From the Department of Chemistry Massachusetts Institute of Technology
Cambridge, Massachusetts, U.S.A.

Problems of the Statistical Thermodynamics of Dilute Polymer Solutions*

By W. H. STOCKMAYER

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SUMMARY:

The current status of the statistical thermodynamics of dilute solutions of chain polymers is reviewed, with particular attention to the interactions between single chain molecules and solvents and to the mutual interactions of two chains.

With respect to the problems of one and two chains, the following topics are considered: the potential of mean force between chain segments and its dependence on the solvent; relationship between lattice and continuum theories; comparison between machine calculations and analytical theories of chain dimensions; exact series and approximate or semi-empirical theories of the osmotic second virial coefficient, and comparison with the experimental data; effects of polydispersity; behavior in mixed solvents. Higher virial coefficients and phase separation are also briefly discussed.

ZUSAMMENFASSUNG:

Der heutige Stand der statistischen Thermodynamik der verdünnten Hochpolymerlösungen wird betrachtet. Folgende Probleme werden diskutiert: das Potential der Durchschnittskraft zwischen Kettenelementen und seine Abhängigkeit von dem Lösungsmittel; die Beziehungen zwischen Gittermodell und Kontinuum-Modell; ein Vergleich zwischen *Monte-Carlo*-Rechnungen und analytischen Theorien der Dimensionen von Kettenmolekülen; verschiedene Theorien des zweiten osmotischen Virialkoeffizienten; der Einfluß der Molekulargewichtsverteilung; das Verhalten in Mischungen von Lösungsmitteln; der dritte Virialkoeffizient und die Phasentrennung.

The object of this paper is to examine certain selected aspects of the statistical thermodynamics of solutions of flexible chain molecules. Since the model proposed by MEYER¹) led HUGGINS²) and FLORY³) to the first successful quantitative theories of polymer solutions at equilibrium, the experimental and theoretical efforts in this field have been very numerous. The books by FLORY⁴) and TOMPA⁵) give rather complete accounts up to about 1954. Here we must be more selective and restrict

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ourselves to some important problems encountered principally in dilute solutions.

1. *Interactions of Solute Molecules and Chain Segments*

One of our purposes is to compare calculations based on explicit lattice models with more formal theories involving integrals over molecular distribution functions. Since the latter are not restricted to any particular model, they must embrace the lattice theories as special cases, as we shall now more specifically recall.

Thorough treatments of molecular distribution functions are given by MÜNSTER[6]) and by HILL[7]), whose treatment we follow. For simplicity, we first consider a classical monatomic substance. Here we shall need only the "generic" singlet and pair distribution functions $\rho^{(1)}(r_1)$ and $\rho^{(2)}(r_1,r_2)$, so defined that $\rho^{(1)}(r_1)\, dr_1$ gives the probability that an unspecified molecule lies in the volume element dr_1 at r_1 and $\rho^{(2)}(r_1,r_2)\, dr_1\, dr_2$ gives the probability that a molecule is in dr_1 at r_1 and another simultaneously is in dr_2 at r_2. These functions are so normalized that

$$\int\limits_{(V)} \rho^{(1)}(r_1)\ dr_1 = N \tag{1.1}$$

$$\iint\limits_{(V)} \rho^{(2)}(r_1, r_2)\, dr_1\, dr_2 = N^2 - N \tag{1.2}$$

where N is the number of molecules. When an open system is treated by the grand canonical ensemble, the average values $\overline{N^2}$ and $\overline{N}$ are to be used, and this leads by means of the well-known formula for the density fluctuation to the equation:

$$\frac{1}{\rho V} \iint\limits_{(V)} \left[\rho^{(2)}(r_1,r_2) - \rho^{(1)}(r_2)\, \rho^{(1)}(r_2)\right] dr_1\, dr_2 = \varkappa\rho kT - 1 \tag{1.3}$$

where $\varkappa$ is the isothermal compressibility, kT has its usual meaning, and ρ is the average number density $\overline{N}/V$. For convenience the above equation is sometimes expressed in terms of the pair correlation function $g^{(2)}$ defined by

$$g^{(2)}(r_1,r_2) = \rho^{(2)}(r_1,r_2)/\rho^{(1)}(r_1)\, \rho^{(1)}(r_2) \tag{1.4}$$

For a fluid, $\rho^{(1)}$ is independent of position and reduces to ρ, while $g^{(2)}$ becomes the familiar radial distribution function $g(\mathbf{r})$ which depends only on the separation $r = |r_1 - r_2|$. In this case, (1.3) reduces to the familiar **Ornstein-Zernike** equation

$$\rho \int_0^\infty [g(r)-1]\, 4\pi r^2 dr = \varkappa\rho kT - 1 \tag{1.5}$$

For liquids below their normal boiling points, the quantity $\varkappa\rho kT$ is only about 0.01 or 0.02, and is therefore negligible compared to unity in first approximation.

