

INTRAMOLECULAR INTERACTIONS IN POLYMER CHAINS

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1. INTRODUCTION

As is known, polymer molecules consisting of large numbers of repeating monomeric units are long chains, ordinarily made of carbon atoms (the chains may also contain atoms of other elements). Because of the limited free rotation about the single bonds of the polymer chains, each polymer molecule may have an enormous number of different conformations. Hence the experimental mean values of various quantities characterizing the molecule must be calculated by averaging over all possible conformations of the molecule (these quantities depend on the values of the corresponding quantities for the monomeric units).

Each conformation of the chain is defined by the set of angles ϕ_i which characterize the rotations of the various links of the chain (Fig. 1) about the neighboring links, as measured from a certain given position. Ordinarily, this position is taken to be the so-called trans-conformation of the links in the chain. Here, the links $i-2, i-1$ and i lie in a plane, and link i is parallel to link $i-2$ (Fig. 1) The probability of a given macro-state of the chain (e.g., that defined by the distance between the ends of the chain) obviously depends both on the number of micro-states corresponding to it (the micro-states being defined by the set of angles ϕ_i), and on the energies of these micro-states. If rotation about the bonds in the chain were completely free, all possible sets of angles ϕ_i would correspond to the same energy. Then the probability of the macro-state would be determined solely by the number of micro-states corresponding to it, i.e., by an entropy factor alone. If the various sets of ϕ_i 's correspond to different energies, then the probability of

the macro-state of the chain is also determined by energetic factors.

On the basis of the analogy between the conformations of a polymer chain and the paths traversed by diffusing particles, we may state that in the general case, the distribution function for the vector h between the ends of the chain has the form

$$W(\mathbf{h}) = \frac{1}{8\pi^3} \int_{-\infty}^{+\infty} e^{-i(\mathbf{p}, \mathbf{h})} A_Z(\mathbf{p}) d\mathbf{p}, \tag{1}$$

where

$$A_Z(\mathbf{p}) = \prod_{k=1}^Z \int_{-\infty}^{+\infty} \tau_k(\mathbf{l}_k) e^{i(\mathbf{p}, \mathbf{l}_k)} d\mathbf{l}_k. \tag{2}$$

Here Z is the number of links in the chain, and $\tau_k(\mathbf{l}_k)$ is the probability that the k -th link is characterized in magnitude and direction by a vector \mathbf{l}_k . In the simplest case, the directions of the vectors \mathbf{l}_k are distributed at random, i. e., the functions $\tau_k(\mathbf{l}_k)$ are spherically symmetrical (as well as being identical for all links). The Eqs. (1) and (2) for $Z \gg 1$ lead to a Gaussian distribution function for h , in agreement with the law for random flight:

$$W(\mathbf{h}) = \left(\frac{3}{2\pi\overline{h^2}}\right)^{\frac{3}{2}} e^{-\frac{3\mathbf{h}^2}{2\overline{h^2}}} \tag{3}$$

where

$$\overline{h^2} = Zb^2, \tag{4}$$

and b is the length of one link. We point out that in this case, $\overline{h^2} \sim Z$. That is, if the chain consists of a large number of links, the root-mean-square length is much smaller than the maximum length.

Equations (3) and (4) are valid, in particular, for a hypothetical chain consisting of freely-jointed links of fixed length b . In real polymer chains, the links form fixed valence angles (ordinarily approximately tetrahedral, i. e., about $109^\circ 30'$). However, from the general theory of the probability of linked events (the theory of Markoff chains) it follows that, whenever the orientation of each link depends only on a limited number of preceding links (small compared with the total number of links in the chain), the distribution function $W(\mathbf{h})$ is expressed by (3) as before. Here, now $\overline{h^2}$ must be taken to be the mean-square distance between the ends of the chain, as calculated with the fixed valence angles taken into account. It is given by ³

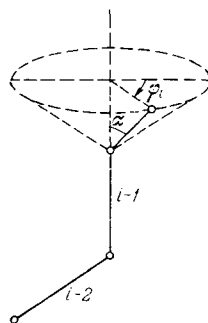


FIG. 1. Internal rotation angles in a polymer chain.

$$\overline{h^2} = Nl^2 \frac{1 + \cos \alpha}{1 - \cos \alpha}, \quad (5)$$

where N is the number of links in the chain, l is the length of a link, and $(\pi - \alpha)$ is the valence angle. In other words, in the case, which we have described, the real chain may be replaced by a chain consisting of freely-jointed statistical elements, and having a root-mean-square length coinciding with that of the real chain. This fact was first pointed out by W. Kuhn² in his classical paper which laid the foundations for the statistical physics of polymers. Equation (3) was obtained by Zimm⁴ for a chain with fixed valence angles and free rotation by direct derivation.

Equation (3) is valid only under the conditions that $Z \gg 1$ and that h is significantly less than the maximum chain length $h_{\max} = Zb$. In particular, this may be seen from the fact that the equation leads to a finite probability of values of h greater than h_{\max} , which is meaningless. A more exact derivation was carried out by W. Kuhn and F. Grun⁵ for a freely-jointed chain, taking into account the fact that, when h approaches h_{\max} , the distribution of the orientations of the links is not spherically symmetrical. This derivation gave, in place of (3),

$$W(h) = B \exp \left[-\frac{1}{b} \int_0^h \beta dh \right], \quad (6)$$

where

$$\beta = L^{-1} \left(\frac{h}{Zb} \right) = 3 \frac{h}{Zb} + \frac{9}{5} \left(\frac{h}{Zb} \right)^3 + \frac{297}{175} \left(\frac{h}{Zb} \right)^5 + \dots \quad (7)$$

is the inverse of the Langevin function, and B is a normalizing constant. When $h \ll Zb$, (6) and (7) go over into (3), but when $h = Zb$, they give $W(h) = 0$ while for $h > Zb$, $W(h)$ becomes meaningless, as must be the case.

Equations (6) and (7) show that, for large values of h , $W(h)$ depends not only on $\overline{h^2} = Zb^2$, but separately on Z and b . In order to apply these equations to real chains, we must point out the method of calculating the number Z and length b of the statistical elements of the effective freely-jointed chain which serves as a model for the real chain. W. Kuhn² suggested that Z and b should be calculated from the conditions that the mean-square and maximum lengths of the real and freely-jointed chains are equal:

$$\left. \begin{aligned} Zb^2 &= \overline{h^2}, \\ Zb &= h_{\max} \end{aligned} \right\} \quad (8)$$

$\overline{h^2}$ and h_{\max} being referred to the real chain). A conformation corresponding to that of the fully-extended chain is ascribed to these same statistical elements. Equations (8) imply that we have re-

placed the gradually-decreasing correlation between the orientations of the links in the real chain by the following situation: the orientations of several neighboring links within one statistical element are completely correlated, while correlations between the orientations of links belonging to different elements are nil. The application of (6) to real chains is not at all self-evident, since it was obtained for freely-jointed chains and, in distinction from (3), may not be directly generalized to the case of a chain with correlated orientations of neighboring links. However, as has been shown in papers by M. V. Vol'kenshtein and the author⁶ and by T. M. Birshtein⁷ based on model calculations Eq. (6) is valid with good accuracy over the entire range of h for a chains with correlated orientations of neighboring links as well.

Up to now, the subject has been that of chains with fixed valence angles but with free internal rotation; in these chains all sets of internal-rotation angles ϕ_i compatible with the fixed bond-lengths and the known values of the valence angles are equally probable. Obviously, this model corresponds to neglecting the interactions of all atoms and groups of atoms which are not directly joined by valence bonds. Yet, it is well known, that atoms and groups of atoms interact with each other. Here, for molecules which have neither free electric charges nor hydrogen-bonding groups (we shall consider only molecules of this type in this article), the interactions in question are the ordinary van der Waals interactions, which are appreciable only at very short distances.

In line with what has been said above, the interactions between atoms or groups which are not directly joined are divided into two classes. To the first class belong the interactions between atoms or groups at distances which are small on the average, and which depend on one or a few internal-rotation angles ϕ_i (short-range interactions). These interactions basically have the character of repulsions between atoms or groups with overlapping electron clouds, and lead to the appearance of hindrance of internal rotation (since the values of the angles ϕ_i corresponding to greater overlap of the electron clouds ordinarily correspond to greater energies). Naturally, short-range interactions are characteristic not only of macro-molecular compounds but also of substances of small molecular weight, where they lead to the appearance of a hindering potential for internal rotation and to the well-known phenomenon of rotational isomerism, which is highly essential in understanding the thermody-

dynamic and spectroscopic properties of molecules. Detailed accounts of the experimental facts and theoretical conceptions concerning hindered internal rotation and rotational isomerism in substances of low molecular weight are to be found in the monographs of Mizushima⁸ and M. V. Vol'kenshtein.⁹

To the second class of interactions belong the interactions between atomic groups which are separated on the average by considerable distances, but which may by chance approach each other in the process of random bending of the chain, and which interact at the moment of approach (long-range interaction). The most essential part of the long-range interaction is a result of the fact that no pair of atoms may occur simultaneously in the same volume element. Hence, these interactions have been named in the literature volume effects. Obviously, it is precisely the long and flexible polymeric chains for which volume effects are characteristic, since it is only in this case that atoms which are distant on the average may by chance approach each other to distances of the order of their van der Waals radii.

This article is primarily devoted to the long-range interactions. The short-range interactions have been discussed in the above-mentioned monograph of M. V. Vol'kenshtein,⁹ as well as in some earlier review articles^{10, 11}; hence we shall limit ourselves here to a brief discussion of the latter.

2. SHORT-RANGE INTERACTIONS IN POLYMER CHAINS

Experiment shows that the short-range interactions that lead to the hindrance of internal rotation show a very strong influence on the properties of macromolecules in solution. In Table I are given the experimental data on the ratios of the root-mean-square dimensions $(h^2)^{1/2}$ of linear macromolecules in an ideal solvent (under conditions in which the influence of long-range interactions are eliminated) to the root-mean-square dimensions $(h^2 \text{ free rot.})^{1/2}$ calculated for the case of free rotation. (Unless otherwise specified, the valence angles are considered to be tetrahedral, i. e., $109^\circ 30'$.) In the fourth column is given the method of determination of the dimensions: light-scattering (LS) or viscosity (V). The methods for determining the dimensions of macromolecules by light-scattering and intrinsic viscosity will be described below, in Secs. 5 and 6. The dimensions of molecules determined from intrinsic viscosities differ somewhat from those commonly given in the literature, since we have used the theoretical rather than the empirical value of the Flory coefficient in the equation relating the intrinsic

viscosity to the dimensions of macromolecules (for the basis of this, see below, Sec. 6). The table does not include data obtained by extrapolation from non-ideal solvents by the method proposed by Krigbaum.^{134, 227} From Table I it follows that the dimensions of real macromolecules in solution are appreciably greater than those of macromolecules with free rotation. That is, the internal rotation in the chains is considerably hindered.

Other characteristics of macromolecules in solution depending on the degree of hindrance of internal rotation are the root-mean-square dipole moment and the mean optical anisotropy of the chain. (the latter is measured by the method of flow birefringence).^{38-42*} In Table II are given the ratios of the root-mean-square dipole moment of the chain to that of a freely-jointed chain: $\mu_0^2 = nm_0^2$ (n is the number of polar groups, and m_0 is the dipole moment of a group). For chains of the type $(-CH_2-CR_2-)_n$, μ^2 for a chain with tetrahedral valence angles and free internal rotation is equal to μ_0^2 ,⁸⁴ while for chains of the type $(-CH_2-CHR-)_n$ with tetrahedral valence angles, it is equal to $(11/12)\mu_0^2$.^{43, 45} We see that for almost all of the studied polymers, $\mu^2 < \mu_0^2$. This is natural, since the polar groups ordinarily repel on one another strongly (because of their sizes). Because of this, for most conformations of the chain, the dipole moments of neighboring polar groups are directed in opposite directions. Thus they partially compensate each other. We note that, as has been shown by Benoit and his associates,^{49, 50, 53} the dipole moments of macromolecules in solution are practically independent of the long-range interactions.

In Table III, taken from reference 55, are given the ratios of the mean optical anisotropy $\overline{\Delta A}$ of the chain to that of a chain with fixed valence angles and free rotation. The latter optical anisotropy is equal to^{54, 55}

$$\overline{\Delta A}_{\text{free rot.}} = \left(a_{zz} - \frac{a_{xx} + a_{yy}}{2} \right) \frac{11 + 9 \cos \alpha}{20 \sin^2 \alpha} - (a_{xx} - a_{yy}) \frac{3}{40(1 + \cos \alpha)}, \quad (9)$$

*As is shown by experiment, the mean optical anisotropies of a chain which are determined for the rubber-like state by means of the photoelastic effect are more or less close to the mean optical anisotropies of the same chain in solution. Besides, as has been shown by K. Z. Fattakhov⁴³ and by G. P. Mikhailov and L. L. Burshtein⁴⁴, the values of the root-mean-square dipole moment of a macromolecule measured in the rubber-like state practically coincide with the values measured in solution. Hence, in Tables II and III, results are also given of measurements of root-mean-square dipole moments and mean optical anisotropies in the rubber-like state.

TABLE I. Root-mean-square distances between the ends of macromolecules in solution.

Polymer	Monomer unit of the chain	$(\overline{h^2}/h^2_{\text{free rot.}})^{1/2}$	Method	Reference
Polyisobutylene	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{CH}_3 \end{array}$	2.3 1.7-1.8	LS, V	12 13-15
Polystyrene*	$\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{C}_6\text{H}_5 \end{array}$	2.2-2.4	LS, V	12,14-25
Polymethylmethacrylate	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{O}=\text{C} \\ \\ \text{O}-\text{CH}_3 \end{array}$	2.0-2.2	LS, V	26-28
Polyethylmethacrylate	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{O}=\text{C} \\ \\ \text{O}-\text{CH}_2-\text{CH}_3 \end{array}$	1.9	LS	29
Polybutylmethacrylate	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{O}=\text{C} \\ \\ \text{O}-(\text{CH}_2)_3-\text{CH}_3 \end{array}$	2.1	LS	30
Polyhexylmethacrylate	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{O}=\text{C} \\ \\ \text{O}-(\text{CH}_2)_5-\text{CH}_3 \end{array}$	2.4	LS	31
Polyoctylmethacrylate	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{O}=\text{C} \\ \\ \text{O}-(\text{CH}_2)_7-\text{CH}_3 \end{array}$	2.3	LS	32

*Unless stated otherwise, the data for polymers of the type $(-\text{CH}_2-\text{CHR}-)_n$ are for atactic polymers (see below).

where a_{pq} are the components of the polarizability tensor** of the monomeric unit along the principal axes of the trans-chain (the z axis lies along the chain axis, and the x axis lies in the plane of the chain). In the fourth column of Table III is given the method of determination of $\overline{\Delta A}$: dynamo-optic (DO) or photoelastic (PE) effect. We must note that Table III does not pretend to be complete. It does

not include the data for polyisobutylene, for which the value of $\overline{\Delta A}$ was determined solely from deviations in the valence angles from tetrahedral and deviations from the valence-optical scheme.

**In the calculation of the a_{pq} 's, values of the polarizability of bonds proposed by Debye were used (see, for example, reference 9).

TABLE II. Root-mean-square dipole moments of macromolecules in solution and in the rubber-like state.

