

THEORETICAL STUDIES
ON
DILUTE POLYMER SOLUTIONS

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HIROMI YAMAKAWA

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HIROMI YAMAKAWA

DEPARTMENT OF TEXTILE CHEMISTRY,
KYOTO UNIVERSITY

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INTRODUCTION

The object of chemical physics, or the molecular theory of the properties of substances, is to build a bridge between the microscopic and macroscopic worlds; that is, to interpret^{the} the macroscopic properties or behaviors of substances from the standpoint of their structure on the molecular and atomic levels, and, to the contrary, to get the informations about the molecular structure from the macroscopic properties with the aid of the theory. This principle for a study, of course, must be applied to high polymers as well as low molecular weight substances. Accordingly, in this article, the properties of polymer solutions will be treated from a "molecular-theoretical" standpoint.

Various physical and physico-chemical properties of polymer solutions may be divided into two classes, those of dilute and concentrated solutions. The first class, which is closely related to the character of solute polymer in dilute solutions such as the molecular size and shape, will be observed in the measurements of the viscosity, light scattering, osmotic pressure, etc., and the second will include the co-operative phenomena such as the phase separation, swelling, solubility, etc. For convenience, here our attentions will be focused on the properties of "dilute" polymer solutions except polyelectrolyte solutions.

In about 1950, the theoretical system of dilute polymer

solutions has almost been established by many researchers, especially by Flory. As is well known, it is the so-called "excluded volume effect" that two elements, or segments, of a polymer chain, possibly remote from one another in sequence along the chain, cannot occupy the same space simultaneously. The main contribution of Flory in this field consists in the introduction of this effect into the polymer chain statistics, and in having indicated that the behavior of a real polymer chain is essentially different from that of Markoffian. And this theory has immediately been applied to the interpretation of osmotic pressure, intrinsic viscosity, and other properties of dilute polymer solutions by Flory himself and his co-workers with a qualitatively satisfactory result. However, in his theory, the connection of segments, or the spatial correlation between segments has not completely been taken into consideration, and thereby there remain several deviations of the theories from experiments unsolved we believe. Another defect of his theories consists in the inclusion of the phenomenological parameters uneliminated. Hence we find it necessary to re-examine the theory of dilute polymer solutions from a more rigorous and molecular standpoint of statistical mechanics.

Thus, the aim of this work is not only to describe systematically the various properties of dilute polymer solutions, related to the excluded volume effect, by the molecular or mo-

del constants, but also to give a quantitative interpretation for the experimental results which cannot be explained by the published theories.

Before entering into the subject, we here conveniently summarize the present study. As for the model of polymer solution, the pearl-necklace model with the continuous medium approximation will be employed throughout this article. The final expressions all are expressed in a power series in the excluded volume parameter z .

In Chapter I, ~~to~~ make clear the nature of the excluded volume effect, the distribution function for distance R_{kl} between segments k and l of a polymer chain, its $2m$ -th moment $\langle R_{kl}^{2m} \rangle$, the mean square radius of gyration $\langle S^2 \rangle$, and the mean square distance $\langle S_k^2 \rangle$ between segment k and the molecular center of mass are calculated by using Ursell-Mayer-Tera-moto's method of expanding the chain phase integral. The results obtained are of non-Markoffian character at any temperature but the Flory point, and are qualitatively consistent with the experimental data of lattice chain obtained by direct counting of its configurations. In Chapter II, the angular distribution of scattered light is calculated using $\langle R_{kl}^{2m} \rangle$, and the influence of the volume effect upon light scattering measurement is discussed somewhat in detail.

In Chapter III, the osmotic second virial coefficient A_2 is calculated following the general solution theory of

McMillan and Mayer. Account is taken not only of the intermolecular interaction but also of the intramolecular interaction of segments or the excluded volume effect. The results show that the molecular weight dependence of A_2 is improved at least in the vicinity of the Flory temperature in comparison with the theories of Flory-Krigbaum and Isihara-Koyama.

In Chapters IV and V, theories of the intrinsic Viscosity $[\eta]$ and frictional coefficient ζ are developed on the basis of the Kirkwood and Riseman scheme. The results show that, if α is the linear expansion factor of the polymer coil, the intrinsic viscosity is asymptotically proportional to α^2 for the free-draining case and $\alpha^{2.43}$ for the impermeable case. This implies that even in the limit for impermeable molecule, the hydrodynamic radius of the polymer coil is not proportional to its statistical radius.