Now consider, for contrast, a perfectly ordered lattice. The singlet density is discontinuous and vanishes except at lattice sites:

$$\rho^{(1)}(r_1) = \sum_i \delta(r_1 - Ri) \tag{1.6}$$

where R_i is the position of the i^th^ lattice point. Also, the pair correlation function is unity when r_1 and r_2 are at two different lattice points, zero when both molecules are at the same lattice point, and need not be defined otherwise. Substitution into (1.3) then leads to the result

$$\int \rho^{(1)}(r_1)[g^{(2)}(r_1, Ri)-1]\, dr_1 = -1 \tag{1.7}$$

as is intuitively obvious since the perfect lattice obviously corresponds to a classical absolute zero of temperature. The point we wish to emphasize, however, is that even the most extreme form of the lattice model, although notoriously deficient in many respects[8]), gives a value for the integral of (1.3) which differs only slightly, for dense fluids at low temperature, from the exact value given by (1.5). In the next section this fact permits us to compare analytical expressions for the mean dimensions of chain molecules with those obtained from machine calculations for the lattice model. Conversely, it is clear that essentially no information can be obtained about the functional form of the radial distribution function g(r) from the value of the integral in (1.5), as long as $\varkappa\rho kT \ll 1$.

Distribution functions for systems of polyatomic molecules are discussed by **Hill**[7]). If the molecules are "rigid" (no internal rotations or vibrations of large amplitude) the rotational coordinates can be treated classically and symbolically absorbed in r_1, while the (intramolecular) vibrations can usually be completely ignored. For long flexible chain molecules, the customary pearl necklace model corresponds to treating the interactions between two non-bonded beads (chain segments), whether in the same chain or in two different chains, as those of rigid molecules. The bonding between adjacent beads must of course be appropriately expressed in the complete distribution function of a chain[9,10]) as must all vicinal interactions governing the internal rotations about chain bonds. Detailed study of the last-named interactions has recently[11,12]) been stimulated by the great interest in stereospecific polymers. These details are also essential to formulate the statistical thermodynamics of undiluted polymers[13]). For dilute polymer solutions their effect is contained in the dependence on polymer structure, solvent and temperature of the "unperturbed" root-mean-square distance *a* between adjacent beads of the random-flight model, and we shall not be able to consider them further.

Treatments of the statistical mechanics of solutions in terms of molecular distribution functions[14–16]) lead to the now familiar analogy between osmotic pressure and gas pressure, first exploited for polymer solutions by ZIMM[9]) and subsequently pursued by many authors (cf. Section 3). As is well known, the effects of interactions between rigid solutes, or between non-bonded segments of polymer chains, are expressed for sufficiently dilute solutions in terms of the binary cluster integral[17]):

$$\beta = \int_0^\infty [1-g^*(r)]\, 4\pi r^2 dr \qquad (1.8)$$

where $g^*(r)$ is the correlation function for solute particles (or segments) at infinite dilution in the chosen solvent. Frequently the result is stated in terms of the pair potential of average force[7]), defined by

$$w(r) = -kT \ln g^*(r) \qquad (1.9)$$

It is all too tempting to forget that $w(r)$, although formally taking the place of a potential energy for solute-solute interactions, depends intimately on solvent-solute and solvent-solvent interactions as well. Also, $w(r)$ is a complicated function of separation (and perhaps orientation) even in the simplest systems. Consider, for example, a classical fluid mixture of monatomic isotopes, obviously an ideal solution. In this case $g^*(r)$ is exactly the radial distribution function $g(r)$ for any pair of molecules in the fluid, and thus would undulate at short range, as would $w(r)$, even if the molecules were hard spheres without attraction.

It can also be seen from (1.5) that, with the neglect of compressibility, β is equal in this case to the molecular volume ρ^{-1}, a well known result[9,16]) for an ideal solution.

It is again instructive to consider the extreme lattice model. If the species of a lattice solution mix randomly and without change in lattice energy, the correlation function behaves as for a pure lattice, leading to the equivalent of (1.8):

$$\beta = \rho^{-1} \int [1-g^*(r_1,Ri)]\, \rho^{(1)}\, (r_1)\, dr_1 = \rho^{-1} \tag{1.10}$$

with the aid of (1.7), again the ideal solution.

The above examples should make it clear that (in analogy with the earlier discussion of pure fluids) very little can be learned about $g^*(r)$ or $w(r)$ from values of β over a restricted range of temperature. Thus, *any* function $w(r)$ with a repulsive core at small r and attraction for some range of r must give positive β at high T, negative β at low T and vanishing β at an intermediate BOYLE or FLORY temperature Θ. Special and analytically convenient forms for $w(r)$, such as that employed by KURATA, YAMAKAWA, and TERAMOTO[18]), therefore have no great fundamental significance, but almost any such function can be used with impunity, provided its short-range nature is preserved, as required by the inequality

$$\beta \ll (\overline{R^2})^{3/2} \tag{1.11}$$

where $\overline{R^2}$ is the mean square displacement length of the chain molecule considered. It is physically quite unrealistic, however, to speculate about the detailed temperature dependence of β by using such a special simple form for $w(r)$, e.g., a LENNARD-JONES 6–12 function[19]); nor can the parameters derived from such expressions be regarded as any more significant from a molecular standpoint than macroscopic parameters such as FLORY's[4]) Θ and ψ_1.