Polymer	Monomer unit of the chain	$(\mu^2 \mu_0^2)^{1/2}$	Reference
Poly-p-chlorostyrene	$\begin{array}{c} \text{---CH}_2\text{---CH---} \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{Cl} \end{array}$	0.65—0.75	43, 45, 46
Poly-p-bromostyrene	$\begin{array}{c} \text{---CH}_2\text{---CH---} \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{Br} \end{array}$	0.71	43
Poly-p-iodostyrene	$\begin{array}{c} \text{---CH}_2\text{---CH---} \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{I} \end{array}$	0.71	43
Poly-o-chlorostyrene	$\begin{array}{c} \text{---CH}_2\text{---CH---} \\ \\ \text{C}_6\text{H}_3 \\ \quad \text{Cl} \end{array}$	1.3	43
Poly-o-bromostyrene	$\begin{array}{c} \text{---CH}_2\text{---CH---} \\ \\ \text{C}_6\text{H}_3 \\ \quad \text{Br} \end{array}$	1.1	43
Polyvinylchloride	$\begin{array}{c} \text{---CH}_2\text{---CH} \\ \\ \text{Cl} \end{array}$	0.87	45, 47
Polymethylmethacrylate	$\begin{array}{c} \text{CH}_3 \\ \\ \text{---CH}_2\text{---C---} \\ \\ \text{O=C} \\ \\ \text{O---CH}_3 \end{array}$	0.73—0.81	44, 48—51

to a significant extent by the flexibility of the chains.⁶⁷⁻⁶⁹ Hence, it is of considerable interest to establish a quantitative connection between the properties of macromolecules in solution and their flexibilities.

The influence of hindrance of internal rotation on the dimensions of macromolecules in solution was first taken into account in the paper of S. E. Bresler and Ya. I. Frenkel,⁷⁰ who proposed that in real macromolecules rotation about the single bonds does not take place at all, but rather, only

rotational oscillations about the trans-configurations of neighboring links. An alternative approach was suggested by M. V. Vol'kenshtein,⁷¹ who proposed the rotational-isomer model of the polymeric chain. According to this model, in the rotation about each bond in the chain, only certain discrete conformations (rotational isomers) are realized in practice. Recently, the existence of rotational isomers in polymer chains was proved experimentally by V. N. Nikitin and B. Z. Volchek,⁷²⁻⁷⁴ who found spectroscopically a transi-

TABLE II. (Continued)

Polymer	Monomer unit of the chain	$(\mu^2 \mu_0^2)^{1/2}$	Reference
Polyethylmethacrylate	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{O}=\text{C} \\ \\ \text{O}-\text{CH}_2-\text{CH}_3 \end{array}$	0.77-0.79	44
Polypropylmethacrylate	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{O}=\text{C} \\ \\ \text{O}-(\text{CH}_2)_2-\text{CH}_3 \end{array}$	0.75-0.77	44
Polyisopropylmethacrylate	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{O}=\text{C} \\ \\ \text{O}-\text{CH} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	0.78-0.81	44
Polybutylmethacrylate	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{O}=\text{C} \\ \\ \text{O}-(\text{CH}_2)_3-\text{CH}_3 \end{array}$	0.74-0.77	44
Polyphenylmethacrylate	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{O}=\text{C} \\ \\ \text{O}-\text{C}_6\text{H}_5 \end{array}$	0.74	48
Poly-p-chlorophenylmethacrylate	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{O}=\text{C} \\ \\ \text{O}-\text{C}_6\text{H}_4-\text{Cl} \end{array}$	0.59	48
Polyoxyethylene	$-\text{CH}_2-\text{CH}_2-\text{O}-$	0.87	50, 52

tion of certain rotational isomers into others on stretching a polymer, as had been predicted previously^{6, 75, 76} by M. V. Vol'kenshtein and the author (see also reference 77). Recently the author⁷⁸ proposed a quantitative theory of the spectroscopic manifestations of changes in the rotational-isomeric composition of the chain.

The rotational-isomer model of M. V. Vol'kenshtein served as the basis of a method of

calculating the influence of short-range interactions on the physical properties of macromolecules in solution (the dimensions, the dipole moments, and the optical anisotropy). Here it was shown that in quantitative calculations one must not limit the study to the approximation on which the first papers in the field⁷⁹⁻⁸⁷ were based; in those papers the rotation about neighboring bonds in the chain were considered to be

TABLE III. Mean optical anisotropies of macromolecules in solution and in the rubber-like state.

Polymer	Monomer unit of the chain	$\frac{\Delta A}{\Delta A \text{ free rot.}}$	Method	Reference
Polyethylene	$-\text{CH}_2-\text{CH}_2-$	4.6-6.8*)	PE	56, 57
Polyvinylchloride	$-\text{CH}_2-\underset{\text{Cl}}{\text{CH}}-$	1.8	PE	58
Atactic polystyrene	$-\text{CH}_2-\underset{\text{C}_6\text{H}_5}{\text{CH}}-$	2-15 **) 2.2-17	PE DO	58-63 64-66, 231
Isotactic polystyrene	$-\text{CH}_2-\underset{\text{C}_6\text{H}_5}{\text{CH}}-$	3.0-22 **)	DO	65
Poly-p-chlorostyrene	$-\text{CH}_2-\underset{\text{C}_6\text{H}_4\text{Cl}}{\text{CH}}-$	2.6-8.3 **) 3.5-11**	PE DO	63 231
Poly-o-chlorostyrene	$-\text{CH}_2-\underset{\text{C}_6\text{H}_3\text{Cl}_2}{\text{CH}}-$	1.6-19 **)	PE	63
Poly-2,5-dichlorostyrene	$-\text{CH}_2-\underset{\text{C}_6\text{H}_3\text{Cl}_2}{\text{CH}}-$	1.8-46 **) 2.9-73**	PE DO	63 231
Poly-3,4-dichlorostyrene	$-\text{CH}_2-\underset{\text{C}_6\text{H}_3\text{Cl}_2}{\text{CH}}-$	3.5-15 **) 3.1-13	PE DO	63 66

*The range of values results from the variation in the experimental data.
**The range of values is the result of various assumptions as to the freedom of rotation of the phenyl groups.

independent of one another. This approximation amounts to neglecting the interactions of all atoms and groups except those immediately connected to the bond about which rotation is taking place. As was shown by the author and Yu. A. Sharonov^{88, 89} in polymers with heavy side-groups of the type $(-\text{CH}_2-\text{CR}_2-)_n$ (e.g., polyisobutylene) or $(-\text{CH}_2-\text{CHR}-)_n$ (e.g., polystyrene), a fundamental role is played by the interaction between the heavy R-groups, depending not on one, but rather on two

successive angles of internal rotation. Hence, the concept of rotational isomerism in polymers of this type must be referred not to the individual links, but to the monomeric units, which consist of two links.⁸⁹ A theory of the dimensions, dipole moments, and optical anisotropy of macromolecules divided into independent monomeric units, rather than independent links, was developed in references 88, 90, and 91.

In the next approximation, it was found neces-

sary to take into account also the correlation of conformations of neighboring monomeric units brought about by interactions of the nearest non-neighboring heavy groups, together with other interactions depending on three or four successive internal-rotation angles. (Interactions depending on a larger number of internal-rotation angles may be considered already to be volume effects.) The method of calculating the stated correlation is based on the application of the matrix method of the Ising model (as applied in the theory of ferromagnetism); this method was proposed by Yu. Ya. Gotlib⁹² and developed subsequently by T. M. Birshtein and the author.⁹³⁻⁹⁵ In distinction from the methods used in references 79--88, this method is essentially based on the rotational-isomeric approximation. Hence, it is not applicable in those cases in which the rotational-isomeric approximation turns out not to be adequate, due to a large degree of freedom of rotation within the limits of a monomeric unit.⁹¹

The basic problem which must be solved in order to compare the theory given above with experiment is the determination of the stablest conformations of the monomeric units of the macromolecule in solution, and the energy differences between them. Unfortunately, the status of the theory of intramolecular interactions of atoms not joined by valence forces does not yet permit us to rely upon theoretical predictions of these quantities for any of the complex molecules. Nevertheless, in a number of cases it is possible to decide on the stablest conformations of the monomeric units on the basis of the conformations of chains in the crystalline state, as was proposed by the author and Yu. A. Sharonov.⁸⁹ Indeed, the conformations of polymer chains in crystals are as a rule determined by intramolecular interactions, rather than by the requirements of intermolecular packing. (The exceptions are chains with a high degree of freedom of internal rotation, such as the polyethers.) This standpoint, on which reference 89 was based, was recently supported by a detailed argument by Bunn and Holmes,⁹⁶ who analyzed from this point of view the crystal conformations of a large number of polymer chains (see also reference 97). Hence it follows that also in the free macromolecules in solution, those conformations which are characteristic of the crystalline state must be favored.

What has been said, of course, must not be understood to mean that polymer chains in solution have planar or helical structures. In order

that the chain in solution should have the form of a helix, rather than a random coil, the helical structure must be stabilized by hydrogen bonds, as takes place, for example, in polypeptides.⁹⁸ When hydrogen bonds are absent, the thermal motion of the macromolecules is more than sufficient to convert them into the random-coil form. However, the structure of short sections of the chains is similar to their crystalline structure. One might say that the short-range one-dimensional order in the free polymer chain in solution is analogous to the long-range one-dimensional order in the crystalline chain -- a situation quite equivalent to the relation between a liquid and a crystal.

In those cases in which the macromolecules crystallize as helices, rather than as planar trans-chains,* there are two energetically equivalent conformations, corresponding to right-hand and left-hand helices. Correspondingly, such macromolecules in solution may be considered as consisting of short sections of right-hand and left-hand helices. A comparison based on this model between the equation for the dimensions of molecules of isotactic polystyrene and experiment⁹³ shows that the rigid helical segments contain three monomeric units on the average.

The most essential results of the above-mentioned series of papers was the establishment of the fact that the properties of macromolecules of the $(-\text{CH}_2-\text{CHR}-)_n$ type in solution depend essentially on their stereochemical structure, i. e., on the distribution of the R-groups with respect to the extended chain. Polymers of this type with regular distributions of the R-groups (stereospecific polymers) were first obtained by Natta;⁹⁹⁻¹⁰² they have a number of exceedingly valuable technical properties. This has recently attracted much attention to the methods of estimating the degree of stereospecificity of macromolecules. Consideration of the influence of short-range interactions on the properties of macromolecules in solution has led to the possibility of using these properties as the basis of one of these methods. This method is applicable, in distinction, e. g., to the x-ray method, to molecules with a low degree of stereospecificity.¹⁰³ It was shown in a recent paper by V. N. Tsvetkov and S. Ya. Magarik⁶⁵ that the optical anisotropy of isotactic polystyrene (i. e., polystyrene in which all the phenyl groups are attached to one side of the chain) is about 1.5 times as great as the optical

*Referring, in particular, to isotactic polymers of the type $(-\text{CH}_2-\text{CHR}-)_n$ (see below).

anisotropy of ordinary polystyrene. Recently, indirect data¹⁰⁴ were also obtained, according to which the molecular dimensions of isotactic polystyrene, undisturbed by long-range interactions (see below), are also somewhat greater than the molecular dimensions of atactic polystyrene. Analogous results have apparently been obtained also for polypropylene.¹⁰⁵

Obviously, even when short-range interactions are taken into account, the orientation of each link in the chain depends only on a limited number of preceding links. Hence, all that was stated in the Introduction about macromolecules with fixed angles and free rotation is applicable to macromolecules with short-range interactions, when they consist of a large number of links. In particular, when $h \ll h_{\max}$, the Gaussian distribution for h is valid for them, as before.* Here, h^2 is taken to denote the square of the distance between the ends of the chain, as calculated with hindered rotation taken into account. In other words, short-range interactions only increase the effective length of the chain, just as fixed valence angles do, but they do not change the relations between the dimensions of the chain and other physical properties depending on the dimensions (in particular, the hydrodynamic properties or the angular dissymmetry of light-scattering intensity). As we shall see below, this constitutes a very important distinction between short-range and long-range interactions.

In chains with hindered internal rotation, different sets of internal-rotation angles correspond to different energies. In view of this, the physical meaning of Eq. (3) for these chains differs: $\ln W(h)$ in this case is proportional not to the entropy, but to the free energy of the chain. A change in h is accompanied by a change in the set of internal-rotation angles, which involves both a change in energy and an additional change in the entropy of the chain. As was shown by M. V. Vol'kenshtein and the author,^{75, 76} for small values of h these changes compensate for one another, so that the change in the set of internal-rotation angles has no influence on the free energy of the chain. Equation (3) thereby retains its significance. The change in energy of the chain on changing h is directly manifested experimentally by the fact that the elastic force which appears on stretching a bulk polymer does not have a pure entropy character, in spite of the generally-

accepted conception. M. V. Vol'kenshtein and the author^{75, 76} have predicted the existence of an energetic elastic force, which in polymers with considerable hindrance of rotation should be comparable in magnitude to the total force (see also reference 77). This theoretical prediction was confirmed experimentally in a paper by Flory, Hovee, and Ciferri.¹⁰⁶ They found, on stretching irradiation-cross-linked polyethylene in the rubber-like state, that an energetic force arises, equal to about half of the total force in absolute magnitude. Thus, short-range interactions in polymer chains determine not only the properties of macromolecules in solution and their crystallizabilities (which was discussed above), but also have a considerable effect on the thermomechanical properties of bulk polymers. We must note that in the ordinary rubbers, built of very flexible chains (polyisoprene, polydimethylsiloxane), these effects must be considerably less than in polyethylene.

3. LONG-RANGE INTERACTIONS IN POLYMER CHAINS; APPROXIMATE THEORY

We shall now include in our discussion the long-range interactions between atomic groups in the polymer chain which approach each other accidentally. When atoms approach within very small distances, strong repulsion forces arise between them and prevent the coincidence of the two atoms within one and the same volume element. We may easily convince ourselves that a large fraction of the possible microconfigurations of a non-material filament corresponding to a given macroconfiguration (the distance between the ends) is forbidden for a real macromolecule. This is because no pair of atoms in the chain may occur in one and the same volume element in these microconfigurations. It is also obvious that the percentage of forbidden microconfigurations will be especially large for high coiled macroconfigurations corresponding to small distances between the ends of the chain. In this case, the density of atoms and the probability of their contacts are relatively large. Hence, volume effects must lead to deviations from the Gaussian distribution for the distance between the ends of the chain by increasing the relative probability of large values of this distance.

Thus, the repulsive forces between atomic groups in the chain lead to an expansion of the macromolecule in the solvent; this decreases the probability of contacts between atoms and may therefore be considered as having an entropy

*When h is comparable to h_{\max} , one may, as before^{6, 7}, use as an approximation the Langevin distribution (6) and (7), taking (8) into account.

character. However, this process is opposed by attractive forces acting between segments of the chain. These latter forces are greater, as a rule, than the attractive forces between chain segments and molecules of the solvent. Hence, from the energetic standpoint the polymer-polymer contacts are more favorable than the polymer-solvent contacts. This leads to a contraction of the molecule, with ejection of the solvent from it. In poor solvents (in which the energy difference between these types of contacts is especially large) this contraction may completely compensate for the entropy expansion of the macromolecule. Then its dimensions will be determined exclusively by short-range interactions, i. e., by the flexibility of the chain (the so-called θ -point of Flory; see below). Naturally, the expansion of the macromolecule is also opposed by the ordinary statistical elastic force associated with the fact that large distances between the ends correspond to relatively small numbers of microconfigurations of a non-material chain.