Finally, in Chapter VI, a thorough comparison of the present theories with experimental data is made, taking solutions of polystyrene in cyclohexane as an example. The results prove that the theories are very fitted for structural interpretation of experimental data.

Chapter I. CHAIN CONFIGURATION

§ 1. 1. Introduction

Whether the introduction of the long-range excluded volume effect into the polymer chain statistics changes the Markoffian character of the chain or not, proposes an interesting problem in both mathematical and statistical-mechanical senses, and has close relation to the various properties of the solution. In 1949, Flory¹⁾ and Suzuki²⁾ have independently developed approximate theories of this effect and indicated that the mean square end-to-end distance $\langle R^2 \rangle$ or the mean square radius of gyration $\langle S^2 \rangle$ of a chain of N links becomes asymptotically proportional to a power of N higher than the first. That is,

$$\langle R^2 \rangle \propto N^{1+\varepsilon} \quad (0 < \varepsilon < 0.2) \quad (1.1)$$

Hence, the polymer chain can never be regarded as the Markoffian. This is inevitably of importance for theoretical interpretation of the intrinsic viscosity and other physico-chemical properties of the solution.

Accordingly, a number of ways of approach has been presented to this problem since that time. In 1951, Teramoto³⁾ has developed a more rigorous theory based on the Ursell-Mayer method of imperfect gas theory, and derived an expression for

$\langle R^2 \rangle$, which is qualitatively in agreement with the Flory prediction mentioned above:

$$\langle R^2 \rangle = Na^2 \left(1 + \frac{4}{3} Z - \dots \right) \quad (1.2)$$

with $Z = \left(\frac{3}{2} \pi a^2 \right)^{3/2} \beta N^{1/2}$, (1.3)

where a is the length of a link and β is the volume excluded to the center of a segment by the presence of another. This equation has subsequently been established by many researchers,^{4) 8)} especially by Zimm, Stockmayer and Fixman,⁹⁾ and we have now the expressions not only for $\langle R^2 \rangle$ but also for $\langle S^2 \rangle$.⁹⁾

$$\langle S^2 \rangle = \frac{1}{6} Na^2 \left(1 + \frac{134}{105} Z - \dots \right). \quad (1.4)$$

However, most of the published work has been confined to the problem of the asymptotic behavior of $\langle R^2 \rangle / N$. Furthermore, except some tentative attempts,¹⁰⁾ we have not yet a reliable experimental verification of these equations. This unfortunate situation seems to arise in part from the circumstances that the effect of a heat of interaction

between solvent and polymer has not explicitly been taken into consideration and that the corresponding expressions for observable quantities such as the osmotic second virial coefficient A_2 , intrinsic viscosity $[\eta]$, etc. but $\langle S^2 \rangle$ have

not yet been established.

Thus, in this chapter, making some refinements to the interaction between solvent and polymer segment, we calculate the various statistical quantities of a single polymer chain in dilute solution based on the Ursell-Mayer-Teramoto method³⁾ not only to make clear the detailed nature of the excluded volume effect but also to derive the expressions for A_2 , $[\eta]$, etc. in later chapters.

§1. 2. Model and Segment Distribution Functions

Consider a linear chain composed of $N + 1$ spherical segments of diameter b , in which the segments are connected by N links of a constant length a one after the other and are attached numbers $0, 1, 2, \dots, N$ from one end to the other; and assume the chain to be completely flexible (pearl-necklace model).^{*} For the sake of brevity, let us denote the coordinate of segment i by the symbol (i) , and the total coordinates of a particular set of n segments by the symbol $\{n\}$. If the continuous medium approximation is adopted, the total potential energy $U\{N+1\}$ of the system is given by the sum of pair interactions between non-adjacent segments:

* The "short-range" interferences, such as fixed valence angles and hindered rotation about bonds, between neighboring elements of actual polymer chain will be discussed in the last chapter.

$$U\{N+1\} = \sum_{i < j} u(R_{ij}) \equiv \sum u_{ij}, \quad (1.5)$$

where $u(R_{ij})$ represents the potential of mean force between segments i and j as a function of the distance R_{ij} between these segments. In the present lack of knowledge of functional form of $u(R_{ij})$, we may assume as an approximation that*

$$u(R) = \begin{cases} \infty & \text{if } 0 \leq R \leq b, \\ -u_0 \exp(-3R^2/2d^2) & \text{if } R > b, \end{cases} \quad (1.6)$$

which is shown in Fig. 1. Here u_0 is an energy parameter, being positive in a poor solvent (endothermic solution) and negative in a good solvent (exothermic solution). Another parameter d is assumed to be somewhat smaller than a , for $u(R)$ is expected to be of short-range nature.

