1*: a compilation of thermodynamic and conformational parameters obtained in this laboratory<sup>55, 56</sup> on branched polystyrenes, stars and combs, in two solvents at temperature  $\Theta$  defined by a vanishing second virial coefficient. The data show that dimensions of the comb molecules are abnormally large in comparison with those predicted from random-flight statistics and the known value of  $\langle s^2 \rangle_0/M$  for linear chains. The differences are too large to be accounted for by uncertainty as to the precise structure and heterogeneity of the branched samples. The value of  $\Theta$  appears to be little affected by branching but the decrease for star A-51 and the increase for comb A-68;4 seem to be outside errors in measurement. In all cases for which data are available, but one,  $\psi_1$  is decreased by branching; and in comb A-68;4 the change is very large.

One's first impulse is to explain (or explain away) the data by attributing the anomalies to local effects that arise because every branch point in a chain is, unavoidably, a chemically foreign entity. These effects would be specific to the chemical structure of the branch points and could not be predicted from a general statistical theory. However, even if such local effects were ever important, they would have to be progressively 'diluted out' as the molecular weight is increased with the number of branches held constant—just as end-group effects in linear chains vanish at such high molecular weights that the anomalous groups become an inappreciable fraction of the molecule. It is conceivable that such a dilution effect is revealed in the

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Polymer <sup>a</sup>	Structure	$f$	$M \times 10^{-4}$ (Branches) <sup>b</sup>	$M \times 10^{-4}$ (Backbone) <sup>b</sup>	$M \times 10^{-4}$ (Polymer)	Solvent <sup>c</sup>	$g$ (Calc.) <sup>d</sup>	$\frac{\langle s^2 \rangle_{0,br}}{g \langle s^2 \rangle_{0,lin}}$	$\theta_{br} - \theta_{lin}$	$\frac{\psi_{1,br}^e}{\psi_{2,lin}}$
OW	Star	3	11.2	—	34.8	C	0.778	—	0	0.62
A-48:2	Star	4	40.0	—	190	D	0.625	0.95 <sup>f</sup>	0	—
A-51	Star	6	5.6	—	33.0	D	0.444	0.89 <sup>f</sup>	—	1.00
A-53:2	Comb	24	4.6	133	250	D	0.561	—	-2.0	0.90
						D		1.31	0	0.59
						C		1.21	—	—
A-53:3	Comb	21	4.6	133	223	D	0.593	1.32	—	—
A-68:4	Comb	22	12.0	133	395	D	0.395	1.52	+2.1	0.36
						C		1.48	+1.3	0.25

<sup>a</sup>Data on Sample OW from ref. 55; all others from ref. 56. <sup>b</sup>Experimental molecular weights (light scattering) of precursor chains. <sup>c</sup>C = cyclohexane; D = cis-decalin. <sup>d</sup>Calculated from random flight statistics for regular stars and random combs. <sup>e</sup>Subscripts 'br' and 'lin' designate properties of comparable branched and linear chains. <sup>f</sup>These values rectify a computational error in ref. 56.

data for stars;  $\psi_1$  for star A-48:2 is the same as that for linear chains and this sample has much longer branches than the other two. It is difficult to see, however, how the comb data can be reconciled with a specific effect of branch points: it would have to be very large when less than one monomer unit in 1700 in the entire chain, or less than one in 500 in the backbone chain, is the locus of a branch point.

The seemingly inescapable conclusion is that the data on branched molecules are evidence of a fundamental inadequacy in the statistical treatment of intramolecular and intermolecular interactions. The primary conformational effect of branching is to cause the domain of the branched chain in solution to be smaller than that of the linear chain of the same mass and thus to contain a higher average density of segments. If we recall that the unperturbed state is one in which intersegmental attractions and repulsions are by no means absent, even though the net effect averaged over all conformations vanishes, it is not difficult to imagine that a large change in mean segment density could upset the balance of forces and result in behaviour at variance with that of linear chains. Assuming that a branched chain might have different statistical parameters from a linear one, we can examine possible correlations. For example, the data in *Table 1* suggest that the combination  $\psi_{1,br}[\langle s^2 \rangle_{0,br}/g\langle s^2 \rangle_{0,lin}]^2$ , (for branched and linear chains of the same mass) might be approximately independent of branching. If this is correct, it may be rationalized by considering the quantities  $\beta_0$  and  $nb$  to be invariant with branching while  $n^2\beta_0$  (which is proportional to  $\psi_1$ ) decreases in proportion as  $n^2b^4$  increases. The increase in chain dimensions might be attributed to the increased segment density; and the decrease in  $\psi_1$ , which means a smaller temperature coefficient for  $A_2$ , suggests that their greater segment density makes two branched chains interact as 'harder' molecules than linear chains.