The approximate theory of long-range interactions, based on the qualitative conceptions presented above, was proposed in 1949 by Flory,¹⁰⁷ and perfected by him later in conjunction with Fox¹⁰⁸ and Orofino.^{109*} A calculation of the degree of expansion of the macromolecule at equilibrium, corresponding to the free-energy minimum, was carried out by Flory on the basis of a lattice model of the solution. In this model, the molecules of the solute and the solvent are considered to be distributed over the points of some regular lattice. In itself, the lattice model does not introduce large errors into the theory, since we are interested only in the interactions of nearest neighbors, whereas short-range order is present in any real solution. A more serious error is introduced by the fact that we are compelled to use the very same lattice for the solute, the solvent, and the solution, ignoring the actually-existing differences in short-range order.¹⁹ Besides, as will be seen below, the specific parameters of the lattice model do not enter into the final equations.

Application of the lattice model to polymer solutions requires that the macromolecule be divided into segments whose dimensions coincide with those of the solvent molecules. The distribution of the segments with respect to the center of gravity of the chain, volume effects being

absent, may be approximated by the Gaussian function*

$$\delta x_j = x \left(\frac{\beta_0}{V^{\frac{1}{3}} \pi} \right)^3 e^{-\beta_0^2 S_j^2 / 4\pi S_0^2 \delta S_j}, \quad (10)$$

where δx_j is the number of segments in a spherical shell of radius S_j and thickness δS_j , x is the total number of segments, and $\beta_0^2 = 3/(2\overline{R_0^2})$. ($\overline{R_0^2}$ is the mean-square radius of gyration of the chain; the zero subscript indicates the absence of volume effects.) The influence of volume effects on the distribution of the segments with respect to the center of gravity is described in Flory's theory by the simple following assumption: All of the segments which occur in the spherical shell between radii S_j and $S_j + \delta S_j$ before the expansion are transferred upon expansion into the spherical shell between radii αS_j and $\alpha(S_j + \delta S_j)$, where $\alpha = (\overline{R^2}/\overline{R_0^2})^{1/2}$ (the hypothesis of uniform expansion of the coil).

The number of segments δx_j allocated to the spherical shell is the same as the number of configurations of the corresponding fraction of the solution (if a solvent molecule can occupy only one cell), and is equal to

$$\Omega_j = \prod_{i=0}^{\delta x_j - 1} (z - 1)(1 - f_i), \quad (11)$$

where $f_i = i/\delta n_{0j}$ is the fraction of the cells which are forbidden to the $(i + 1)$ -th segment by reason of being occupied by the preceding i segments; δn_{0j} is the total number of cells in the j -th spherical shell, and z is the coordination number of the lattice. Hence, the entropy of the transition from a system containing completely ordered polymer plus solvent (this state corresponds to a single configuration) to the solution is equal to (calculated for the j -th spherical shell):

$$\delta S_j = k \ln \Omega_j = -k \left(\delta n_{1j} \ln v_{1j} - \delta x_j \ln \frac{z-1}{e} \right), \quad (12)$$

where δn_{1j} is the number of solvent molecules in the j -th spherical shell, and $v_{1j} = \delta n_{0j} / \delta n_{0j}$ is the volume fraction of the solvent. The second term on the right-hand side of (12) remains even in the absence of the solvent ($\delta n_{1j} = 0$), and thus amounts to the entropy of disorientation of the chain segments. Hence, the entropy of mixing of the disorientated segments with the solvent molecules is equal to $-k\delta n_{1j} \ln v_{1j}$.

The heat of mixing of the segments with the

*A more detailed presentation of Flory's theory may be found in his monograph¹⁹ (see also¹⁰).

*Actually this distribution is more complicated,^{110, 111} but the Gaussian is a good approximation.

solvent molecules in the j -th shell is equal to

$$\delta H_{Mj} = \Delta\omega_{12} p_{12}^j = kT \chi_1 \delta n_{1j} v_{2j}, \quad (13)$$

where $\Delta\omega_{12}$ is the change in energy on forming each new contact of a chain segment with a solvent molecule, $\chi_1 = z\Delta\omega_{12}/kT$, and p_{12}^j is the number of such contacts. The latter is approximately equal to $zv_{1j}\delta x_j = zv_{2j}\delta n_{1j}$

Consequently, the change in free energy upon mixing for the j -th shell is

$$\delta F_{Mj} = kT \{ \delta n_{1j} \ln(1 - v_{2j}) + \chi_1 \delta n_{1j} v_{2j} \}. \quad (14)$$

The degree of expansion of the molecule at equilibrium is determined from the condition: $\partial\Delta F/\alpha = 0$, in which δF_{Mj} depends on α by the relation

$$\delta n_{1j} = \frac{4\pi\alpha^3 S_j^2 \delta S_j (1 - v_{2j})}{V_1}, \quad (15)$$

where v_{2j} is the volume fraction of polymer in the j -th shell, and V_1 is the volume of a solvent molecule. From (14) we obtain (with an accuracy up to terms in

$$\frac{\partial(\delta F_{Mj})}{\partial(\delta n_{1j})} = -kT \left(\frac{1}{2} - \chi_1 \right) v_{2j}^2. \quad (16)$$

Here, the terms $\frac{1}{2}$ and χ_1 are characteristic of the entropy and heat of mixing, respectively. Since the entropy of mixing, generally speaking, cannot be reduced to a quantity that can be calculated from the lattice model (in particular, there may be entropy effects associated with nearest-neighbor interactions), the term $\frac{1}{2}$ must be replaced by an empirical parameter ψ_1 . On introducing in addition the energy parameter $\theta = 2\chi_1 T$ (which has the dimensions of a temperature), we obtain in place of (16)

$$\frac{\partial(\delta F_{Mj})}{\partial(\delta n_{1j})} = -\psi_1 kT \left(1 - \frac{\theta}{T} \right) v_{2j}^2, \quad (17)$$

which is applicable far beyond the limits of validity of the lattice model.

The change in the elastic free energy ΔF_{elas} also enters into the expression for the total free energy of the expanded chain. This is easy to calculate from the hypothesis of uniform expansion of the coil:

$$\Delta F_{\text{elas}} = kT \left[\frac{3}{2} (\alpha^2 - 1) - \ln \alpha^3 \right] \quad (18)$$

By using (15), (17), and (18) we obtain from the condition of minimum ΔF the following equation for the degree of expansion α at equilibrium:

$$\alpha^5 - \alpha^3 = 2C_M \psi_1 \left(1 - \frac{\theta}{T} \right) V \bar{M}, \quad (19)$$

where

$$C_M = \frac{27}{2^{3/2} \pi^{3/2}} \frac{\bar{v}^3}{N_A v_1} \left(\frac{\bar{h}_0^2}{M} \right)^{-3/2} \quad (20)$$

Here, \bar{v} is the specific volume of the polymer, v_1 is the molar volume of the solvent, M is the molecular weight of the polymer, N_A is Avogadro's number, and \bar{h}_0^2 is the mean square of the distance between the ends of the chain in the absence of volume effects. (The quantity \bar{h}_0^2/M does not depend on the molecular weight, and serves as a measure of the flexibility of the chain). We must stress that (19) refers to a macromolecule in an infinitely dilute solution. As the concentration increases, α rapidly approaches unity, since the expansion of the molecule caused by the interaction between its segments is compensated by a contraction caused by the interaction with segments of different molecules. A theory of the concentration dependence of α has been proposed by Krigbaum.²²⁹

Equation (19) relates α to the molecular weight of the polymer, the temperature, the flexibility of the chain, and the thermodynamic parameters ψ_1 and θ , which are characteristic of the given polymer-solvent pair. These parameters are empirical; however, not only the interactions of segments within one molecule depend on them, but also the interactions between segments belonging to different molecules. This permits us to determine the parameters in an independent fashion. A measure of the intermolecular interaction is furnished by the second virial coefficient in the series expansion of the osmotic pressure as a function of the concentration

$$\frac{\pi}{c} = RT \left(\frac{1}{M} + A_2 c + \dots \right). \quad (21)$$

If intermolecular interactions are absent, $A_2 = 0$, and the solution behaves as an ideal solution, that is, it obeys the van't Hoff Law. A presentation of the theory of the second virial coefficient of polymer solutions would be outside the topic of this review. We shall only indicate that the theory concerning A_2 , which has been developed by Flory together with Krigbaum and Orfino,^{19, 109, 112} and which is completely analogous in its physical assumptions and model utilized to the theory of intramolecular interactions presented

above, gives the result^{109*}

$$A_2 = \frac{16\pi}{3^{3/2}} \frac{N_A (\bar{R}^2)^{3/2}}{M^2} \ln \left(1 + \frac{\sqrt{\pi}}{4} X \right), \quad (22)$$

where

$$X = \frac{1}{4} \left(\frac{3}{\pi} \right)^{3/2} \frac{\bar{v}^2}{N_A v_1} \cdot \frac{M^2}{(\bar{R}^2)^{3/2}} \Psi_1 \left(1 - \frac{\theta}{T} \right). \quad (23)$$

Hence, at the θ -point, $A_2 = 0$, i.e., the polymer solution behaves as an ideal solution (in such cases the polymer is said to be in an ideal solvent). As is clear from (19), α simultaneously becomes unity. That is, intramolecular interactions have no influence on the dimensions of the macromolecule. Thus, the influence of the effects associated with inter- and intramolecular interactions between segments vanish at one and the same point. The close connection between intra- and intermolecular interactions may be expressed even more clearly by combining (19), (22), and (23). This gives¹⁰⁹

$$A_2 = 4\pi^{3/2} N_A \frac{(\bar{R}^2)^{3/2}}{M^2} \Psi(\alpha), \quad (24)$$

where

$$\Psi(\alpha) = \frac{4}{3\sqrt{3}\pi} \ln \left[1 + \frac{\sqrt{\pi}}{2} (\alpha^2 - 1) \right]. \quad (25)$$

Equations (24) and (25), containing only α , A_2 , the molecular weight, and the undisturbed dimensions of the chain, directly connect the degree of expansion of the macromolecule in various solvents with the thermodynamic properties of these solvents, as characterized by A_2 .

Obviously, the higher the characteristic temperature θ (often called the Flory temperature), the poorer the solvent is. This is because the energy loss Δw_{12} is greater on replacing the polymer-polymer and solvent-solvent contacts by polymer-solvent contacts (we recall that $\theta \sim X \sim \Delta w_{12}$).^{**}

In good solvents, θ is lower than the freezing point of the solvent, and thus at all experimental temperatures, $T > \theta$, and hence, $A_2 > 0$, and $\alpha > 1$. As we choose poorer solvents, θ ap-

*In reference¹⁰⁹, (19) and (22) are somewhat more complicated, owing to inclusion of the next term in the series expansion of $\partial(\delta F_{Mj})/\partial(\delta n_{1j})$ as a function of v_{2j} . However, the role of the correction terms is small, so that we may neglect them (especially for large molecular weights). We also note that the existence of these correction terms does not change the relation between α and A_2 , as determined by (24).

**If $\Delta w_{12} < 0$, that is, mixing is energetically favored, then $\theta < 0$, and hence, it loses the physical meaning of a temperature.

proaches the experimentally-attainable temperature range, so that A_2 and α decrease. At $T = \theta$ (ideal solvent), $A_2 = 0$, and $\alpha = 1$, while at $T < \theta$, $A_2 < 0$, and $\alpha < 1$. Hence the dimensions of macromolecules in solution are greater in better solvents.

We must keep in mind the fact that it is impossible to carry out an experiment at a temperature considerably lower than the θ -point, since phase separation sets in (the polymer precipitates). The theory of fractionation (see, e.g., reference 19) shows that the critical solution temperature of polymers of high molecular weight is related to the molecular weight by

$$\frac{1}{T_c} = \frac{1}{\theta} \left(1 + \frac{b}{VM} \right) \quad (26)$$

(b is a constant). Hence, θ is the critical solution temperature for the polymer at infinite molecular weight. At finite but large values of M , T_c is only a few degrees below θ , so that it is experimentally impossible to attain values of A_2 much less than zero, or values of α much less than unity. We might say that in poor solvents, the macromolecules "prefer" to combine with other molecules and precipitate, rather than to contract into tight coils. We note that both of the characteristics of the temperature θ mentioned above (the point at which $A_2 = 0$, and the limit of T_c as $M \rightarrow \infty$) are made use of in determining this temperature experimentally.

Flory's theory leads to three basic qualitative conclusions:

1. In an "ideal" solvent (θ -point), the dimensions of chains are determined by their flexibilities alone. In order to test this conclusion from the theory experimentally, it is essential to select solvents with θ -points near each other, since the flexibility of the chain itself may depend on the temperature (due to shift in the equilibrium of rotational isomers). In this regard, great possibilities arise from mixtures of poor and good solvents; by varying the composition, one may shift the θ -point in any necessary direction. In Fig. 2 are plotted the quantities $K = [\eta]_{\theta}/\sqrt{M}$, measured for polystyrene in various ideal solvents ($[\eta]_{\theta}$ is the intrinsic viscosity at the θ -point). As is shown by the theory of the viscosity of polymer solutions (see below), $[\eta]_{\theta}/\sqrt{M}$ is proportional to $(h_0^2/M)^{3/2}$. Along the abscissa is plotted the temperature corresponding to the θ -point. We see that the values measured in different solvents, even with nearby θ -points, differ by about 20%. Here the greatest values of K correspond to mixed solvents containing benzene or

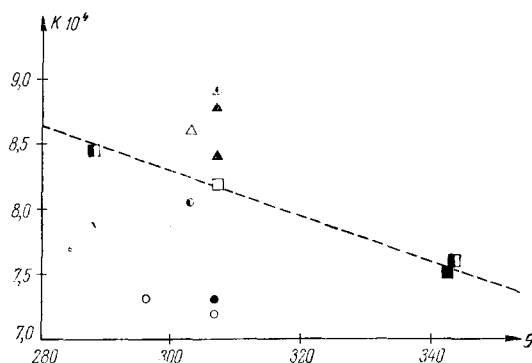


FIG. 2. The relation of $K = [\eta]_0 / M$ for polystyrene to the temperature θ .

Triangles--data obtained in mixtures of toluene with methanol (\blacktriangle ^{24, 113}) and with n-heptane (\triangle ¹⁹), and in mixtures of benzene with methanol (\blacktriangle ^{113, 114}); squares--data obtained in cyclohexane (\square ¹⁴), methylcyclohexane (\blacksquare ¹⁹), ethylcyclohexane (\blacksquare ¹⁹), and mixtures of cyclohexane with CCl_4 (\blacksquare ¹⁹); circles--data obtained in mixtures of methyl-ethylketone with methyl (\bullet ¹⁹) and isopropyl (\circ ^{23, 113}) alcohols, and in mixtures of p-dioxan with methyl alcohol (\bullet ¹¹³). The dotted straight line is drawn through the squares.

toluene, molecules which structurally resemble the side-groups of the polystyrene chain. On the other hand, the lowest values of K correspond to mixtures of methylethylketone and p-dioxan with alcohol. Especially convincing data are found in the paper of Bianchi, Magnasco, and Rossi¹¹³ who studied identical fractions of polystyrene in various mixed solvents (at $\theta = 34^\circ\text{C}$), and obtained values differing among themselves by 20%. The intermediate position is occupied by solvents containing cyclohexane or its derivatives. For this group of solvents, it was possible to vary the θ -point over a rather wide range. This made it possible to show a regular decrease of K with increasing temperature (the dotted line in the figure). This decrease apparently is to be explained by an increase in the fraction of the energetically-less-favorable twisted conformations of the chain. The observed dependence of the values of K on the solvent is not necessarily evidence of incomplete compensation of the influence of long-range interactions on the dimensions of the chains, since the flexibility of the chains itself, which is determined by short-range interactions, may depend on the solvent within certain limits.