For the model described, the problem is formally the same as that of imperfect gases, namely the evaluation of a phase integral $\Omega_2(R_{kl}, N)$:

$$\Omega_2(R_{kl}, N) = \int \exp(-\sum u_{ij}/kT) d\{N+1\} / d(k) d(l), \quad (1.7)$$

* Teramoto³⁾ has employed the hard sphere potential and Zimm et al.⁹⁾ have adopted the assumption of short-range nature of $u(R)$ without giving its explicit form.

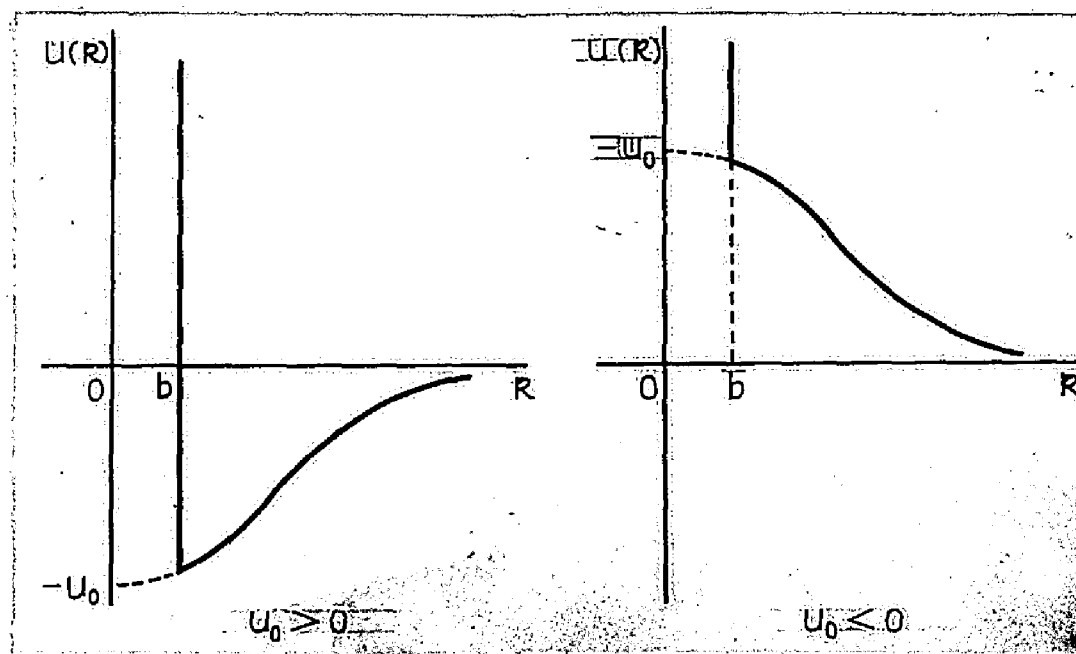


Fig. 1. Schematic representation of the potential $u(R)$ of mean force between two segments.

where k is the Boltzmann constant, and T is the absolute temperature. The integration extends over all the possible configurations under the conditions of constant link length and of fixing segment k to origin and segment l to a point at distance $R_{kl} = |R_{kl}| = |(l) - (k)|$ from the origin. (The symbol $d\{N+1\}/d(k) d(l)$ indicates that the integration goes over all coordinates except those of the specified segments k and l .)