2. *Dimensions of Chain Molecules*

It now seems well established that the configurations of flexible chain molecules deviate from the statistics of random flights because of the interactions between non-bonded segments, as measured by the cluster integral or "excluded volume" β of Section 1. The effects of these interactions are often expressed in terms of the expansion factor[4]) α, conveniently defined*) by

$$\alpha^2 = \overline{R^2}/\overline{R_0^2} \qquad (2.1)$$

where R^2 is the mean square displacement length of a chain and R_0^2 is its value in the absence of such interactions, i.e. at $T = \Theta$ where $\beta = 0$. Provided that clusters of three or more segments can be ignored, as seems almost certain, the expansion factor for long chains is a function of a single variable[10]), which may be written

$$\begin{aligned} z &= (3/2\pi\overline{R_0^2})^{3/2}\,\beta n^2 \\ &= (3/2\pi)^{3/2}\,\beta a^{-3}\,n^{1/2} \qquad (2.2)\end{aligned}$$

for a chain of n segments, where *a* as earlier is the unperturbed effective length of a link. The function is known only for small z:

$$a^2 = 1 + \frac{4}{3}z - \left(\frac{16}{3} - \frac{28\pi}{27}\right)z^2 + - - \qquad (2.3)$$

the linear term having been derived many times and the quadratic term being due to FIXMAN[22]). It seems unlikely that many more terms in this series will yield to exact treatment.

FLORY long ago[23]) obtained by means of an approximate theory the closed expression

$$\alpha^5 - \alpha^3 = 2C_M M^{1/2}\,\psi_1\,(1 - \Theta/T) \qquad (2.4)$$

When the notations are brought into correspondence[24]), we find

$$\beta = 2V_1\psi_1\,(1 - \Theta/T) \qquad (2.5)$$

where V_1 is the molecular volume of the solvent, and finally (2.4) becomes

$$\alpha^5 - \alpha^3 = Cz \qquad (2.6)$$

where the constant C has the value $3^{3/2}/2 = 2.60$, or about twice that needed to secure agreement with the exact series (2.3) for small z.

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*) For the purpose of this discussion the difference between variously defined expansion factors, caused by the non-GAUSSian character of the chain, can be ignored. However, for an exact interpretation of frictional properties, this difference is very important, as discussed in the paper of M. KURATA[20,21]).

Several derivations of the form (2.6) have now been given[25,26]) which lead to alternative values for C, but it is difficult to assess the validity of the approximations used. No alternative closed expression for $\alpha(z)$ has been proposed.

It is found[21]) that if C is set equal to 4/3, thus forcing agreement with the linear term in (2.3), the coefficient of z^2 in the expansion of (2.6) is in fair agreement (2.67 compared to 2.08) with the correct value. Moreover, this value of C was demonstrated[24]) to agree with the experimental results for at least one system near the Θ-point, and other examples are now known[18]) which give similar agreement. The proposal[24]) to adopt this revised value of C in general was not accepted by OROFINO and FLORY[27]), who supposed that at higher values of α and z the original constant would be superior. We shall now show, however, that the most recent *Monte Carlo* calculations of WALL and his co-workers[28]) are in distinctly better agreement with the lower value of C.

The calculations of WALL and ERPENBECK are for a diamond lattice with unit step length. From Section 1, the appropriate value of β is the volume per lattice point, which is $(4/3)^{3/2}$ for this lattice, while the effective link length *a* is $\sqrt{2}$ for the tetrahedral valence angle. The

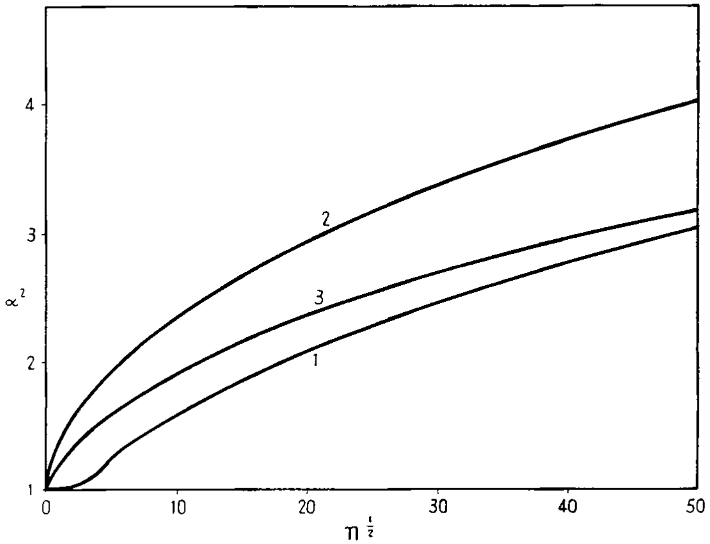

Fig. 1. Expansion factors on a diamond lattice plotted as α^2 against $n^{1/2}$: Curve 1, *Monte Carlo* calculations of WALL and ERPENBECK; Curve 2, FLORY's theory eq. (2.6) with C = 2.60; Curve 3, FLORY's theory with C = 1.33

resulting value of z is $\pi^{-3/2}\, n^{1/2}$, and the corresponding plots of α^2 against $n^{1/2}$ are shown in Fig. 1 for both $C = 2.60$ and $C = 1.33$. For comparison with these curves, the results of WALL and ERPENBECK[28]) are also plotted. These authors fitted their numerical results, extending up to $n \simeq 800$, by the equation

$$\log_{10} \overline{R^2} = 0.15 + 1.18 \log_{10} n \tag{2.7a}$$

but these are represented almost as well by

$$\log_{10} \overline{R^2} = 0.10 + 1.20 \log_{10} n \tag{2.7b}$$

which has the virtue of agreeing with the asymptotic form of (2.6). In the absence of excluded volume effects, the dimensions of chains with tetrahedral valence angles are given by

$$\overline{R_0^2} \cong 2n - \frac{3}{2} \tag{2.8}$$

which with (2.7b) leads to

$$\log_{10} \alpha^2 = -0.20 + 0.20 \log_{10} n + 0.326\, n^{-1} \tag{2.9}$$

the equation used in plotting curve 1 of Fig. 1. It is seen that (2.6) gives higher results than the *Monte Carlo* curve for both values of C, but the lower value is considerably the better at all values of α. It is interesting to remark that for very high *n* curve 3 falls below curve 1, but since this occurs several decades beyond the range of the numerical work it is at present without significance.