2. The dimensions of macromolecules are larger in better solvents. This conclusion is confirmed by a large amount of experimental material concerning all of the studied systems, without exception. In good solvents, the dimensions of chains are 1-1/2 to 2 times larger than

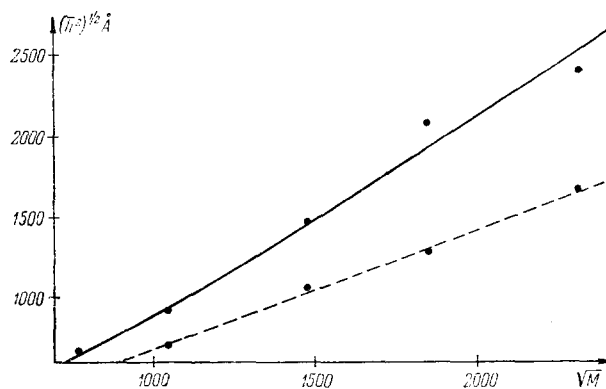


FIG. 3. The relation of the dimensions of polystyrene molecules to the molecular weight in a θ -solvent (dotted curve) and in a good solvent (solid curve).²²

they are at the θ -point. As an example, in Fig. 3 is shown the relation of $(\bar{h}^2)^{1/2}$ for polystyrene molecules to M in cyclohexane at 34°C (solvent at the θ -point) and in toluene at 20°C (good solvent). In addition, α is somewhat less than unity near the point of precipitation of the polymer ($T < \theta$), in agreement with the theory.

3. The root-mean-square dimensions of chains increase more rapidly with the molecular weight than \sqrt{M} (at $T > \theta$). In fact,¹¹⁵ it follows from (19) that $\alpha^2 \sim M^\epsilon$, where $\epsilon = (\alpha^2 - 1)/(5\alpha^2 - 3)$. (When $\alpha \rightarrow \infty$, $\epsilon \rightarrow 0.20$, and $(\bar{h}^2)^{1/2} \sim M^{(1+\epsilon)/2} \sim M^{0.60}$.)

This conclusion from the theory is also confirmed by numerous experimental studies. In particular, in reference 22, the value $\epsilon = 0$ was obtained for polystyrene in a solvent at the θ -point (cyclohexane at 34°C). In a series of gradually better solvents (cyclohexane at 43°C and 57°C , and toluene at 20°C), the values obtained were, respectively $\epsilon = 0.005, 0.07$, and 0.22 . In addition, with flexible molecules and large values of M , values of ϵ exceeding the theoretical limit of 0.20 by more than the experimental error have never been observed.

The fact that experiment clearly indicates that the dependence of \bar{h}^2 on M is stronger than a linear proportionality has a further significance. This lies in the fact that the earlier statistical theories of volume effects¹¹⁶⁻¹²⁴ led to the incorrect conclusion that, when volume effects are taken into account, $\bar{h}^2 \sim M$. (A critique of some of these papers is given in reference 10.) It is interesting to note that the question of the dependence of \bar{h}^2 on the number of links, volume effects being taken into account, has also been studied by another method. Here, the polymer chain was simulated by non-self-intersecting paths generated by electronic computers¹²⁵⁻¹³⁰. It was shown in reference 130 that, for a three-dimensional cubic

lattice, $\overline{h^2} \sim N^b$, where $b \approx 1.22$; here the number N of steps did not exceed 64. Wall, Hiller, and Atchison¹²⁶ have developed a method which permits one to estimate the asymptotic behavior of $(\overline{h^2}/N)$ as $N \rightarrow \infty$. It turned out that the asymptotic behavior of $\overline{h^2}$ is characterized by a considerably weaker power function of N than is found at small values of N . Thus, five three-dimensional lattices of various types were studied in paper 127. In these, for small values of N , b is approximately 1.22. Nevertheless, as $N \rightarrow \infty$, $\overline{h^2}/N$ approaches a finite limit. However, this approach is exceedingly slow (in one of the lattices studied, $\overline{h^2}/N$ attains 99% of its limiting value at $N = 10^7$, and in another of the lattices, at $N = 10^{30}$). Thus, the asymptotic behavior of $\overline{h^2}$ cannot be found experimentally with real macromolecules. Besides, as was shown in reference 128, the asymptotic behavior of $\overline{h^2}/N$ is considerably dependent on the value of the excluded volume assigned to each step, so that a small increase in the latter may lead to divergence in $\overline{h^2}/N$ as $N \rightarrow \infty$.

What has been stated shows that Flory's theory reproduces the basic features of the intramolecular interactions in macromolecules in a qualitatively correct manner. Nevertheless, the degree of quantitative agreement between the theory and experiment leads us to desire something better. Above all, it follows from Flory's theory that the quantity $(\alpha^5 - \alpha^3)/\sqrt{M}$ cannot depend on the molecular weight. Experiment shows that this is false, as is shown in particular by Fig. 4 (see reference 131). Here, data for solutions of polystyrene in toluene²² and polyvinylacetate in methylethylketone³³ are plotted; these data were obtained by the light-scattering method of Zimm (see below). We see that actually $(\alpha^5 - \alpha^3)/\sqrt{M}$ increases with M . Data given in Flory's monograph,¹⁹ based on the less reliable method of determining A_2 from the intrinsic vis-

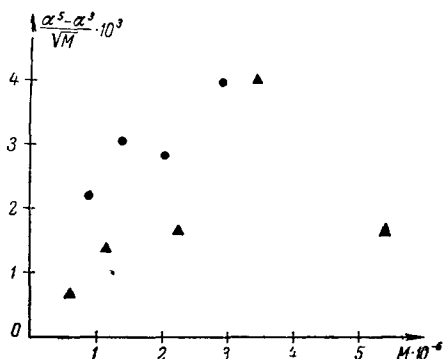


FIG. 4. The relation of $(\alpha^5 - \alpha^3)/\sqrt{M}$ to M for polystyrene in toluene²² (triangles) and polyvinylacetate in methylethylketone³³ (circles).

cosity, also indicate that $(\alpha^5 - \alpha^3)/\sqrt{M}$ is not constant.

On the other hand, Flory's equation¹⁹ permits us to calculate α directly if we know the thermodynamic parameters ψ_1 and θ of the system. As was stated above, θ may be measured by an independent method, and χ_1 determined from the second virial coefficient. Orofino and Flory¹⁰⁹ showed that the values of χ_1 determined from α and from A_2 are of the same order of magnitude, although the discrepancies between them are appreciably greater than the experimental error. The same result may be obtained by a direct test of (25), as is done in Fig. 5 (see reference 132). The dotted curve in the figure corresponds to (25), while the points are the experimental data.^{21, 33, 133-135} In most of the experimental studies used here,¹³³⁻¹³⁵ R^2 was determined from the intrinsic viscosity, while in references 21 and 33 it was determined directly by the light-scattering method of Zimm.

Figure 5 shows that the relation between A_2 and α derived in the papers by Flory and his associates does not agree quantitatively with experiment. This is especially noticeable in the range of α close to unity (poor solvents), where the Flory-Krigbaum-Orofino theory predicts too gradual an increase of A_2 with increasing α (i. e., with increasing temperature). This is shown graphically by Fig. 6 (see reference 132), in which the temperature dependence of A_2 (taken from reference 21) is plotted directly. We must add that at large values of α , the Flory-Krigbaum-Orofino theory leads to very large values of A_2 , also not in agreement with experiment. In particular, according to this theory, for $\alpha = 2.4$, $\Psi(\alpha) = 0.72$, whereas experiment²⁵ gives a value of only 0.35.

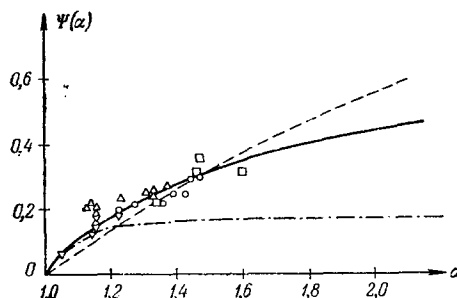


FIG. 5. The relation of $\Psi(\alpha) = (\frac{1}{4} \pi^3 / 2 N_A) A_2 M^2 / (R^2)^{3/2}$ to $\alpha = (R^2 / R_0^2)^{1/2}$. —····— Flory-Krigbaum-Orofino theory [Eq. (25)]; - - - - Casassa-Markowitz theory [Eq. (57)]; ——— theory of the author and Yu. E. Eizner [Eq. (58)]. Experimental data: Δ — polystyrene in toluene,¹³³⁻¹³⁵ \diamond — polystyrene in butanone,¹³⁵ \circ — polyisobutylene in cyclohexane,¹³³ \square — polyvinylacetate in methylethylketone³³, ∇ — polystyrene in cyclohexane.²¹

It is essential that one should be able in principle to determine the quantity ψ_1 from the value of A_2 near the θ -point independently of any model theory of A_2 . Indeed, (22) can be rewritten in the form

$$A_2 = \frac{\bar{v}^2}{v_1} \psi_1 \left(1 - \frac{\theta}{T}\right) F(X), \quad (27)$$

where

$$F(X) = \frac{4}{V\pi X} \ln \left(1 + \frac{V\pi}{4} X\right) = 1 - \frac{V\pi}{8} X + \dots \quad (28)$$

We see that $F(X) \rightarrow 1$ and $A_2 \rightarrow (\bar{v}^2/v_1) \psi_1 (1 - \frac{\theta}{T})$ as $T \rightarrow \theta$. Thus, the limiting expression for A_2 contains no numerical parameters, and as may be shown, is not connected with any concrete model. Hence, in the calculation of ψ_1 for polyisobutylene in benzene, Stockmayer¹³⁶ made use of data for A_2 obtained in the immediate neighborhood of the θ -point¹³³. The value which he obtained ($\psi_1 = 0.30$) turned out to be twice as large as the value of ψ_1 obtained from α by (19). This means that the numerical coefficient of C_M in the series expansion of α^2

$$\alpha^2 = 1 + 2C_M \psi_1 \left(1 - \frac{\theta}{T}\right) \sqrt{M} - \dots \quad (29)$$

must be reduced by about one-half. In fact, the experimental data for α which Stockmayer used were obtained from the intrinsic viscosity¹³, whereas it is just in the vicinity of the θ -point that this method may lead to large errors (see below). However, Fig. 6 shows that the conclusion drawn by Stockmayer is also valid in the determination

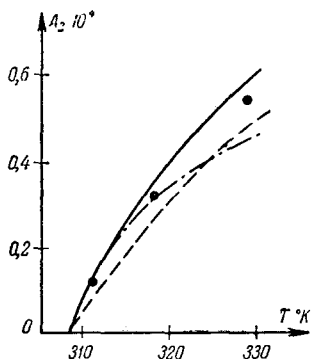


FIG. 6. The temperature-dependence of A_2 near the θ -point; ---- Flory-Krigbaum-Orofino theory, -.-.- Casassa-Markowitz theory, ——— theory of the author and Yu. E. Eizner, ● — experimental data (polystyrene in cyclohexane²¹).

of the dimensions of macromolecules by the light-scattering method of Zimm.

4. LONG-RANGE INTERACTIONS IN POLYMER CHAINS; A PRECISE THEORY

We saw above that Flory's theory is not in quantitative agreement with experiment. This is quite natural, since a number of coarse assumptions were made in deriving it. In fact, a real polymer chain, which is a sequence of connected segments, is replaced in this theory by a cloud of segments distributed about the center according to a Gaussian law. The fact that the exact distribution law of the segments with respect to the center of gravity^{110, 111} is replaced by a Gaussian law apparently in itself has no substantial effect on the results of the theory. [In any case, the introduction of the exact distribution law¹³⁷ into the calculation of A_2 gives results¹³⁸ which are very little different from those given by Eq. (22).] However, the replacement of the real chain by a cloud of segments deprives us of the possibility of taking into account the correlation between contacts between different pairs of segments. This leads to substantial errors.

A rigorous theory of the influence of volume effects on the dimensions of macromolecules may be developed for the case in which the volume effects may be considered as a small correction. It has been developed in the papers of a number of authors,^{139-146, 151} who started either with the Fokker-Planck equation or with the calculation of the partition function of the chain. We shall present schematically below the derivation of equations for \bar{k}^2 and R^2 , based on the latter method (for a more detailed derivation, see reference 131). We shall examine the "pearl necklace" model, in which the model of the chain is a system of interacting segments joined by non-material freely-jointed bonds. This model is widely used in the physics of polymer solutions; the centralization of the interactions at separate points along the chain apparently does not lead to large errors, provided that the number of these points is sufficiently large.

The distribution function for the coordinates of any pair of segments in the chain has the form

$$f(p, t) = \int \dots \int f\{k\} \frac{d\{k\}}{d(p) d(t)}, \quad (30)$$

where (p) is the coordinate set of the p -th segment, and

$$f\{k\} = f^0\{k\} e^{-\frac{V\{k\}}{RT}} \quad (31)$$

is the complete distribution function for the coordinates of all segments in the chain. ($V\{k\}$ is the interaction energy of all the segments.) Considering, as usual, that

$$V\{k\} = \sum_{i < j} u(\mathbf{r}_{ij}) \quad (32)$$

and that $U(\mathbf{r}_{ij})$ decreases rapidly with increasing distance $r_{ij} = |\mathbf{r}_{ij}|$ between the segments, we obtain

$$e^{-\frac{V\{k\}}{RT}} = 1 - \sum_{i < j} \phi(\mathbf{r}_{ij}) + \sum_{i < j} \sum_{\substack{i' < j' \\ (i < i')}} \phi(\mathbf{r}_{ij}) \phi(\mathbf{r}_{i'j'}) - \dots, \quad (33)$$

where the functions $\phi(\mathbf{r}_{ij}) = 1 - \exp[-u(\mathbf{r}_{ij})/RT]$ differ from zero only for small values of r_{ij} .