In the absence of intersegmental force, $\Omega_2(R_{kl}, N)$ reduces to the corresponding phase integral $\Omega_2^{(0)}(R_{kl}, N)$ for the ideal chain of N links:

$$\Omega_2^{(0)}(R_{kl}, N) = \int d\{N+1\} / d(k) d(l). \quad (1.8)$$

For $\Omega_2^{(0)}(R_{kl}, N)$, we may assume

$$\Omega_2^{(0)}(R_{kl}, N) = (4\pi a^2)^N (\beta_{kl}^3 / \pi^{\frac{3}{2}}) \exp(-\beta_{kl}^2 R_{kl}^2), \quad (1.9)$$

$$\beta_{kl}^2 = 3/2(l-k)a^2,$$

where $(4\pi a^2)^N$ is the phase integral of this chain which is allowed to have all the configurations without fixing the specified segments k and l . The assumption (1.9) becomes asymptotically valid as $(l-k)$ becomes large. It is noted here that, if $\{n\} = (i), (j), \dots, (t)$, we have

$$\begin{aligned}\Omega_n^{(0)}(\{n\}, N) &= \int d\{N+1\} / d\{n\} \\ &= (4\pi a^2)^{N+l-t} \Omega_2^{(0)}(R_{ij}, j-i) \Omega_2^{(0)}(R_{jk}, k-j) \cdots \Omega_2^{(0)}(R_{st}, t-s). \quad (1.10)\end{aligned}$$

Now, if we introduce a short-range function χ_{ij} defined by

$$\chi_{ij} = \exp(-u_{ij}/kT) - 1, \quad (1.11)$$

the integrand of Eq. (1.7) can be expanded in the form,

$$\exp(-\sum u_{ij}/kT) = 1 + \sum \chi_{ij} + \sum \sum \chi_{ij} \chi_{st} + \cdots; \quad (1.12)$$

then,

$$\Omega_2(R_{kl}, N) = \Omega_2^{(0)}(R_{kl}, N) + \Omega_2^{(1)}(R_{kl}, N) + \cdots, \quad (1.13)$$

$$\Omega_2^{(1)}(R_{kl}, N) = \sum_{i < j} \int \chi_{ij} d\{N+1\} / d(k) d(l).$$

Integrating with respect to the coordinates except (k), (l), (i) and (j), with keeping Eq. (1.10) in mind, we obtain

$$\int \chi_{ij} d\{N+1\} / d(k) d(l)$$

$$\begin{aligned}
&= (4\pi\alpha^2)^{N+i-l} \int \chi_{ij} \Omega_2^{(0)}(\mathbb{R}_{ij}, j-i) \Omega_2^{(0)}(\mathbb{R}_{jk}, k-j) \\
&\quad \times \Omega_2^{(0)}(\mathbb{R}_{kl}, l-k) d(i) d(j) \quad \text{if } 0 \leq i < j \leq k, \\
&= (4\pi\alpha^2)^{N+k-l} \int \chi_{ij} \Omega_2^{(0)}(\mathbb{R}_{kl}, l-k) \Omega_2^{(0)}(\mathbb{R}_{ij}, j-i) \\
&\quad \times \Omega_2^{(0)}(\mathbb{R}_{jl}, l-j) d(i) d(j) \quad \text{if } k \leq i < j \leq l,
\end{aligned} \tag{1.14}$$

Fig. 2 shows the cluster diagrams corresponding to each expression in Eq. (1.14). The integrals of this type can be readily evaluated by the Fourier and inverse transformations.¹¹⁾ An example is taken of the case $k \leq i < j \leq l$ below. If the Fourier transform of the integral

$$\begin{aligned}
J(\mathbb{R}_{kl}) &= \int \chi_{ij} \Omega_2^{(0)}(\mathbb{R}_{kl}, l-k) \Omega_2^{(0)}(\mathbb{R}_{ij}, j-i) \\
&\quad \times \Omega_2^{(0)}(\mathbb{R}_{jl}, l-j) d(i) d(j)
\end{aligned} \tag{1.15}$$

is denoted by $H(q)$, the inverse transform $J(\mathbb{R}_{kl})$ is given by

$$J(\mathbb{R}_{kl}) = \frac{1}{8\pi^3} \int \exp(-i\mathbf{q} \cdot \mathbb{R}_{kl}) \cdot H(\mathbf{q}) d\mathbf{q} \tag{1.16}$$

with

$$H(\mathbf{q}) = h_1(\mathbf{q}, i-k) h_2(\mathbf{q}, j-i) h_1(\mathbf{q}, l-j),$$