Similar calculations, though over a much more restricted range of *n* can be based on the older results of WALL, HILLER, and ATCHISON[29]) for the simple cubic lattice, and lead to similar results. We thus again conclude that (2.6) with $C = 1.33$ (or perhaps better, $C = 1.28$ to agree with the radius of gyration, as opposed to the displacement length) is the best available expression for the expansion factor of an isolated chain molecule in solution.

The above discussion is largely concerned with chain molecules in good solvents, for which $\beta > 0$, but the case of strong net attractions ($\beta < 0$) between the polymer segments should also be considered. A case of great interest is found in those natural and synthetic polypeptides which can form stable helices in solution. The special statistical mechanics of the helix-coil transformation in such (necessarily stereospecific) macromolecules is already well developed$^{30-33}$), but will not be discussed here.

It can be expected that even atactic chain molecules must collapse to a rather dense form (very small α) if the net attraction between their parts becomes sufficiently large. LANGMUIR, for example, long ago pointed out^{34}) that, because of the intramolecular VAN DER WAALS forces, hydrocarbon chains in a dilute gas must on the average be rolled up into spheres with a density comparable to that of the liquid phase. An exact theory of this effect would be prohibitively difficult. A very rough value of the "collapse point" is afforded by the observation that equation (2.6) has no positive real roots unless z is more positive than a critical value:

$$z^* = -\frac{2}{3C}\left(\frac{3}{5}\right)^{5/2}$$

which with the preferred value of C corresponds to $z^* = -0.14$. When $z > z^*$, there are two positive real roots, of which the larger corresponds to the observable state of the chain, but for $z < z^*$ only the completely collapsed coil is stable. This prediction is not without interest, for example in connection with the mechanism of polymerization in precipitating media, but it is not easily verified under equlibrium conditions because the solubility of the polymer is too low.

The dimensions of branched molecules cannot be considered here, but an unresolved conflict may be mentioned. According to a formula of PTITSYN^{35}) as quoted by VOLKENSTEIN^{11}), the expansion factor of a branched polymer exceeds that for a linear chain of the same molecular weight, but FIXMAN^{22}) came to the opposite conclusion in evaluating the linear term in z for a cruciform molecule. It seems best for the experimental study of branching to avoid this problem by working at the Θ-temperature.

3. *The Second Virial Coefficient*

In this section we restrict ourselves to a brief physical discussion of recent theories of the osmotic second virial coefficient, A_2, as defined by the osmotic pressure expansion:

$$P/c\,RT = M^{-1} + A_2c + A_3c^2 + \cdots \tag{3.1}$$

in which P is the osmotic pressure, M the molecular weight of the solute, and c the concentration expressed as mass of solute per unit volume of solution. The general formulation of A_2 as a definite integral over molecular distribution functions was first given for flexible chain polymers by ZIMM[9]). Since there are several excellent recent discussions[36–38]) of this mathematical foundation it will not be treated in detail here.

According to the original lattice theories[2,3]) A_2 should be independent of molecular weight; but the first steps toward a theory of dilute polymer solutions[39,9]), reinforced by better experimental results, clearly showed that A_2 is a decreasing function of M. It is perhaps discouraging to admit that in spite of almost fifteen years of further effort there still is no completely satisfactory theory of the function $A_2(M)$. The study of this function remains a central problem of polymer solution theory, for as long as the functional dependence of A_2 on M (and also, it must be emphasized, on molecular weight distribution) is not firmly established, it is impossible to discuss unambiguously the interactions of chain segments with each other and with solvents.

In almost all the existing theories of A_2, the molecular model requires the introduction of two parameters. These have already been encountered in the discussion of single chains, and are the effective unperturbed segment length a and the cluster integral β, or equivalent quantities*). For the interaction of two identical chains, these theories may all be cast into the form

$$A_2 = (N_0\beta n^2/2M^2)\,h(z) \tag{3.2}$$

where N_0 is AVOGADRO's number, and n and z are defined as in equation (2.2). The function $h(z)$ starts from unity at $z = 0$ and decreases monotonically with increasing z. It seems useful, before discussing this function in more detail, to ask whether the existing experimental data support the assumption that two parameters are sufficient. To investigate this question we may first combine equations (2.1) and (2.2) with (3.2) to obtain the result

$$\frac{A_2M^2}{N_0(\overline{R^2})^{3/2}} = \left(\frac{2\pi}{3}\right)^{3/2}\frac{z\,h(z)}{2\alpha^3} \tag{3.3}$$

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*) It may be objected that the segment size must be chosen, and hence that the number of segments n in the molecule constitutes a third parameter. However, as remarked elsewhere[24]), the combinations βn^2 and na^2, which alone occur in the final equations for long chains, are invariant to the choice of segment size, so that there are only two significant parameters. It is thus permissible and convenient to follow FLORY by choosing a segment to have the same volume as a solvent molecule.