If we limit the series to the linear term, i. e., if we neglect simultaneous contacts of two or several pairs of segments (we can do this, provided that the volume effects are only a small correction), we obtain

$$f(p, t) = f^0(p, t) - \sum_{i < j} I_{pt}(i, j), \quad (34)$$

where

$$I_{pt}(i, j) = \int \int f^0(p, t, i, j) \phi(\mathbf{r}_{ij}) d(i) d(j), \quad (35)$$

and $f^0(p, t, i, j)$ is the distribution function for the coordinates of four segments. Making use of the fact that $f^0(p, t, i, j)$ is practically constant in the narrow interval in which $\phi(\mathbf{r}_{ij}) \neq 0$, we have

$$I_{pt}(i, j) = v_0 \omega_{pt}(i, j), \quad (36)$$

where

$$v_0 = \int_{-\infty}^{+\infty} \phi(\mathbf{r}_{ij}) d\mathbf{r}_{ij} = \int_{-\infty}^{+\infty} [1 - e^{-\frac{u(\mathbf{r}_{ij})}{RT}}] d\mathbf{r}_{ij}, \quad (37)$$

and

$$\omega_{pt}(i, j) = \int_{-\infty}^{+\infty} f_{r_{ij}=0}^0(p, t, i, j) d\mathbf{r}_{ij}. \quad (38)$$

Equations (34)–(38) permit us in principle to calculate the distribution function for the distance between any pair of segments in the chain, and the mean values of any of the functions of this distance. In particular, we obtain for the distance between the ends of the chain

$$\bar{h}^2 = \bar{h}_0^2 \left(1 + \frac{4z}{3} - \dots \right), \quad (39)$$

where

$$z = \left(\frac{3}{2\pi} \right)^{3/2} \frac{V_x^- v_0}{a^3} \quad (40)$$

(x is the number of segments in the chain, a is the effective length of a link joining adjacent segments). The distribution function for h has the form^{131, 147}

$$W(h) = W_0(h) \left[1 + \sqrt{6\pi} z \frac{h}{(\bar{h}_0^2)^{1/2}} - 4z \right], \quad (41)$$

where $W_0(h)$ is a Gaussian function. Study of (41) shows that the function $W(h)$ has a sharper maximum than the effective Gaussian function giving the same value of \bar{h}^2 . On the other hand, if we calculate the mean squares of the distances between any pairs of segments in the chain \bar{r}_{pt}^2 with the aid of (35)–(38), we may obtain an equation for the mean square of the radius of gyration of the chain:

$$\bar{R}^2 = \frac{1}{N^2} \sum_{p < t} \bar{r}_{pt}^2 = \bar{R}_0^2 \left(1 + \frac{134}{105} z - \dots \right). \quad (42)$$

It follows from (39) and (42) that volume effects have a somewhat stronger effect on \bar{h}^2 than they do on \bar{R}^2 , such that $\bar{h}^2 = 6\bar{R}^2(1 + 6z/105)$ when they are taken into account. (For Gaussian chains, $\bar{h}_0^2 = 6\bar{R}_0^2$.) Hence, the expansion of macromolecules in good solvents is not completely isotropic: in this process their degree of prolongation is increased somewhat. This is confirmed by study of the equation for \bar{r}_{pt}^2 , from which it follows that volume effects have a stronger influence on the distances between segments which are widely separated from each other than they do on the distances between relatively close segments. A certain increase in the degree of prolongation in better solvents must have an effect on the optical properties of macromolecules in solution, but especially on the form birefringence, which is brought about by the orientation of nonspherical particles having an intermediate index of refraction differing from the index of refraction of the medium.^{42, 148} The statistical theory¹⁴⁹ shows that the ratio of length to diameter for Gaussian chains is equal to two; this is confirmed by the experiments of V. N. Tsvetkov and E. V. Frisman¹⁵⁰ on the form effect. An increase in the degree of prolongation in better solvents must in principle be associated with a certain increase in the form effect. In a paper by V. N. Tsvetkov and S. Ya. Lyubina²³² it was shown that this effect is extremely slight, so that, to a first approximation, the expansion of the polymer coil can be considered to be isotropic.

We shall now consider the physical meaning of the parameter v_0 which appears in the equation for z . One may see from (37) that v_0 has the dimensions of volume, and is determined by the potential of interaction between a pair of segments in the chain. If the segments were rigid spheres of diameter d_0 (that is, $u(\mathbf{r}_{ij}) = \infty$ when $r_{ij} < d_0$, and $u(\mathbf{r}_{ij}) = 0$ when $r_{ij} > d_0$), v_0 would equal $4\pi d_0^3/3$, that is, the volume forbidden for the center of one sphere due to the presence of another sphere there. In the general case of an arbitrary $u(\mathbf{r}_{ij})$, v_0 has the meaning of the effective excluded volume of a segment in the chain. Obviously, the potential $u(\mathbf{r}_{ij})$ is positive for small values of r_{ij} (repulsion), and negative for larger values (attraction). Correspondingly, v_0 can be resolved into two components, positive and negative, which, in general, will show different temperature dependences. Hence, at a certain temperature (corresponding to the θ -point of Flory), they may cancel one another. Here, we take the value for $r_{ij} \rightarrow \infty$ as the zero point for $u(\mathbf{r}_{ij})$, as is customary. Then, just as in Flory's theory, since the segments are surrounded by solvent molecules the essential point is the compensation between the forces of repulsion between the segments and the attraction forces in excess of those existing between the segments and the solvent molecules*.

The relation between v_0 and the thermodynamic parameters of the system may be most easily established by comparing the expressions for A_2 at values of T close to θ , the expressions being taken from the thermodynamic theory of Flory, Krigbaum, and Orofino [Eq.(27)] and from the statistical theory based on taking rigorously into account the interactions of segments joined in the chain**. The rigorous statistical theory, first proposed by Zimm¹⁵¹ and subsequently developed in the papers of Albrecht¹⁵² and Yamakawa,^{153, 154} gives

$$A_2 = \frac{N_1 x^2 v_0}{2M^2} F(z), \quad (43)$$

where***

$$F(z) = 1 - 2,865z + \dots \quad (44)$$

*The cancellation takes place, of course, not between the stated forces per se, but between their influences on the microconfiguration of the chain.

**As has already been noted, the expression for A_2 near the θ -point does not depend on the model used.

***One can easily see that $F(z) = (\alpha^3/z)\Psi(\alpha)$.

We note that the approximate Flory-Krigbaum-Orofino theory [see Eq. (29)] gives in these terms: $F(z) = 1 - 1,15z + \dots$

Equating (27) to (43) at $T \rightarrow \theta$, at which $F(X)$, $F(z) \rightarrow 1$, we obtain^{131, 136}

$$v_0 = 2 \frac{V_S^2}{V_1} \Psi_1 \left(1 - \frac{\theta}{T} \right) \quad (45)$$

(V_S is the volume of a segment in the chain). Hence,

$$z = \frac{4}{3V_S^2} C_M \Psi_1 \left(1 - \frac{\theta}{T} \right) \sqrt{M}. \quad (46)$$

When equation (46) is taken into account, the exact equation (39) for $\alpha^2 = \bar{h}^2/\bar{h}_0^2$ becomes

$$\alpha^2 = 1 + \frac{16}{9V_S^2} C_M \Psi_1 \left(1 - \frac{\theta}{T} \right) \sqrt{M}. \quad (47)$$

In this equation, the numerical coefficient of C_M is close to unity. As was shown at the end of the preceding paragraph, this is in agreement with experiment [in Flory's theory, the coefficient of C_M was equal to two; see (29)].

On the basis of the above discussion, Flory's equation (19), can be written in the form

$$\alpha^5 - \alpha^3 = \frac{3V_S^2}{2} z, \quad (48)$$

This expression may be obtained from the exact Eq. (39), if we assume that the volume effects cause an α -fold increase in the length of each link. Indeed, the quantity z in the right-hand side of (39) has the meaning of the number of contacts between segments per unit volume of the undisturbed chain. Since $z \sim \alpha^{-3}$, then, in order to extend (39) to the case of large volume effects, it is sufficient from this viewpoint to replace z by z/α^3 . This gives¹⁴²

$$\alpha^5 - \alpha^3 = \frac{4z}{3}, \quad (49)$$

which differs from the equation of Flory (48) only in the numerical coefficient. Also, as follows from his conclusions, this equation will give a correct first term in the series expansion of α as a function of z .

We can show that we can attain about 4/3 of the value of the constant in an equation of the type of (48) or (49) within the framework of the Flory theory (i. e., without taking into account the connection of the segments into a chain), if we take

into account the non-Gaussian character of the distribution function for h in an approximate manner. Such a treatment was carried out in 1952 by M. V. Vol'kenshtein and the author¹⁵⁵ (see also reference 10), who, just as Flory did, began with a Gaussian distribution of the segments with respect to the center of gravity [see Eq. (10)]. However, this distribution was considered for a chain having a fixed distance h between its ends. The mean square of the radius of gyration of a Gaussian chain with a distance h between its ends is equal¹⁵⁵ to $R_h^2 = h_0^2/12 + h^2/12$. On considering that volume effects increase h^2 and R^2 in the same ratio, we obtain, when volume effects are taken into account: $R_h^2 = h^2/12 + h^2/12 = a^2 h_0^2/12 + h^2/12$.

Thus, the distribution of the segments with respect to the center of gravity, which is determined by the magnitude of R^2 , turns out to depend on the distance between the ends of the chain. This permits us to take into account the relation of the free energy of expansion of the chain to h , and to obtain the distribution function for h in the form

$$W(h) = W_0(h) \exp \left[-3 \sqrt{6} \frac{z}{a^3} \frac{1}{\left(1 + \frac{h^2}{h_0^2}\right)^{3/2}} \right] \quad (50)$$

[$W_0(h)$ is a Gaussian function]. The distribution function (50), just like the exact distribution function (42), has a sharper maximum than the effective Gaussian function giving the same value of h^2 . The calculation of h^2 with the aid of the distribution function (50) leads to an integral equation for a^2 , which can be approximated well by the equation¹³¹

$$a^5 - a^3 = \phi(z) z, \quad (51)$$

where $\phi(z)$ increases from 1.15 to 1.30 as z increases. Obviously, (51) is very close to (49), which results from the exact theory with the assumption of a uniform expansion of the coil.

The series expansion of (49) as a function of z gives

$$a^2 = 1 + \frac{4z}{3} - \frac{8z^2}{3} + \dots \quad (52)$$

In addition, the exact equation obtained by Fixman¹⁴⁴ by the method outlined above [see (34)–(38)], but taking the square terms into account, has the form

$$a^2 = 1 + \frac{4z}{3} - 2.08z^2 + \dots \quad (53)$$

A comparison of (52) and (53) shows that the assumption of uniform expansion of the coil is not

adequate. We stated above that volume effects have a stronger influence on the distances between distant segments than they do on those between close segments. Hence the various parameters of the chain having the dimensions of length will, in general, depend in differing manners on the volume effects (as we have already seen above in the example of h^2 and R^2).

The author¹³¹ proposed the following approximate method for taking the effect of non-uniform expansion of the coil on the $a-z$ relation into account. A possible measure of the non-uniformity of the expansion of the coil is the difference in the coefficients of z^2 in (52) and (53). In order to obtain the correct coefficient for z^2 , we must replace the quantity z in equation (39) by z/a_{eq}^3 , rather than by z/a^3 . Here, $a_{\text{eq}}^2 = 1 + \beta z - \dots$. On comparing the equation

$$a^2 = 1 + \frac{4z}{3a_{\text{eq}}^3} = 1 + \frac{4z}{3} - 2\beta z^2 + \dots \quad (54)$$

with (53), we obtain $a_{\text{eq}}^2 = 1 + 1.04z - \dots$. That is, $a_{\text{eq}} < a$. Replacing z in the last equation by z/a_{eq}^3 , we obtain

$$a_{\text{eq}}^5 - a_{\text{eq}}^3 = 1.04z, \quad (55)$$

while

$$a^5 - a^3 = \frac{4z}{3} \frac{a^3}{a_{\text{eq}}^3}. \quad (56)$$

Equations (55) and (56), which replace (49), show that $(a^5 - a^3)/z$ is not constant, as in Flory's theory, but increases almost 1-1/2 times as z increases (when $z \rightarrow 0$, $a^3/a_{\text{eq}}^3 \sim 1$, while when $z \rightarrow \infty$, $a^3/a_{\text{eq}}^3 \rightarrow 1.45$). In particular, this means that the quantity $(a^5 - a^3)/\sqrt{M}$ must increase with the molecular weight of the polymer. As we have seen above (see Fig. 4), this agrees with experiment*. In Fig. 7 is shown the dependence of a^2 on z as given by (55) and (56) (solid curve), and by (49) (dotted curve). We see that taking non-uniform expansion of the coil into account leads to an increase in a (for a given z).

We note that taking non-uniform expansion of the coil into account also leads to an essential change in the form of the theory of the second virial coefficient, significantly improving the agreement of this theory with experiment. As has already been noted above, the Flory-Krigbaum-Orofino theory does not reproduce the quantitative relation between a and A_2 , especially in poor solvents (see Fig. 6). Re-

*In a paper by Krigbaum²²⁸, another attempt was made to explain the dependence of $(a^5 - a^3)/\sqrt{M}$ on M . For a critique of this paper, see reference 131.

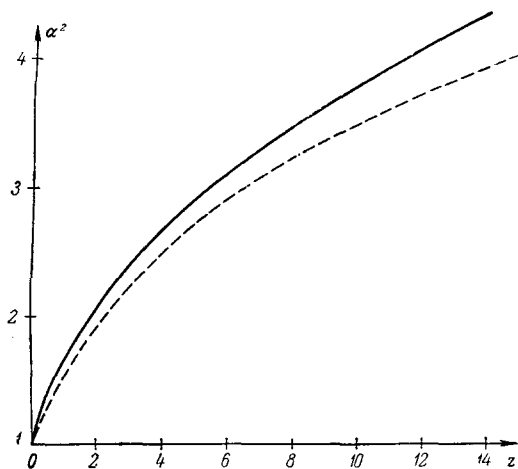


FIG. 7. The relation of α^2 to z , taking into account the non-uniform expansion of the coil by Eqs. (55) and (56) (solid curve), and with the assumption of uniform expansion [Eq. (49), dotted curve].

cently, this theory was improved by Casassa and Markovitz,¹⁵⁶ who replaced the Gaussian distribution of segments with respect to the center of gravity by a Gaussian distribution with respect to an arbitrary intermolecular contact, thus roughly taking into account the linking of the segments in the chain. The result obtained by Casassa and Markovitz may be expressed by means of Eq. (24), where

$$\Psi(\alpha) \cong \frac{1}{5.68} \left(1 - e^{-\frac{5.68z}{\alpha^3}} \right), \quad (57)$$

and z is related to α by (49). The relation between the Flory-Krigbaum-Orofino equation (25) and the Casassa-Markovitz equation (57) is in a certain sense analogous to the relation between Flory's equations (19) and (48) for α and the corrected Flory equation (49), "adjusted" by the correct coefficient for the linear term in the series expansion in terms of α . A comparison of the Casassa-Markovitz theory with experimental data in poor solvents is shown in Fig. 6. Here one sees that the Casassa-Markovitz theory agrees with experiment better in this region than does the Flory-Krigbaum-Orofino theory. However, in good solvents the Casassa-Markovitz theory does not give quantitative agreement with experiment (see Fig. 5).

Equation (57) was obtained, strictly speaking, for a Gaussian chain, while the influence of volume effects was roughly taken into account by replacing z by z/α^3 ; this corresponds to the hypothesis of uniform expansion of the coil. The degree of validity of this hypothesis may be estimated from the value of the coefficient of z^2 in

the series expansion of $F(z)$ [see (43)--(44)]. This coefficient is the sum of a quantity resulting from ternary intermolecular contacts (equal to 9.726, see reference 152) and another quantity resulting from the influence of single intramolecular contacts on double intermolecular contacts. A trivial calculation of this influence, amounting to the replacement of z in the linear term by z/α^3 , gives a contribution of 5.73 to the z^2 coefficient¹⁵². A precise estimate of only part of these influences gave^{153, 154} a value of 8.78, while an approximate calculation of all the influences¹³² gave 12.58. This shows that the quantity z must be replaced by z/α_{eff}^3 , rather than by z/α^3 , in the given case (α_{eff} being less than α). Considerations similar to those presented above in the derivation of equations (55)–(56) led the author and Yu. E. Eizner¹³² to replace the Casassa-Markovitz equation (57) by the equation

$$\Psi(\alpha) \cong \frac{1}{5.68} \left(1 - e^{-\frac{5.68z}{\alpha_{\text{eff}}^3}} \right), \quad (58)$$

where $\alpha_{\text{eff}}^2 = 1 + 2.93z/\alpha_{\text{eq}}^3$, α_{eq} being expressed by Eq. (55). Here the relation between z and α is defined by (55) and (56). Comparison of (58) with experiment, as shown in Figs. 5 and 6, indicates that the experimental data relating to good solvents are in significantly better agreement with the theory which takes non-uniform expansion of the coil into account.