The data and such intuitive explanations are obviously outside the possibilities for the two parameter theory, in which it is presumed that  $n$ ,  $b$ , and  $\beta$  are independent of branching. Thus it is necessary to consider from a basic point of view how the requirements of the theory can logically be relaxed. One likely possibility might be to abandon the postulate of pairwise additivity of segment interactions by introducing an additional temperature-dependent excluded volume parameter  $\beta'$  to account for any difference between the interaction energy for a trio of segments and that for three pairs. A formalism for this has been worked out by Yamakawa<sup>57</sup> for linear chains and can very readily be extended to branched models. In this version the perturbation treatment leads to a series in powers of  $\beta$  and  $\beta'$ . The first term, corresponding to the single-contact approximation in equation 17 is<sup>58</sup>:

$$A_2 = N_A n^2 [\beta + (\frac{3}{2})^{\frac{1}{2}} (5.224 - 2Cn^{-1})(\pi b_0^2)^{-\frac{1}{2}} \beta'] / 2M^2 \quad (55)$$

where  $C$  depends on branching (for linear chains,  $C = 4$ ). With  $C \ll n^{\frac{1}{2}}$ , as will usually be the case, equation 55 exhibits no appreciable effect due to branching. If  $\beta$  and  $\beta'$  vanish at the same temperature  $\Theta$ , as Yamakawa assumes, higher terms in the series have to vanish simultaneously in such fashion that the temperature dependence of  $A_2$  at  $T = \Theta$  cannot be affected

by branching. Consequently this approach does not account for the thermodynamic behaviour of branched chains; and the fact that only the usual segment length  $b_0$  appears in the theory assures that the anomalies in molecular dimensions remain unexplained.

In a somewhat similar spirit one might introduce concentration-dependent potentials of average force between segments<sup>59</sup>. The view attributing the anomalous effects of chain-branching to the intermolecular segment concentration prompts such an approach, but this possibility has not been explored.

A quite different attack on the problem of branched chains is implicit in a paper by Vrij<sup>60</sup> on the conformation of linear chains. Vrij's argument, which follows a derivation of Debye<sup>61</sup>, is based on the idea that the total free energy of a chain conformation must include contributions from gradients of segment density in the chain domain. The procedure, slightly modified<sup>62</sup>, is as follows. A segment  $i$ , at a point denoted by  $\mathbf{r}$  drawn from the origin of coordinates, is picked as a reference point; its total potential  $\phi_i$  is taken as the sum of pairwise interactions with every other segment in the chain. Each pair interaction is governed by the potential of average force  $u(s)$ , a function of the distance  $|s|$  from segment  $i$ . The number-density of segments,  $\rho(\mathbf{r} + \mathbf{s})$ , is expanded in Taylor's series about the locus of segment  $i$ . Multiplication of the series by  $u(s)$  and integration over space gives a series expression of  $\phi_i$ . Another integration, to sum  $\phi_i$  over all  $i$ , gives the total free energy  $\Theta$  of a conformation defined by the segment density function  $\rho(\mathbf{r})$ :

$$\Phi = \frac{\beta''kT}{2} \int [\rho(\mathbf{r})]^2 d\mathbf{r} + \frac{\beta'''kT}{12} \int \rho(\mathbf{r}) \nabla^2 \rho(\mathbf{r}) d\mathbf{r} + \dots \quad (56)$$

where

$$\beta''kT = \int_0^\infty 4\pi s^2 u(s) ds \quad (57)$$

and

$$\beta'''kT = \int_0^\infty 4\pi s^4 u(s) ds \quad (58)$$

The derivation of equation 56 is quite general, assuming only additivity of segment pair interactions. It can obviously be extended to an expression for the free energy of a bimolecular cluster. Equally obviously, equation 56 does not of itself provide definite results; but it does have important implications. It contains two 'exclusion' parameters  $\beta''$  and  $\beta'''$  that will not vanish at the same temperature, except in the special case that  $u(s)$  vanishes for all  $s$ ; and both are multiplied by integrals over chain conformation that depend on molecular weight and branching. Since  $\beta''$  and  $\beta'''$  can hardly enter in the same way into expressions for intramolecular and intermolecular interactions, the temperature at which the unperturbed chain size is attained need not correspond to that for which the second virial coefficient vanishes; and both temperatures may depend on molecular weight and branching.

With the Gaussian-sphere model for a linear polymer chain, equation 56 leads to modifications of Flory's well known theory of chain expansion<sup>5</sup>

(that which gives  $\alpha^5 - \alpha^3 \propto z$ ) and of the Flory-Krigbaum theory of the second virial coefficient. Using these theories, and making a surmise about the magnitude of  $\beta'''$ , Vrij concludes that in ordinary systems the temperature at which  $A_2$  vanishes is not sensibly affected (so that  $\Theta$  need not be redefined) but that unperturbed chain dimensions might be attained only at a temperature measurably below  $\Theta$ , except at very high molecular weight where the effect of  $\beta'''$  vanishes. Whether such an essentially minor correction to a treatment already based on a highly simplified molecular model can have any quantitative significance may be open to question; but it is elementary to show that if it is real for a linear chain, the effect will be greater in a branched chain of the same molecular weight: at  $T = \Theta$ , the branched molecule will be more expanded than the linear one<sup>62</sup>.