Recalling from (2.3) that there is an unique relation between α and z, we see that a plot of the dimensionless left-hand member of (3.3) against α, which can be obtained from light scattering measurements, should produce a single "reduced" curve for all well-fractionated polymers in all solvents. Since light scattering data for the computation of α are not so readily available, we have preferred to evaluate $\overline{R^2}$ and α from intrinsic viscosity data by means of the FLORY-FOX relations[4])

$$[\eta]\, M = \Phi\, (\overline{R^2})^{3/2} \tag{3.4}$$

$$[\eta]/[\eta]_\Theta = \alpha^3 \tag{3.5}$$

It is now well established, both experimentally[40]) and theoretically[20,38,41]), that the exponent of α in (3.5) is somewhat less than 3, and hence that Φ is not strictly constant but decreases with increasing molecular weight or solvent power. However, since the newer theory still makes the ratio $[\eta]/[\eta]_\Theta$ a function only of α, except for quite low values of the "draining parameter" of the intrinsic viscosity calculation, the use of the FLORY-FOX relations should not seriously hinder the construction of a reduced curve. By combining equations (3.3) to (3.5), we obtain

$$\frac{A_2 M}{[\eta]} = \frac{N_0}{2\Phi}\left(\frac{2\pi}{3}\right)^{3/2} \frac{z\, h(z)}{\alpha^3} = f(\alpha) \tag{3.6}$$

A plot inspired by equation (3.6) is shown in Fig. 2, where $A_2M/[\eta]$ is plotted against (α^2-1) from the experimental data selected by OROFINO and FLORY[27]). The values of $[\eta]_\Theta$ required to compute α were taken from FLORY's book[4]) with the exception of those for polymethyl methacrylate, which come from the work of CHINAI and BONDURANT[42]). The experimental points shown in the graph certainly do not lie very closely on a single curve, but if the data for methyl methacrylate polymers (represented by squares) are omitted the remaining points define a fairly definite curve. With regard to the methacrylate results, it may be pointed out that the agreement with the other polymers would have been even poorer if we had used the $[\eta]_\Theta$ values given in FLORY's book*) instead of the lower figures of CHINAI and BONDURANT. If the true $[\eta]_\Theta$ were still lower by about 10 %, or if the viscosity "drainage parameter" were abnormally low for this polymer, the discrepancy could be explained without abandoning the two-parameter theory of A_2. It would obviously

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*) Reference [4]), p. 618, Table XXXIX.

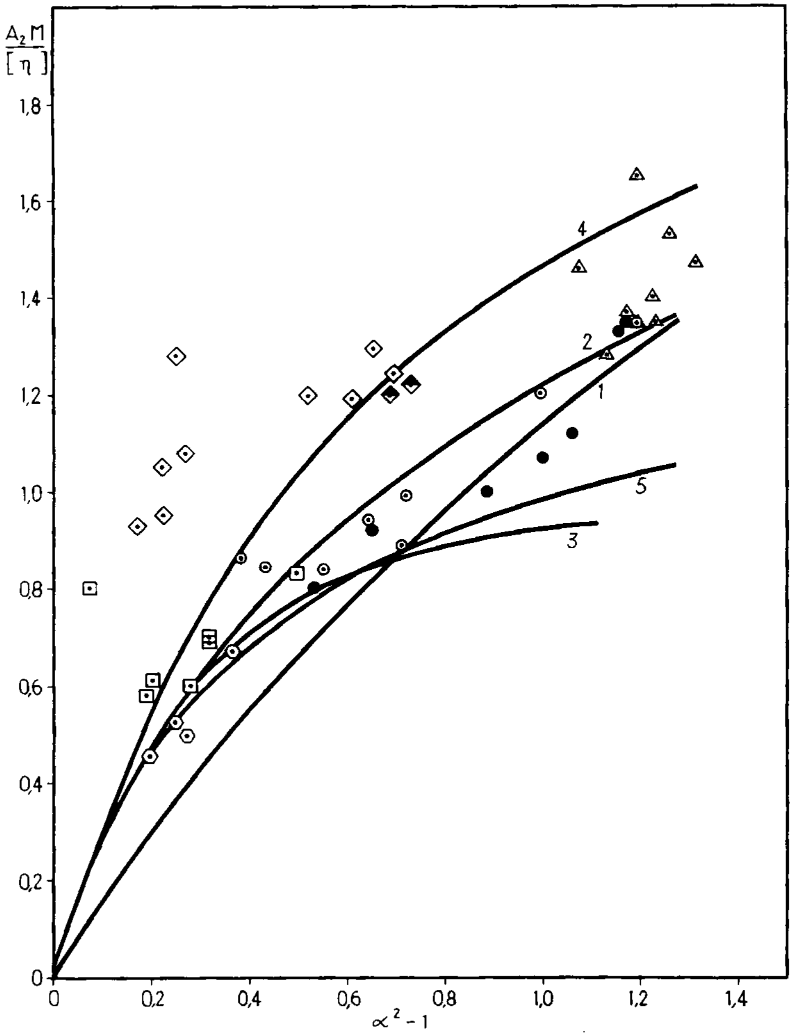

Fig. 2. Reduced second osmotic virial coefficients, plotted as $A_2M/[\eta]$ against (α^2-1). Reference numbers and equations refer to the text.