Krigbaum²²⁷ proposed a semi-empirical relation connecting $\overline{R^2}$, $\overline{R_0^2}$ and A_2 . This relation, which was obtained by combining Eqs. (40), (42), and (43) [for $F(z) = 1$], has the form

$$\frac{(\overline{R^2})^{\frac{3}{2}}}{(\overline{R_0^2})^{\frac{3}{2}}} = \frac{\overline{R^2}}{\overline{R_0^2}} + 3 \frac{134}{105} \frac{1}{(4\pi)^{3/2}} \frac{A_2 M^2}{N_A} \quad (59)$$

Krigbaum's equation was obtained by combination of equations which are valid only in the immediate vicinity of the θ -point, and extrapolation of its use into the region of good solvents is theoretically invalid. Nevertheless, its experimental corroboration is not bad. Indeed, according to this equation (if we neglect for convenience the insignificant difference between $\overline{h^2}/\overline{h_0^2}$ and $\overline{R^2}/\overline{R_0^2}$)

$$\Psi(\alpha) = \frac{1}{2} \left(1 - \frac{1}{\alpha^3} \right), \quad (60)$$

which is rather close to (58). While this coincidence is undoubtedly simply the result of compensation of various factors omitted in Krigbaum's equation, it shows that this equation may be used to estimate $\overline{R_0^2}$ when the values of $\overline{R^2}$, A_2 ,

and M are known²³⁰.

5. LONG-RANGE INTERACTIONS AND LIGHT-SCATTERING IN POLYMER SOLUTIONS

We saw above that long-range interactions lead to deviations from the Gaussian distribution function for distances between segments of the chain. Here, the volume effects have different influences on different pairs of links ("non-uniform expansion of the coil"). However, the ordinary theories of the properties of macromolecules in solution (light-scattering, hydrodynamic properties, etc.) are based on the assumption that the distribution function for the distance between any given pair of segments in the chain is Gaussian. Hence, strictly speaking, these theories are applicable only to macromolecules in ideal solvents. The generalization of these theories to the properties of macromolecules in good solvents is commonly based on the explicitly or implicitly formulated assumption that the influence of volume effects may be reduced to an increase in the length of a link in the chain, the Gaussian statistics being preserved.

In the precise determination of the dimensions of macromolecules by light-scattering or hydrodynamic properties, one must generalize the theory of these phenomena in a way which takes into account the non-uniform expansion of the coil due to long-range interactions. The pertinent results are presented in this and in the next paragraphs.

As is known, light scattering by molecules of dimensions comparable with the wavelength of the light shows a characteristic angular dissymmetry: the scattering in the forward direction is greater than that in the backward direction. This is associated with the fact that there is a phase difference between the waves scattered by different regions of one given molecule. This difference is greater in backward than in forward scattering, so that the waves scattered in the backward direction interfere with one another to a large degree. The resulting angular dissymmetry of the scattered light is the greater, the greater the ratio of the dimensions of the molecule to the wavelength of the light. Thus, this dissymmetry may be used to determine the dimensions of the molecule. The addition of the amplitudes of the waves scattered at a given angle ϑ from the various atoms in the molecule gives the following expression for the ratio of the light intensity scattered at the angle ϑ to that scattered at a zero angle (see, e. g., reference 157):

$$P(\vartheta) = \frac{I_{\text{scat}}(\vartheta)}{I_{\text{scat}}(0)} = \frac{1}{N^2} \sum_{p, t=1}^N \left(\frac{\sin \mu r_{pt}}{\mu r_{pt}} \right), \quad (61)$$

where N is the number of atoms in the molecule, $\mu = (4\pi/\lambda') \sin(\vartheta/2)$, λ' is the wavelength of the light in the given medium, and r_{pt} is the distance between the p -th and the t -th atoms.

In order to average over all the conformations of the macromolecule, as is done on the right-hand side of (61), in general, we must have a definite assumption of a model of the structure of the chain. However, the light-scattering at small angles may be interpreted also independently of the model, since at small angles (i. e., small values of μ), (61) becomes

$$P(\vartheta) = 1 - \frac{\mu^2}{3} \frac{1}{N^2} \sum_{p < t} \bar{r}_{pt}^2 + \dots = 1 - \frac{\mu^2 \bar{R}^2}{3} + \dots, \quad (62)$$

Here, the result does not depend on the structure of the chain, but is related directly to the definition of the mean square radius of gyration. A method of determining the dimensions of macromolecules, proposed by Zimm¹⁵⁸, is based on (62). We now make use of the fact that the experimentally measured relative intensity $I(\vartheta)$ of the scattered light (at unit distance from the scattering center) is connected to $P(\vartheta)$ by the relation (see, e. g., reference 19)

$$\frac{Kc}{I(\vartheta)} = \frac{1}{M_w P(\vartheta)} + 2A_2c + \dots \quad (63)$$

(c is the concentration of the polymer; $K = (2\pi^2/\lambda'^4 N_A) n_0^2 (dn/dc)^2$; and n_0 are, respectively, the indices of refraction of the solution and the solvent; and M_w is the weight-average molecular weight of the polymer). We may then determine $P(\vartheta)$ by plotting $Kc/I(\vartheta)$ as a function of $\sin^2(\vartheta/2) + kc$, where k is an arbitrary constant. Now, we carry out a double extrapolation to $c = 0$ and $\vartheta = 0$. The curve extrapolated to $c = 0$ gives $1/M_w \cdot P(\vartheta)$; the extrapolation to $\vartheta = 0$ permits us, according to (62), to determine \bar{M}_w from the intercept on the axis of ordinates, while \bar{R}^2 is determined from the initial slope of the curve.

Zimm's method, in principle, permits us to determine M_w and \bar{R}^2 independently of model conceptions of the structure of the chain. However, in practice it is by no means always possible to carry out a reliable extrapolation to $\vartheta = 0$, since the measurements are ordinarily carried out at $\vartheta = 30^\circ - 150^\circ$ (stray light and scattering by dust interfere with the measurements at lower angles). For large molecular weights, the quan-

tity $\mu^2 \bar{R}^2$ is not small at $\theta \approx 30^\circ$, so that we must not limit the series expansion of the equation for $P(\theta)$ to the first two terms. In order to interpret light-scattering data at finite angles, we must calculate $P(\theta)$ in finite form, and this requires models for the structure of the chain.

In the simplest model, the distances between all the scattering centers obey a Gaussian distribution function. In this case

$$\left(\frac{\sin \mu r_{pt}}{\mu r_{pt}} \right) = e^{-\frac{1}{6} \mu^2 r_{pt}^2} \quad (64)$$

Considering that $\bar{r}_{pt}^2 = |t - p| \alpha^2$, we obtain from (61) and (64)

$$P(\theta) = \frac{2}{x^2} (e^{-x} - 1 + x), \quad (65)$$

where $x = \mu^2 \bar{R}^2$. Equation (65) was first obtained by Debye¹⁵⁹, and was the basis of the method which he proposed for determining \bar{R}^2 from the ratio of values of $P(\theta)$ measured at two different angles (commonly 45° and 135°). Undoubtedly, the Gaussian distribution function is not valid for distances between atoms which are close to each other in the chain. However, attempts to take into account the rigidity of short segments of the chain, as have been made by Peterlin¹⁶⁰ and other authors,¹⁶¹⁻¹⁶³ show that this effect has little influence on the form of the curve for $P(\theta)$, provided that the contour length of the molecule is sufficiently greater (hundreds of times) than the length of the rigid region.

Since volume effects cause a greater increase in the distances between distant segments in the chain, it follows that they must appreciably distort the form of the $P(\theta)$ curve. Indeed, (61) shows that the scattering at large angles is determined principally by nearby pairs of segments, since the waves scattered by distant pairs of segments interfere with one another, due to the large phase difference. [The corresponding terms in the double summation on the right-hand side of (61) are small.] Hence, volume effects must have a weaker influence on the light intensity scattered at large angles than on that scattered at small angles. In other words, for a given \bar{R}^2 , the volume effects decrease the angular dependence of the light-scattering intensity.

The qualitative considerations given above are confirmed by corresponding calculations carried out by the author.¹⁶⁴ Later, analogous results*

*In reference 166 the theory is generalized to the case of polydisperse molecules.

were obtained by Benoit^{165, 166} and by Hyde, Ryan, and Wall¹⁶⁷. These theories¹⁶⁴⁻¹⁶⁷ are based on Eq. (64), which is based on a Gaussian distribution function for r_{pt} . The fact that volume effects cause a greater increase in the distances between distant segments is taken into account in these theories by replacing the equation $\bar{r}_{pt}^2 = |t - p| \alpha^2$ by the equation $\bar{r}_{pt}^2 = |t - p|^{1 + \epsilon'} \alpha^2$ (see also reference 168). In reference 164, ϵ' , which must actually be a function of p and t , was assumed to be equal to the parameter ϵ defined by the relation: $\bar{h}^2 \sim M^{1 + \epsilon}$. [As was stated above, according to Flory's theory,¹⁵⁵ $\epsilon = (\alpha^2 - 1)/(5\alpha^2 - 3)$.] In references 165--167, ϵ' was considered to be an empirical parameter, independent of p and t .

The substitution of the equation $\bar{r}_{pt}^2 = |t - p|^{1 + \epsilon} \alpha^2$ into (64) and (61) gives, instead of the Debye function (65), the following function

$$P(\theta) = \frac{2}{1 + \epsilon} \left\{ \kappa^{-\frac{1}{1 + \epsilon}} \left(-\frac{\epsilon}{1 + \epsilon}, \kappa \right)! - \kappa^{-\frac{2}{1 + \epsilon}} \left(\frac{1 - \epsilon}{1 + \epsilon}, \kappa \right)! \right\}, \quad (66)$$

where $\kappa = x(1 + 5\epsilon/6 + \epsilon^2/6)**$, and $(q, \kappa)! = \int_0^\kappa \exp(-r) r^q dr$ are incomplete Γ -functions, tabulated in reference 167. Figure 8, taken from reference 164, shows that, for identical initial slopes, the curve for $P^{-1}(\theta)$ constructed by means of (66) lies under the curve constructed by means of (65). This is in agreement with the qualitative concepts presented above.

It follows from the Debye equation (65) that the dependence of P^{-1} on μ^2 is characterized by an initial slope $s_0 = R^2/3$, and an asymptote with $s_\infty = \bar{R}^2/2$ so that $s_0/s_\infty = 2/3$. According to the theories of reference 164--167, the curve for $P^{-1}(\theta)$ does not have an asymptote, while the ratio of the initial to the final slope of this curve is equal to

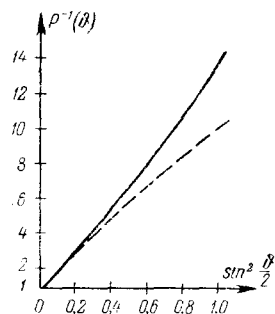
$$\frac{s_0}{s_\infty} = \frac{2}{3} \Phi \left(\frac{(\bar{R}^2)^{1/2}}{\lambda'}, \epsilon \right), \quad (67)$$

where

$$\Phi = \left(\frac{(\bar{R}^2)^{1/2}}{\lambda'}, \epsilon \right) = \frac{\Gamma \left(\frac{1}{1 + \epsilon} \right)}{\left(1 + \frac{5\epsilon}{6} + \frac{\epsilon^2}{6} \right)^{\frac{1}{1 + \epsilon}}} x_{\max}^{\frac{\epsilon}{1 + \epsilon}}. \quad (68)$$

**The distinction between κ and x is associated with the fact that, as shown by Peterlin¹⁶⁸, $\bar{h}^2 = 6R^2(1 + 5\epsilon/6 + \epsilon^2/6)$ in the approximation under discussion. (Compare with the equation $\bar{h}^2 = 6R^2(1 + 6z/105)$ obtained above by the rigorous method.)

FIG. 8. The relation of $P^{-1}(\theta)$ to $\sin^2(\theta/2)$ for $(R^2)^{1/2}/\lambda' = 1$ and $\epsilon = 0.18$, according to the Debye theory (solid curve) and the theory of the author (dotted curve).



The relations of ϕ to $(\overline{R^2})^{1/2}/\lambda'$ and to ϵ are given in reference 164. From these it follows that ϕ increases with $(\overline{R^2})^{1/2}/\lambda'$ and with ϵ , and in experimentally possible cases may be of the order of 1.5 to 1.8. Here, $s_0/s_\infty > 1$, that is, $P^{-1}(\theta)$ is not curved upward (as in the Debye theory), but downward (see Fig. 8). The considerable influence of volume effects on the form of the $P(\theta)$ curve leads to the result that the dimensions of chains measured by scattering at large angles with the use of the Debye function are smaller than the true dimensions. Here, as the diagrams in reference 167 show, the error may be quite significant. It is even more essential to take volume effects into account in attempts to estimate the polydispersity and branching of polymer chains from the form of the $P(\theta)$ curve by the methods suggested by Benoit.¹⁶⁹⁻¹⁷² (As was shown in these papers, polydispersity increases the s_0/s_∞ ratio, while branching decreases it.) Obviously, it is proper to use these methods only in poor solvents, in which volume effects may be neglected.

The author has also developed¹⁶⁴ a rigorous theory of the influence of volume effects on the function $P(\theta)$. This theory was also based on Eq. (64), but used the exact expression for $\overline{r_{pt}^2}$ (in the approximation linear in θ). This theory, qualitatively confirms the results of the theory presented above. In particular, it leads to the conclusion that, when volume effects are taken into account, $s_0/s_\infty = \frac{2}{3} a^2$ where $a^2 = \overline{R^2} / \overline{R_0^2}$. However, this asymptotic behavior is attained only at experimentally unrealizable values of $\mu^2 \overline{R^2}$, so that in practice, $2/3 < s_0/s_\infty < \frac{2}{3} a^2$. This result was recently confirmed in a paper by the author and Yu. E. Ėizner¹⁷³ by a rigorous calculation. Here the non-Gaussian character of the distribution function for r_{pt} was taken into account. In reference¹⁷³ and the papers of Yamakawa and Kurata^{145, 146} the influence of volume effects on light-scattering at small angles θ was also studied. It was shown in reference¹⁷³ that, given the same initial slope, volume effects produce a somewhat greater initial curvature of the $P^{-1}(\theta)$ curve in comparison with the

Debye curve. Thus, at small values of θ , the true $P^{-1}(\theta)$ curve lies somewhat above the Debye curve, while at large values of θ , it lies appreciably lower (with the same initial slope).

The experimental testing of the above theory of light-scattering of polymer solutions in good solvents is given in references 25, 166, 167, and 174, 176. Here, as was predicted by the theory, it turned out that, for the same initial slope, the $P^{-1}(\theta)$ curves lay lower in good solvents than in poor solvents; the solutions studied contained high-molecular-weight polystyrene ($M \approx 10^7$) in benzene or toluene (good solvents) or methylethylketone or cyclohexane (poor solvents). Fig. 9, is a diagram illustrating this; it is taken from the paper by V. E. Ėskin,²⁵ who studied this effect especially carefully. One may see from the diagram that in a good

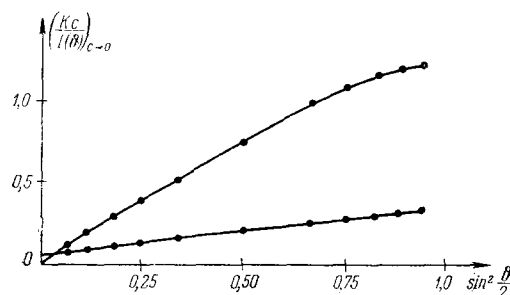


FIG. 9. Angular dependence of light-scattering of polystyrene solutions with $M = 20 \times 10^6$, in toluene at 19°C (upper curve), and in a θ -solvent (cyclohexane at 34.4°C lower curve²⁵).

solvent (toluene), the $P^{-1}(\theta)$ curve is appreciably curved downward at large values of θ ; this agrees qualitatively with the theory presented above. The theoretical curve which best describes the experimental data corresponds to $(\overline{h^2})^{1/2} = 6000 \text{ \AA}$, from which $\alpha = 2.4$. This is in good agreement with the results obtained by Ėskin²⁵ from measurements of the intrinsic viscosity [$(\overline{h^2})^{1/2} = 5800 \text{ \AA}$] and translational diffusion [$(\overline{h^2})^{1/2} = 6000 \text{ \AA}$]. On the other hand, the determination of $(\overline{h^2})^{1/2}$ from the upper curve in Fig. 9 by the ordinary Debye dissymmetry method gives a value of 5000 Å; this discrepancy is significantly outside the limits of error of the experiment. As was shown in reference²⁵, the Debye $P^{-1}(\theta)$ curve corresponding to dimensions of the macromolecule determined from the intrinsic viscosity does not agree at all with the experimental curve. However, the analogous curve, constructed according to the theory taking into account the non-uniform expansion of the coil¹⁶⁴, is in satisfactory agreement with experiment.