We note that  $\beta''$  is a first-order approximation to the excluded volume integral  $\beta$ , obtained by expanding  $\exp \{-u(s)/kT\}$  (see equation 11) and that the second term in equation 56 denotes an excess interaction energy over that obtained by assuming that the local energy density is proportional to the square of the local segment density. The last assumption, common to the various smoothed-distribution models<sup>5, 36</sup> discussed above, is equivalent to the description of the intersegmental interaction in terms of a delta function, as in equation 13. Equation 56, therefore, represents a break with the two-parameter treatments through a relaxation of the strict requirement of short-range interaction. The formalism is not in question, but it remains highly uncertain whether a physically appreciable effect can be accounted for in this fashion.

Berry<sup>56</sup> has studied some of the polymers listed in *Table 1* in good solvents (decalin at  $T > \Theta$  in toluene). I shall not repeat the analysis here but merely note that branching is found to increase  $\alpha$  and to decrease  $A_2$  in the sense predicted from random-flight calculations despite the anomalies in the values of the parameters obtained at  $\Theta$ . For instance, as with an unbranched chain,  $A_2$  remains proportional to  $\alpha^2 - 1$  as both  $A_2$  and  $\alpha$  are varied by changing the temperature; and to a fair approximation the proportionality factor depends on branching in the way predicted by eliminating  $z$  between perturbation expansions for  $A_2$  and  $\alpha^2$ , and retaining only the initial dependence on  $\alpha^2 - 1$ . Further, the magnitudes of  $A_2$  in good solvents can be reasonably correlated, granting some problematical assumptions, by combining  $\psi_1$  and  $\langle S^2 \rangle_0$  obtained at  $\Theta$  with approximate expressions of the form of equation 34 but containing the theoretical values of  $B$  for the branched models.

## CONCLUSION

I have tried in the foregoing discussion to review succinctly the theoretical basis of our present understanding of thermodynamic interactions of flexible-chain polymers in dilute solution and to give some indication of the results of experiment. I have purposely emphasized questions specifically pertinent to the statistical description of chain conformations and have passed over matters of importance less directly related to this. For example, the intersegmental excluded-volume integral  $\beta$  appears throughout; but it is treated



as a parameter to be obtained by independent means, rather than a quantity whose absolute magnitude is to be deduced from physical principles as part of the theory. Conceptually, the last objective can be viewed as belonging to a general theory of fluids, rather than something specific to polymer molecules.

That I have intended the comparisons with experiment to be merely illustrative rather than definitive is my only defence for referring almost exclusively to studies from my own institution. A useful critical analysis of all the relevant experimental literature would require a review far beyond the scope of this one. I think it fair to say, however, that the thermodynamic and molecular-size data for linear polystyrene are as extensive and as reliable as any other available for a particular polymer-solvent system and that recent work from other laboratories serves to confirm the results as correctly representative for ordinary, nonpolar, freely coiling, polymer chains—even though points of interpretation may remain in dispute. As much cannot be said for the behaviour of branched polystyrene documented in *Table 1*; for the effects of branching on the thermodynamic parameters as reported in some other studies<sup>6,3</sup> are in certain respects quite different. In the present state of knowledge it seems bootless to speculate on these discrepancies; reasonable explanations will have to await more extensive and definitive measurements on materials of precisely defined structure.

The challenging questions prompted by the results on branched polymers should stimulate such further studies. In principle, if local segment-concentration effects within a chain domain cause the two-parameter concept to fail for branched chains, it cannot logically be maintained for linear chains. If anomalies are not revealed with linear chains, the reason may just be the circumstance that in a homologous series of linear molecules at a given temperature, molecular weight and segment concentration within the chain domain are not independent variables (and, practically, any change in segment concentration achievable through variation of chain expansion with temperature and solvent is quite limited). Admission of branching as a chain parameter permits radical changes in segment concentration to be made without changing the overall size of the chain domain or the 'goodness' of the solvent. Studies of branched chains should thus permit searching tests of the basic theoretical ideas. Whether elucidation of the behaviour of branched chains will force revisions in the interpretation of observed properties of linear chains remains to be seen. It has already been suggested that measurements of interactions between chains of different length may provide valuable criteria for evaluating approximate theories for the second virial coefficient. It is conceivable that data on such binary solutes or on mixtures of linear and highly branched species might also throw additional light on the more fundamental question of the two-parameter formalism.

In closing, I think it appropriate to call attention to an important new book, Professor Yamakawa's *Modern Theory of Polymer Solutions*, which came to hand as this text was being completed<sup>64</sup>. It provides a comprehensive account of the two-parameter approach to intramolecular and intermolecular interactions, and thence to thermodynamic, configurational, and frictional properties in dilute solutions.

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