Experimental points:

- ○ Polystyrene in toluene
- □ Polystyrene in butanone
- ● Polyisobutylene in cyclohexane
- ⬡ Polyisobutylene in benzene
- △ Polyvinyl acetate in butanone
- ◇, ◆ Polymethyl methacrylate in acetone

Curves:

1. FLORY-KRIGBAUM, with original constants, Eq. (3.9.) — 2. FLORY-KRIGBAUM, with modified constants, Eq. (3.11). — 3. CASASSA[50,52]), Eq. (3.12). — 4. KRIGBAUM[54]), empirical Eq. (3.13). — 5. STOCKMAYER[36]), empirical, Eq. (3.14).

be valuable to repeat the above analysis with light scattering data instead of viscosities. Ignoring this difficulty for the moment, we accept the existence of at least an approximate reduced curve and now consider the merits of the theories which pretend to predict it.

According to the formal theory, A_2 is an integral over all configuration of two chain molecules, and the integrand is proportional to the difference between the actual probability of a configuration and probability that would result if all interactions between the two chains were negligible. ZIMM's expansion$^{16)}$ of this integrand precisely resembles the cluster expansion of the theory of gases (see, for example, references$^{6)}$ and $^{7)}$), involving sums of products of the "short range" functions, $f_{ij} = [g^*(r_{ij}) - 1]$, for individual pairs of chain segments. A product of k such f-functions has a negligible value except when the indicated k pairs of segments are actually quite close to each other, and after integration yields a contribution to A_2 which is proportional to β^k. The sum of all such contributions with a given value of k is usually called the k-contact term. ZIMM evaluated the first two terms, and the third has been treated by ALBRECHT$^{36)}$ and YAMAKAWA$^{37,38)}$ who considered most rigorously the effects of intramolecular contacts within the separate chains. No complete higher terms are known, although certain special types have been studied$^{36)}$. We therefore have, in terms of the function of equation (3.2).

$$h(z) = 1 - 2.865z + 18.51\,z^2 - \cdots \qquad (3.7)$$

where the third term is not quite complete. This expression, like (2.3), is useful only in the vicinity of the Θ-temperature where z is small. It has been tested in this region$^{37,38)}$ with satisfactory results. The corresponding initial slope in Fig. 2 depends on the choice of the viscosity constant Φ, which is further discussed below.

As in the single-chain problem of Section 2, a theory which aims at a closed expression for A_2, suitable for all values of z, must be based on a simplified physical model or on equivalent mathematical approximations. Again the pioneer in the construction of such theories was FLORY, who represented the polymer molecule as a swarm or cloud of segments with a fixed spherically symmetrical distribution about the center of mass, thus smoothing out the chain-like connectivity of the actual macromolecule. In FLORY's first theory of this type$^{39)}$, the segment cloud was chosen to be a sphere of constant density, but this model has not been widely used. Somewhat later, FLORY and KRIGBAUM$^{43,44)}$ constructed their now well known theory based on a GAUSSian distribution of chain segments about the center of mass. Their results were shown by GRIMLEY[17]) to follow from the equivalent mathematical assumption that the complete internal distribution function of a chain of n segments is equal to a product of n independent GAUSSian functions, one for each segment, and all with the same modulus. This assumption does not give the correct[45, 46]) average segment density for a random-flight chain.

ISIHARA and KOYAMA[47]) have repeated the calculation with the proper density function, but the effect of this change on the final result is not very great, and it appears that in general[48]) the precise choice of the density function is not crucial. All smoothed-density theories may therefore be discussed together. A close approximation to the definite integral appearing in the FLORY-KRIGBAUM theory was reported by OROFINO and FLORY[27]). In the notation of this paper, their formula is

$$h(z) = (C_2 z \alpha^{-3})^{-1} \ln(1 + C_2 z \alpha^{-3}) \tag{3.8}$$

with $C_2 = 2.30$.

Tests of the FLORY-KRIGBAUM theory[6, 29]) have shown that it predicts the general magnitude of A_2 quite well if FLORY's theory of the expansion factor is used (in our notation, equation (2.6) with $C = 2.60$), but that A_2 is not predicted to decrease rapidly enough with increasing molecular weight[49]. This may also be seen from the full curve labelled 1 in Fig. 2, which represents the equation

$$\frac{A_2 M}{[\eta]} = 4.14 \log_{10} [1 + 0.885 (\alpha^2 - 1)] \tag{3.9}$$

This equation is obtained from equations (2.6), (3.6) and (3.8), with the numerical constants $C = 2.60$, $C_2 = 2.30$ and $\Phi = 2.2 \cdot 10^{23}$. The last of these figures*) is lower than the theoretical value of $2.87 \cdot 10^{23}$ (strictly[20]) applicable only at $T = \Theta$) but it is more appropriate to calculations for good solvents, and without any allowance for the effects of polydispersity.