6. LONG-RANGE INTERACTIONS AND HYDRODYNAMIC PROPERTIES OF MACROMOLECULES

We shall now consider the influence of non-uniform expansion of the coil on the hydrodynamic properties of macromolecules in solution. Experiment provides us with two types of hydrodynamic characteristics of macromolecules. By studying the translational motion of the molecule through the solution, either in Brownian movement (in the diffusion phenomenon) or under the influence of centrifugal force (sedimentation in the ultracentrifuge), we can determine the translational frictional coefficient of the macromolecule from the diffusion and sedimentation constants. The translational frictional coefficient is related to the diffusion constant by the well-known Einstein equation

$$D = \frac{kT}{F}, \quad (69)$$

and to the sedimentation constant by the equation

$$s = \frac{M(1 - v\rho)}{FN_A} \quad (70)$$

(v is the specific volume of the polymer, and ρ is the density of the liquid). The latter equation may be easily obtained from the condition of equilibrium between the centrifugal force and the frictional force acting on the molecule.

On the other hand, in laminar flow of the liquid, as characterized by a certain velocity gradient, different parts of the molecule will be driven forward by the forces of flow having different velocities. Thus the part of the molecule situated in the region of fastest flow will tend to overtake the part situated in the region of relatively slow flow. As a result, a torque will set on the molecule and cause it to rotate in the current (at the same time, of course, the molecule is carried along by the current with a velocity equal to the flow velocity at the site of its center of gravity). An elementary calculation shows that the angular velocity of rotation of the molecule is equal to one-half of the velocity gradient of the flow. When the molecule rotates in the current, its segments will have definite velocities with respect to the surrounding medium. (This can be seen from the fact that the molecule unavoidably cuts lines of flow when it rotates.) Hence, if we go from the pure solvent to the solution, the frictional energy losses will be greater, due to the additional dissipation of energy in the friction of the segments of the molecule with respect to the solvent. This is manifested macroscopically as an increase in viscosity. The contribution of the individual molecule to this increase may be conveniently characterized by the intrinsic viscosity, which

is the relative increment in viscosity per unit concentration, extrapolated to infinite dilution:

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_c - \eta_0}{\eta_0 c} \quad (71)$$

In addition, the study of flow birefringence of macromolecules makes possible the determination⁴² of the rotational diffusion coefficient D_r . As is shown by theory^{177, 115} and experiment¹⁷⁸ this quantity is related to the intrinsic viscosity by a universal relationship.

A presentation of the theories of the hydrodynamic properties of macromolecules in solution (see reference^{19, 179, and 180}) would extend far beyond the limits of this article, in which we can only characterize briefly the basic results of these theories. A most important element in a theory of the hydrodynamic behavior of macromolecules in solution must be the hypothesis concerning the relation of the motion of the medium surrounding the molecule to the motion of the segments of the molecule. The simplest assumption states that the motion of the medium does not depend at all on the motion of the segments. That is, each segment experiences friction in the surrounding medium, just as if the remaining segments did not exist (model of the free-draining molecule).

Obviously, in this case the frictional force acting on the molecule during its translational motion through the solvent is equal to the sum of the forces acting on all the segments of the molecule. Since all the segments move with the same velocity, this means that the translational frictional coefficient of the molecule is

$$F = x\zeta, \quad (72)$$

where x is the number of segments in the chain, and ζ is the translational frictional coefficient of a segment*. Hence, in this approximation, the translational frictional coefficient is completely independent of the dimensions and structure of the macromolecule, depending only on the molecular weight. On the other hand, the theory of the intrinsic viscosity of free-draining molecules, developed by Huggins¹⁸¹, Debye¹⁸², Hermans,¹⁸³ and Kramers¹⁸⁴ gives the equation

$$[\eta] = \frac{\zeta N_A}{6\eta_0 M_0} \bar{R}^2, \quad (73)$$

where η_0 is the viscosity of the solvent, and M_0 is the molecular weight of a segment. According to

*In studying the hydrodynamic properties of macromolecules, just as in the study of volume effects, the "pearl necklace" model is commonly used, that is, a set of segments joined by non-material bonds.

(73), $[\eta] \sim \overline{R^2}$, i. e., it depends directly on the dimensions of the macromolecule. Here, it follows from the derivation of (73) that in the approximation being considered (with free draining), the relation between $[\eta]$ and $\overline{R^2}$ is universal. That is, it is independent of the structure of the macromolecule.

The opposite limiting case corresponds to a macromolecule which completely carries with it in its motion all of the solvent occurring within it. Thus, it can be treated by the model of a spherical particle, impermeable to the solvent. In this case, the translational frictional coefficient and the intrinsic viscosity of the macromolecule are expressed, respectively, by the well-known equations of Stokes

$$F = 6\pi\eta_0 R_e \quad (74)$$

and Einstein

$$[\eta] = 2.5N_A \frac{V_e}{M} \quad (75)$$

In (74) and (75), R_e and V_e denote the radius and the volume of the effective hydrodynamic sphere respectively.

It follows from (72) and (73) that for a free-draining Gaussian chain, F and $[\eta]$ are proportional to M . On the other hand, for Gaussian chains which are impermeable to the flow of the solvent (if we consider the radius of the effective sphere to be proportional to the radius of gyration of the chain), we obtain the relation that F and $[\eta]$ are proportional to \sqrt{M} . (This is because $R_e \sim \sqrt{M}$, and $V_e \sim M^{3/2}$.) Experimental data obtained for a large number of polymer-solvent systems (see, e. g., reference 19) show that, for flexible chains, $[\eta] \sim M^a$, where $0.5 < a < 0.8$; and $F \sim M^b$, where $0.5 < b < 0.6$. This fact may be explained in two ways, naturally: either by postulating the partial permeability of the chain, whereby the values of a and b are intermediate between the two limiting cases, or by bringing in the non-Gaussian character of the chains. The latter factor leads to a stronger dependence of R_e and V_e of the impermeable molecules on the molecular weight. The second explanation was proposed by W. Kuhn² as early as 1934. However, in view of the fact that practically nothing was known about volume effects at that time, this explanation was immediately abandoned.

In 1948, Kirkwood and Riseman¹⁸⁵ and Debye and Bueche¹⁸⁶ developed a theory of the hydrodynamic properties of macromolecules which are partially permeable by the solvent. Here, Debye and Bueche used as the model of the molecule a

sphere uniformly filled with segments, while Kirkwood and Riseman studied the more realistic model of a Gaussian chain. The results of the Kirkwood-Roseman theory have the form

$$F = \frac{(\overline{h^2})^{1/2} \eta_0}{\frac{2^{5/2}}{(3\pi)^{3/2}} + \frac{\eta_0 (\overline{h^2})^{1/2}}{x\zeta}} \quad (76)$$

and

$$[\eta] = \left(\frac{\pi}{6}\right)^{3/2} N_A X F(X) \frac{(\overline{h^2})^{3/2}}{M}, \quad (77)$$

where $X = x\zeta/(6\pi^3)^{1/2} \eta_0 (\overline{h^2})^{1/2}$, and $F(X)$ is a function tabulated in reference 185 and 187. This function approaches unity as $x\zeta/\eta_0 (\overline{h^2})^{1/2}$ approaches zero, while as $x\zeta/\eta_0 (\overline{h^2})^{1/2} \rightarrow \infty$, it decreases like $1/X$.

For $x\zeta/\eta_0 (\overline{h^2})^{1/2} \ll 1$, (76) and (77) go over, respectively, into (72) and (73) for the free-draining chain, while for $x\zeta/\eta_0 (\overline{h^2})^{1/2} \gg 1$, they give the equations

$$F = P (\overline{h^2})^{1/2} \eta_0, \quad (78)$$

where $P = \frac{(3\pi)^{3/2}}{2^{5/2}} = 5.11$, and $P = (3\pi)^{3/2}/2^{5/2} = 5.11$,

$$[\eta] = \Phi \frac{(\overline{h^2})^{3/2}}{M}, \quad (79)$$

where $\Phi = (\pi/6)^{3/2} N_A [XF(X)]_{X=\infty}$. Equations (78) and (79) are nothing but the Stokes and Einstein equations applied to macromolecules. According to the Kirkwood-Riseman and Debye-Bueche theories, the formulas relating F and $[\eta]$ to M are characterized by exponents a and b (see above), which decrease from 1.0 to 0.5 as $x\zeta/\eta_0 (\overline{h^2})^{1/2}$ increases. These authors consider, on this basis, that the experimental values of a and b are determined by the partial permeability of the chain for the solvent. However, the values of ζ obtained from the experimental values of a and b were one or two orders of magnitude smaller than might have been expected on the basis of Stokes' Law applied to the individual segment.

Flory, Fox, and Mandelkern^{19, 108, 188} have considered the fact that the Kirkwood-Riseman and Debye-Bueche approach completely ignores the role of volume effects. Since volume effects have a considerable influence on the relation of $\overline{h^2}$ to M , the determination of $x\zeta/\eta_0 (\overline{h^2})^{1/2}$ from a and b is quite improper. In addition, the application of Stokes' Law to the individual segments leads to the following numerical estimate¹⁹ of the coefficients in (76):

$$F = \frac{(\overline{h^2})^{1/2} \eta_0}{0.2 + \frac{0.1}{V_e x}} \quad (80)$$

*Einstein's equation for the viscosity of a suspension of spherical particles is commonly written in the form: $(\eta - \eta_0)/\eta_0 = 2.5 \Omega$, where $\Omega = cN_A V_e/M$ is the volume fraction of the particles in the solution.

Hence, at the large molecular weights of interest to us, (78) and (79) must be valid; these pertain to macromolecules which are impermeable to the solvent. From this viewpoint, deviations from proportionality between $[\eta]$ and F , on the one hand, and \sqrt{M} , on the other, must be explained entirely by volume effects, rather than by partial permeability of the molecule. In fact, if we take into account the fact that $\overline{h^2} \sim M^{1+\epsilon}$, where $0 < \epsilon < 0.2$ (see above), we obtain for flexible chains, $[\eta] \sim M^{(1+3\epsilon)/2}$, and $F \sim M^{(1+\epsilon)/2}$. This gives precisely the interval of exponents a and b (respectively 0.5 -- 0.8 and 0.5 -- 0.6) which were observed experimentally.

The crucial experiment that confirmed the validity of the viewpoint of Flory and Fox was the establishment by Flory and his associates^{13, 14, 17, 18, 36, 189} of the fact that in ideal solvents, when volume effects are absent, $[\eta] \sim \sqrt{M}$ (see the résumé of these papers in reference¹⁹). A direct test of (79) was carried out by Flory¹⁹ on the basis of published data.^{16, 26, 186, 190} This showed that this equation is verified by experiment. Here, the empirical value $\Phi = 2.1 (\pm 0.2) \times 10^{21}$ was obtained. With regard to the theoretical value of Φ according to the initial paper of Kirkwood and Riseman,¹⁸⁵ $\Phi = 3.62 \times 10^{21} [(\overline{h^2})^{1/2}]$ being measured in cm, and $[\eta]$ in dl/g). However, this value was obtained by an incorrect solution involved in the theory of the integral equation¹⁹¹. A numerical solution of this equation¹⁸⁷ gave: $\Phi = 3.36 \times 10^{21}$ but there was no estimate of the error of this result. In a paper by Auer and Gardner¹⁹² this equation was solved by an accurate method which they developed* in reference 193. This gave $\Phi = 2.90 \times 10^{21}$ (correction of the allowed error of calculation¹¹⁵ in paper¹⁹² gives $\Phi = 2.86 \times 10^{21}$). Finally Zimm¹⁹⁴ has obtained $\Phi = 2.84 \times 10^{21}$ on the basis of another model of the chain, with a different method of calculation.

In addition, a number of experimental studies have confirmed the constancy of the quantity $[\eta]^{1/3} M^{1/3} \eta_0 / F$, which should be equal to $\Phi^{1/3} / P$, according to (78) and (79). By using the data of reference¹⁸⁸ and¹⁹⁵⁻¹⁹⁸, in which F was determined by the sedimentation method, Flory¹⁹ showed that $\Phi^{1/3} / P = 2.5 (\pm 0.1) \times 10^6$. Substituting in the value $\Phi = 2.1 \times 10^{21}$, we obtain $P = 5.1$, in excellent agreement with theory. The same value of $\Phi^{1/3} / P$ was found in the studies of V. N. Tsvetkov and S. I. Klenin,¹⁹⁹⁻²⁰¹ in which F was determined from the coefficient of translational dif-

fusion, as measured by the method of V. N. Tsvetkov²⁰² (this method permits one to measure the diffusion coefficient at exceedingly small concentrations, which ensures obtaining especially reliable values). Finally, Oth and Desreux²⁰³ and V. N. Tsvetkov and S. I. Klenin²⁰⁴ have subjected (78) to a direct experimental test. (In reference²⁰³ was determined by sedimentation, while in reference²⁰⁴ it was determined by translational diffusion.) They obtained the result that this equation is valid within the experimental limits of error; in complete agreement with theory, P was equal to 5.1.

We see that whereas the theoretical value of P agrees with experiment, the theoretical value of Φ is greater than the experimental value by an amount appreciably outside the limits of error of the experiment. This may be explained by the fact that the theoretical value of Φ (and also that of P) is obtained on the basis of Gaussian statistics, and hence, strictly speaking, pertains only to θ -solvents. In good solvents, the non-uniform expansion of the coil must lead to changes in the values of Φ and P . A theory of the intrinsic viscosity of macromolecules, taking into account the non-uniform expansion of the coil, has been developed by the author and Yu. E. Eizner within the framework of the theories of Zimm²⁰⁵ and of Kirkwood and Riseman.¹¹⁵ Since both approaches give identical results, we shall limit ourselves here to a brief statement of how the non-uniform expansion of the coil is taken into account in the theory of Kirkwood and Riseman¹¹⁵.