Expansion of the logarithm in (3.8) for small z gives, with $C_2 = 2.30$,

$$h(z) = 1 - 1.15\, z + \cdots \tag{3.10}$$

showing in comparison with (3.7) that the magnitude of the double-contact term is seriously underestimated. In analogy with a manoeuvre in Section 2. we may read just the value of the constant in (3.8) to $C_2 = 5.73$, thus securing the correct value of the double-contact term. If we

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*) The value is appropriate to intrinsic viscosities expressed in ml.g.$^{-1}$.

preserve consistency by also taking $C = 1.276$ for equation (2.6), the analog of (3.9) is found to be

$$\frac{A_2M}{[\eta]} = 1.65 \log_{10} [1 + 4.50 (\alpha^2-1)] \qquad (3.11)$$

which is shown as Curve 2 of Figure 2. The improvement over Curve 1, particularly at low z, is apparent.

The above device of adjusting the constants of the smoothed-density expressions to force agreement with the exact perturbation theories for small z gives surprisingly good results for much larger values of z. This is perhaps sufficient justification for its practical use, yet from the theoretical point of view it leaves something to be desired, since in a spherical smoothed-density model all fluctuations of the segment distribution from its long-time average are necessarily ignored, as is the specific chain-like connection of the segments.

CASASSA and MARKOVITZ$^{50)}$ have taken an important step toward an improved theory. They assumed that the conditional probability of a multiple-contact configuration, given the existence of a first contact, may be written as a product of independent pair probabilities. This assumption automatically gives the correct double-contact term. To take approximate account of the effects of intramolecular contacts, CASASSA and MARKOVITZ followed FLORY and KRIGBAUM by assuming GAUSSian probabilities uniformly modified by the expansion factor α. Their treatment then leads to a result approximated to within one per cent by the simple function

$$h(z) = [1 - \exp(-Kz\alpha^{-3})]/Kz\alpha^{-3} \qquad (3.12)$$

with $K = 5.68$. By essentially similar but more intuitive arguments, this expression was also derived by FIXMAN$^{51)}$. Very recently, CASASSA$^{52)}$ has modified the theory by recognizing that after a first intermolecular contact is established the expansion factor α_2 that should be used in the probabilities for subsequent contacts must be greater than α for a single chain. Following FIXMAN's methods$^{22)}$, he computes α_2 for the cruciform structure formed from the two chains by their first contact, and then uses this quantity in place of α in equation (3.12). The value of h(z) is thereby slightly increased, but it remains somewhat low, as can be seen from Curve 3 of Fig. 2, which represents this modified form of (3.12). It must be remembered that no constants in this theory have been empirically adjusted to give improved agreement with the experimental data, and from this point of view it is the best so far proposed.

Another and somewhat different statistical theory taking approximate account of the connected nature of the chain has recently been constructed by Krigbaum and his collaborators[53]). It cannot be discussed further here, but the agreement with experiment is reported to be good.

Two other curves have been drawn in Fig. 2, corresponding to two semiempirical equations:

$$\frac{A_2M}{[\eta]} = 2.27\,(1 - \alpha^{3} - 1) \qquad (3.13)$$

proposed by Krigbaum[54] and

$$\frac{A_3M}{[\eta]} = \frac{3.21\,(\alpha^2-1)}{1 + 2.25(\alpha^2-1)} \qquad (3.14)$$

by the writer (see reference[36])). Both are seen to be inferior to the modified Flory-Krigbaum-Orofino expression (Curve 2) of equation (3.11), which is recommended for practical calculations at the present time.

Orofino and Flory[27]) have elaborated the smoothed-density model by introducing a third parameter corresponding to triple clusters of segments, analogous to the third virial coefficient of a monatomic gas. The greatest effect of the extra parameter is produced at low molecular weights, but it seems in all cases to be rather small.

The effect of molecular weight distribution on A_2 has been much less studied. The double contact term of the perturbation theory can be evaluated without difficulty for two chains of unlike size, but no simple average of the two molecular weights emerges. The Flory-Krigbaum theory predicts that the A_2 value for two different chains can sometimes exceed the values for both like pairs of chains. This prediction seems rather *surprising at first but it has been experimentally verified*[55]).

The temperature dependence of A_2 remains to be discussed. The parameters a and β both depend on T, the dependence of β on T being greater in most cases. Unless the measurements extend over a very wide temperature range, it is very probable that a linear form for β, as in equation (2.5) with constant values of ψ_1 and Θ, will suffice. This does *not* imply a linear dependence of A_2 on T^{-1}, as all powers of β occur in the function h(z) and curvature is to be expected in any case.

We close this section by repeating our opinion that it is imperative to bring the molecular weight problem in the theory of A_2 under better control before speculating too extensively on the magnitudes of interaction parameters such as FLORY's ψ_1 and Θ and their molecular structural significance.

4. *Mixed Solvents*

Only a very restricted topic relating to the behavior of polymers in mixed solvents will be briefly discussed. This is the problem of solvation, which is here understood to mean preferential adsorption of one solvent component to the polymer. The phenomenon is of some practical importance because it affects the determination of molecular weights by several methods, for example by light scattering if the solvent components have different indices of refraction. It is also important in the density-gradient ultracentrifuge method of MESELSON, STAHL and VINOGRAD 56, 57), which is intriguing because of the possibility it offers in principle for the measurements of quite high number-average molecular weights. For both cases the thermodynamic quantity required is the same. With subscripts 1 and 2 for the solvent components and 3 for the polymer, the desired quantity is the limit at vanishing c_3 of

$$\lambda' = \left(\frac{\partial c_2}{\partial c_3}\right)_{T,P,\mu_1} = -\frac{(\partial\mu_2/\partial c_3)_{T,P,c_2}}{(\partial\mu_2/\partial c_2)_{T,P,c_3}} \tag{4.1}$$

where *c* denotes weight concentration and μ chemical potential.

Since the number of segments in contact within a coil is much smaller than the total number of segments, λ' is fortunately independent of the polymer molecular weight. From the FLORY-HUGGINS equations for a ternary system 4), it is predicted to have the form

$$\lambda' = \frac{M_2V_3v_2[\chi_{21}(v_2-v_1) + \chi_{23} - l^{-1}\chi_{13} + l^{-1} - 1]}{M_3V_2[v_1 + l^{-1}v_2 - 2\chi_{21}v_1v_2]} \tag{4.2}$$

where the v_i are volume fractions, $l = V_1/V_2$, V_i molecular volumes and χ_{ij} interaction coefficients. This equation not only states precisely how λ' depends on solvent composition but also indicates that it could be predicted from a knowledge of the three separate binary systems 1–2, 1–3 and 2–3. A recent study 58) by light scattering of the system benzene-cyclohexane-polystyrene has shown, however, that a ternary interaction parameter χ_{123}, which is not found in any binary system, is required to fit the results. This is perhaps not surprising in a system of rather non-spherical even though non-polar solvent molecules. Physically, it means that the interactions of a benzene molecule with a cyclohexane molecule are changed when both are brought near a polystyrene chain. Practically, it complicates the interpretation and prediction of intrinsic viscosities[59]), solubilities[4]) and other properties in mixed solvents.

5. *The Third Virial Coefficient and Phase Separation*

The general statistical theory of concentrated polymer solutions is not considered here, but a discussion of the third osmotic virial coefficient A_3 is appropriate to a treatment of dilute solutions for several reasons[4]): (1) a knowledge of A_3 is very useful in extrapolating experimental results to obtain accurate values of A_2; and (2) a method of obtaining the entropy parameter ψ_1 from phase separation experiments[4]) depends on the value assumed for A_3, as will be indicated.

The theory of A_3 has not to the writer's knowledge been treated since his paper with CASASSA[60]), which gave an approximate treatment based on the smoothed-density model. There the dimensionless ratio A_3/MA_2^2 was evaluated as a function of the expansion parameter α, and was predicted to rise monotonically from zero at $\alpha = 1$ (i.e. at $T = \Theta$) to the hard-sphere value of 5/8 at very large α. From the point of view of the basic statistical theory[16]), it is extremely unlikely that A_3 should vanish exactly at $T = \Theta$, since it contains contributions from the ternary clustering of segments. However, there are many more possibilities for binary clustering, so that at small but non-vanishing z the dominant term should be contributed by configurations in which each of the three chains makes one contact with each of the two others. We have evaluated this term, and find

$$A_3 = 4DN_0^2\beta^2n^4z/3M^3 + \cdots \tag{5.1}$$

where

$$D = \int_0^1\int_0^1\int_0^1\int_0^\xi\int_0^\eta\int_0^\zeta (x + y + z)^{-3/2}d\xi d\eta d\zeta dx dy dz \sim 0.208$$

With the aid of (2.6) and (3.2) this leads to

$$A_3/MA_2^2 = 1.73\,(\alpha-1) + \cdots \tag{5.2}$$

which is to be compared with the relation

$$A_3/MA_2^2 \sim 1.03\,(\alpha-1) + \cdots \tag{5.3}$$

given by the approximate60) theory. This seems quite satisfactory agreement.

The separation of a polymer solution into two liquid phases has been extensively treated by FLORY4). For high molecular weights, it suffices to consider the osmotic pressure series (3.1) terminating at the term in A_3. The first and second derivatives of P with respect to c are simultaneously zero at the critical point, and this gives two relations from which critical concentration and temperature can be found:

$$-A_2 c = M^{-1} = 3A_3 c^2 \qquad (5.4)$$

If we recall that A_3 contains16) a ternary-cluster term A_3^0 independent of M which does not vanish at $T = \Theta$, and that the other terms are negligible in the small temperature range near this point, we may find the critical temperature T_c from

$$-A_2 = (3A_3^0/M)^{1/2} \qquad (5.5)$$

The FLORY expression4) for T_c is obtained only if we replace the function h(z) in (3.2) by unity and use the special FLORY-HUGGINS value $\bar{v}^3/3V_1^2$ for A_3^0, where $\bar{v}$ is polymer specific volume. More generally, we may put

$$A_2 \sim \frac{\bar{v}^2 V_1^{-1}\psi_1(1-\Theta T^{-1})}{1 + EM^{1/2}\bar{v}^2 V_1^{-1}\psi_1(1-\Theta T^{-1})} \qquad (5.6)$$

where E is a constant*) easily obtainable for any assumed value of the double-contact term in A_2. The critical temperature then is given by

$$\bar{v}^2 V_1^{-1} \psi_1 (\Theta T_c^{-1} - 1) [1 + E(3A_3^0)^{1/2}] = (3A_3^0/M)^{1/2} \qquad (5.7)$$

and it is seen that, although a plot of T_c^{-1} against $M^{-1/2}$ may always be extrapolated to find Θ, it is not possible to evaluate the entropy parameter ψ_1 without accurate knowledge of A_3^0. From this point of view, the discrepancy4) between ψ_1 values obtained from precipitation temperatures and those obtained from dilute solution measurements is not surprising.

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* Here we ignore the temperature dependence of *a*.

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