The fundamental equation of the Kirkwood-Riseman theory has the form

$$[\eta] = \frac{N_A \overline{R^2} \zeta}{6 M_0 \eta_0} \Psi, \quad (81)$$

where, for chains of high molecular weight which may be considered impermeable to the solvent

$$\Psi = \int_{-1}^{+1} \phi(\xi, \xi) d\xi, \quad (82)$$

whereas $\phi(\xi, \eta)$ is the solution of the integral equation

$$f(\xi, \eta) = \frac{x\xi}{2} \int_{-1}^{+1} T(\xi, \tau) \phi(\tau, \eta) d\tau. \quad (83)$$

Here, $\xi = 2p/x - 1$; $\eta = 2p'/x - 1$; $\tau = 2t/x - 1$ (p, p' and t are numbers of segments),

$$f(\xi, \eta) = \frac{1}{2} \frac{R_{cp} \cdot R_{cp'}}{R^2} \quad (84)$$

R_{cp} is a vector joining the p -th segment with the center of gravity of the chain), and

$$T(\xi, \tau) = \frac{1}{6\pi\eta_0} \left(\frac{1}{r_{pt}} \right) \quad (85)$$

*The method of Auer and Gardner consists in expanding the desired function, the kernel, and the singularities of the integral equation in a series of Gegenbauer polynomials.

are the components of the average tensor of hydrodynamic interaction (the tensor of Oseen)

For Gaussian chains,

$$\overline{r_{pt}^2} = |t - p| a^2, \quad \left(\frac{1}{r_{pt}} \right) = \left(\frac{6}{\pi} \right)^{1/2} (\overline{r_{pt}^2})^{-1/2},$$

$$f_0(\xi, \eta) = \frac{1}{8} [3(\xi^2 + \eta^2) - 6|\xi - \eta| + 2] \quad (86)$$

and

$$T_0(\xi, \tau) = \frac{1}{V \cdot 3 \cdot \pi^{3/2} \eta_0 (h_0^2)^{3/2} |\tau - \xi|^{1/2}} \quad (87)$$

Solving (82) and (83), with (86) and (87) taken into account, Auer and Gardner¹⁹² obtained Eq. (79) with $\Phi = 2.90 \times 10^{21}$. As was shown in reference 115, the influence of the volume effects on $[\eta]$ by way of their influence on the function $f(\xi, \eta)$ (which characterizes the distribution of the segments with respect to the center of gravity) is small, and we may neglect it. Hence, we must take into account only the influence of non-uniform expansion of the coil on the hydrodynamic interactions of the segments, as characterized by the Oseen tensor. By considering, as before, that $1/\overline{(1/r_{pt})} = (6/\pi)^{1/2} (\overline{r_{pt}^2})^{-1/2}$

but making use of the expression $\overline{r_{pt}^2} = |t - p|^{1+\epsilon} a^2$

(thus approximately taking into account the non-uniform expansion of the coil), the authors of reference 115 obtained in place of (79) the equation

$$[\eta] = \Phi(\epsilon) \cdot 6^{3/2} \frac{(\overline{R^2})^{3/2}}{M} \quad (88)$$

where $\Phi(\epsilon)$ is a coefficient whose dependence on ϵ may be approximated by the equation

$$\Phi(\epsilon) = 2.86 \cdot 10^{21} (1 - 2.63\epsilon + 2.86\epsilon^2) \quad (89)$$

A practically analogous result was obtained by the author and Yu. E. Éizner** within the framework of Zimm's theory²⁰⁵.

We see that the coefficient Φ in (88) is smaller in better solvents. In other words, in better solvents $[\eta]$ increases more slowly than the volume of the macromolecule, as characterized by the quantity $(\overline{R^2})^{3/2}$. This is explained by the fact that $[\eta]$ is proportional to the product $\overline{R^2} \cdot \Psi$

*Since it is not h^2 but R^2 which we measure directly in the light-scattering method (see above), it is more natural to discuss the relation between $[\eta]$ and R^2 (rather than h^2).

**The small differences (namely, according to Zimm's theory, $\Phi = 2.84 \times 10^{21}$ when $\epsilon = 0$) can be explained by the distinction that, in Zimm's theory, the coil is considered to rotate about the center of hydrodynamic resistance, rather than about its center of gravity, as it does in the Kirkwood-Riseman theory.

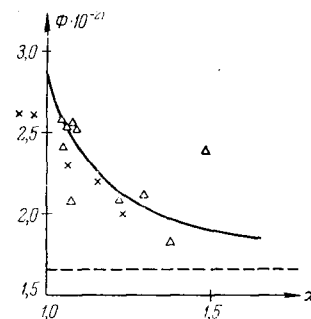


FIG. 10. Relation of the Flory coefficient Φ to the coefficient of expansion of the molecule α . — theoretical curve obtained by the author and Yu. E. Éizner;¹¹⁵ - - - - asymptote of the theoretical curve; experimental data: x²¹ (polystyrene with $M = 3.20 \times 10^6$ in cyclohexane at various temperatures), Δ ¹⁶ (polystyrene with $M = 0.51 \times 10^6$ -- 1.76×10^6 in various solvents).

[see Eq. (81)]. Here, Ψ depends on the quantities $(1/r_{pt})$, which determine the hydrodynamic interactions in the chain. Since volume effects have a stronger influence on distances between more distant segments of the chain, they have less effect on the quantities $(1/r_{pt})$ than on the quantities r_{pt}^2 on which R^2 depends²⁰⁶. It is obvious that distant pairs of segments contribute more to quantities depending on r_{pt}^2 than they do to those depending on $(1/r_{pt})$. The situation in this case is completely analogous to that which occurs in the theory of light scattering (see above), in which the volume effects also have a relatively weak influence on the scattering at large angles, since this is determined by scattering between nearby segments in the chain.

In order to compare the theory presented above with experiment, we shall express ϵ in terms of α , with the aid of the equation: $\epsilon = d \ln \alpha^2 / d \ln M = (\alpha^2 - 1) / (5\alpha - 3)$ ¹¹⁵, which follows directly from the formula $\alpha^5 - \alpha^3 = \text{const.}$. The relation of Φ to α , determined as indicated is shown in Fig. 10, on which are also given the corresponding experimental data.* The agreement between theory and experiment must be recognized to be exceedingly good, considering the relatively coarse way of taking the non-uniform expansion of the coil into ac-

*For the quantitative comparison with the theory, only studies were used in which: R^2 was determined by Zimm's method, an appreciable dependence of $[\eta]$ on the velocity gradient of flow could not be expected, and the polydispersity of the studied polymers (which has a considerable effect on Φ ^{26, 115}) had been estimated. Qualitatively, the decrease of Φ in better solvents may be obtained from the analysis of a large number of experimental studies (see, e.g., references 12, 33, 207, and 208).

count and the absence of any arbitrary parameters in the theory. This pertains especially to the results of the study of Krigbaum and Carpenter²¹, in which a special study was made of the dependence of Φ on the quality of the solvent, and in which a lack of proportionality between $[\eta]$ and $(\overline{R^2})^{3/2}$ was shown for the first time.

The results of the study given above show that the discrepancy between the theoretical and empirical values of Φ (see above) may be explained by the fact that the theoretical value pertained to a θ -solvent, while the empirical value was obtained by Flory by analysis of experiments, most of which were carried out in good solvents, in which Φ is close to 2.1×10^{21} . It also follows from this study that, in the determination of $(\overline{h^2})^{1/2}$ from data on the value of the intrinsic viscosity $[\eta]_{\theta}$ in θ -solvents, one must use the value $\Phi = 2.86 \times 10^{21}$ (rather than 2.1×10^{21}). This will lead to a decrease in the values of $(\overline{h_0^2})^{1/2}$ obtained thus by about 10%. It is also necessary to take into account the dependence of Φ on α in the determination of Φ from the intrinsic viscosity.

The influence of volume effects on the intrinsic viscosity was also studied recently in a paper by Yamakawa and Kurata,^{209, 210} whose theory was limited to the region of small values of z . The study by these authors proceeds from the same physical assumptions as do references¹¹⁵ and²⁰⁵. However, the influence of non-uniform expansion of the coil on the hydrodynamic interaction was taken into account in a relatively coarse manner, and an inexact solution of the integral equation of Kirkwood and Riseman was used. Thus, Yamakawa and Kurata obtained a much weaker dependence of Φ on the solvent, incapable of explaining the experimental data. (For a critique of the paper of Yamakawa and Kurata, see reference¹⁷³.) In addition, we must emphasize that the theory of the author and Yu. E. Eizner apparently exaggerates somewhat the dependence of Φ on α in the region of α close to unity. Indeed, it follows from (89) that, in the vicinity of the θ -point

$$\Phi = 2.86 \cdot 10^{21} (1 - 1.75z + \dots), \quad (90)$$

whereby $[\eta] = [\eta]_{\theta} (1 + 0.16z)$. Since the coefficient of z in the latter equation appears as a small difference between two large quantities, a small error in (90) may lead to a considerable change in this coefficient. In fact, experiment apparently indicates a stronger temperature-dependence of $[\eta]$ near the θ -point than would be expected from the equation $[\eta] = [\eta]_{\theta} (1 + 0.16z)$. Unfortunately, the development of a rigorous theory of the dependence of $[\eta]$ on z encounters enormous difficulties

in calculation, even in the region of small values of z (the solution of an integral equation with a very complex core).

Analogously, a theory may be developed about the influence of volume effects on the translational frictional constant of a macromolecule. A general theory of the translational frictional constant was developed by Kirkwood²¹¹, and is not connected with any special assumptions about the structure of the chain. This theory leads, for a macromolecule impermeable to the solvent, to the expression

$$F = \frac{3\pi\alpha^2\eta_0}{N} \sum_{p, t=1}^N \left(\frac{1}{r_{pt}} \right) \quad (91)$$

For linear Gaussian chains, (91) goes over into (78) with $P = 5.11$. A consideration of the non-uniform expansion of the coil in the theory of the translational friction of a macromolecule was first made by Peterlin.²¹²⁻²¹⁵ He made use of the distribution function for h which he had obtained¹⁴⁷ [see above, Eq. (41)], found an expression for $(1/h)$, and suggested that an expression for $(1/r_{pt})$ may be obtained from it by replacing N by $P|t-p|$. Peterlin's result, referred to the case of small values of z , may be given in the form

$$P = P_0 (1 - 0.31z). \quad (92)$$

Hence, the coefficient P , just like the coefficient Φ , decreases in better solvents. That is, volume effects have a weaker influence on the translational frictional constant F than they do on $(\overline{R^2})^{1/2}$.

Subsequent studies have shown, however, that Peterlin's theory considerably exaggerates the influence of volume effects on P . In the paper of the author and Yu. E. Eizner¹¹⁵, who used the "Gaussian" relation between $(1/r_{pt})$ and r_{pt}^2 , just as in the theory of $[\eta]$, but considered that $\frac{1}{r_{pt}^2} = |t-p|^{1+\epsilon} \alpha^2$, it was shown that

$$P = P_0 \left(1 - \frac{\epsilon}{4} z \right), \quad (93)$$

That is, the decrease in P is not greater than 5% (since $\epsilon \ll 0.2$). It follows from (93) that, in particular, when $z \ll 1$, $P = P_0 (1 - 0.16z)$. That is, the influence of volume effects on P is an order of magnitude smaller than their influence on Φ [cf. Eq. 90], obtained under the same approximations). Finally, in the papers of Stockmayer and Albrecht²¹⁶ and of the author and Yu. E. Eizner¹⁷³, in which the influence of volume effects on P in the region of small values

of z was taken into account by the rigorous method, it was shown that

$$P = P_0(1 - 0.03z), \quad (94)$$

so that, in practice, Flory's equation (78) is obeyed with a sufficient degree of accuracy.

7. CONCLUSION

The results given above of the modern theories of short-range and long-range interactions in polymer chains show that it is absolutely necessary to take these intersections into account in order to explain quantitatively the properties of macromolecules in solution. This is no less true of the properties of bulk polymers, which we have not considered here. Here, the short-range interactions, which determine the flexibility of the chain, are above all responsible for the differences in physical properties of macromolecules of differing chemical and stereochemical structures, while the long-range interactions are responsible for the differences in behavior of macromolecules in different solvents.

The theory of short-range interactions, determining the relation between the structures and properties of chains, has just begun to be developed. On the other hand, the theory of long-range interactions, which establishes the correlation between various properties of chains, is in a relatively better status. Studies in recent years, which have involved taking into account the non-uniform expansion of the coil due to long-range interactions, have led to the elimination of practically all of the appreciable discrepancies between theory and experiment. At present, if we know the dimensions of the molecules of a given polymer in a given solvent, as well as their dimensions in an ideal solvent, and the molecular weight, we can predict the second virial coefficient, the form of the curve of angular dissymmetry of light-scattering, the intrinsic viscosity, and the translational frictional constant with and accuracy not much poorer than the experimental accuracy.

We have considered in this paper only linear macromolecules without free charges or hydrogen-bonding groups. Branching appreciably decreases the dimensions of chains, for a given molecular weight.^{217, 218} This effect is partially compensated by the role of volume effects, which increases with the degree of branching.²¹⁹ Branching also affects the form of the light-scattering curve,^{170, 171} the hydrodynamic properties,^{206, 220, 221, 223} and the second virial coefficient^{220, 222} of molecules of given dimensions and given

molecular weight. (In particular, as is shown by theory^{206, 220, 221, 223} and experiment,^{223, 224} 224 Flory's coefficients Φ and P increase with increasing degree of branching.) At present, we possess a quantitative theory of the influence of branching on all the fundamental characteristics of macromolecules in solution.

With regard to theories of the influence of free charges and intra- and intermolecular hydrogen bonds on the properties of macromolecules in solution, at present we are far from a final solution of this problem, in spite of the large number of studies devoted to these questions. Yet, it is just the properties of charge polymers (polyelectrolytes) and polymers with hydrogen bonds (in particular, polypeptides) which are of special interest to us. This is because, on the one hand, the study of polyelectrolytes and hydrogen-bonded polymers is necessary for the development of a physicochemical theory of biological phenomena.²²⁵ On the other hand, in these polymers many properties are clearly manifested, which are also characteristic of ordinary polymers, but which lead only to relatively subtle effects in the latter. Thus, electrostatic long-range interactions in polyelectrolytes must lead to incomparably larger non-uniformities in the expansion of the coil than take place in the case of the volume effects. This fact has many consequences in the theory of light-scattering, and hydrodynamic and thermodynamic properties of polyelectrolyte solutions. Short-range interactions (intramolecular hydrogen bonds) in polypeptides stabilizes helical chain conformations, so that the helix-coil transition in the one-dimensional systems which are comprised by macromolecules has a cooperative nature (the so-called "intramolecular melting"). We cannot spend time in this article on these interesting phenomena, but refer the reader to reviews on this subject (see, e. g., references 9, 98, and 226). The development of a quantitative theory of the properties of molecules of polyelectrolytes and hydrogen-bonded polymers is undoubtedly one of the most essential problems of modern statistical physics of polymers.

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Translated by M. V. King

Translator's Comments - A review such as this is especially welcome in the field of physics of polymer solutions, which has far outstripped all available monographs, and is difficult to keep up with, even with the aid of review papers. The list of papers cited is extensive, the work both of the Soviet schools, especially the Institut Vysokomolekulyarnykh Soedinenii (Institute of High-Molecular-Weight Compounds), and of Western authors being well represented. However, this large set of references is not complete, even for the limited part of the field of physics of polymer solutions which the author has chosen for his subject. In particular, the book by Tompa¹ on polymer solutions is not cited, nor are any of the papers by that author. This oversight is understandable, but unfortunate, since certain of the chapters in Tompa's book cover much of the same subject matter as this review, and the book contains a similar long bibliography. Actually, to obtain a treatment as thorough as possible of this subject, the reader should refer both to the current review and to Tompa's book.

The author has had to make a choice of emphasis in writing

about such a ramified subject, and has thus given considerably more emphasis to the studies of long-range interactions (volume effects) than to short-range interactions. A unifying theme of much of the treatment is the comparison of the Flory-Krigbaum-Orofino statistical theory of the volume effects in polymer solutions with various more precise theories which have since been proposed. A concept much used by the author in comparing the theories is that of the "non-uniform expansion of the coil", i. e., a detailed critique is given of the concept that the volume effects may be accounted for by assuming that the coil molecule expands uniformly from its ideal configuration to its actual configuration.

Special sections in the review are devoted to discussions of the predictions of light-scattering and hydrodynamic properties given by the various theories, with considerable mathematical treatment and comparison with experiment.

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