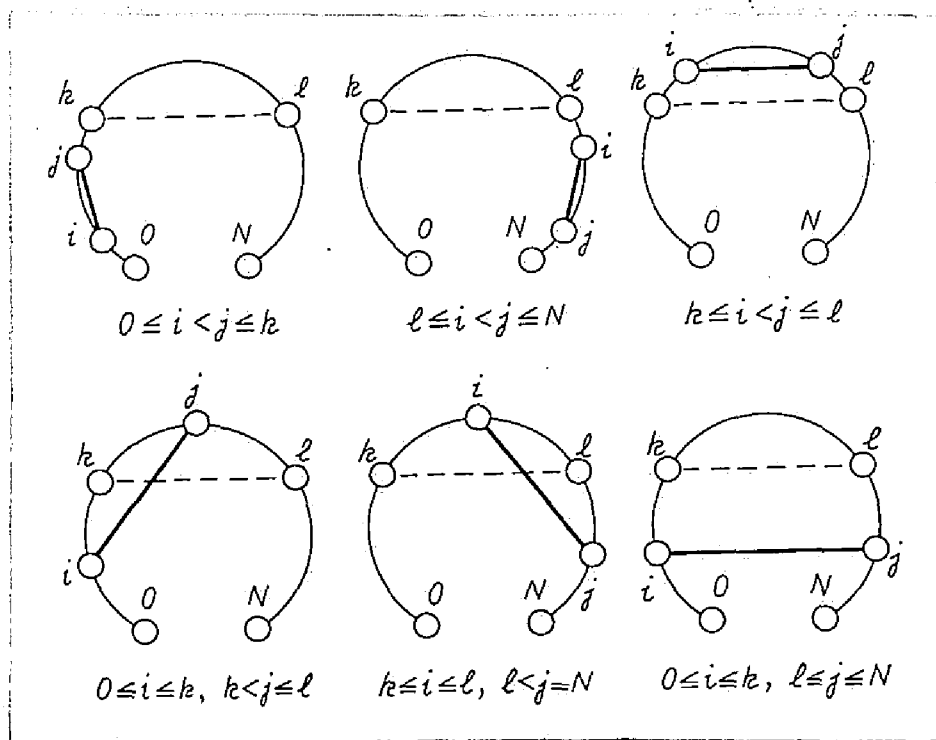


Fig. 2. Cluster diagrams for the single contact integral:

$\int \chi_{ij} d\{N-1\} / d(k)d(l)$. The heavy lines connect the contact segments i and j . The broken lines represent the given distance R_{kl} .

$$h_1(q, i-k) = \int \Omega_2^{(0)}(R_{ki}, i-k) \exp(iq \cdot R_{ki}) dR_{ki},$$

$$h_2(q, j-i) = \int \chi(R_{ij}) \Omega_2^{(0)}(R_{ij}, j-i) \exp(iq \cdot R_{ij}) dR_{ij}, \quad (1.17)$$

$$h_1(q, l-j) = \int \Omega_2^{(0)}(R_{jl}, l-j) \exp(iq \cdot R_{jl}) dR_{jl}.$$

On performing the integrations in Eqs. (1.16) and (1.17), all terms higher than the second of u_0/kT in the expansion of χ_{ij} are neglected. This neglect is justified by the experimental result that the heat of mixing is usually small in polymer solutions. Furthermore, the following approximation is introduced,

$$b \ll d < a. \quad (1.18)$$

This is a necessary condition in order that the imperfect gas-like expansion could be applied: the first condition $b \ll a$ indicates that the volume effect is sufficiently small, and the second condition $d < a$ means the mean force of segmental interaction to be short-ranged, as supposed from Eq. (1.6). Thus, after laborious but straightforward

calculations,* we arrive at**

$$J(R_{kl}) = -[Z/N^{\frac{1}{2}}(j-l)^{\frac{3}{2}}](4\pi a^2)^{l-k}(\gamma_{kl}^3/\pi^{\frac{3}{2}})\exp(-\gamma_{kl}^2 R_{kl}^2), \quad (1.19)$$

$$\gamma_{kl}^2 = 3/2(l-k-j+l)a^2$$

with
$$Z = \left(\frac{6}{\pi}\right)^{\frac{1}{2}} \left(\frac{b}{a}\right)^3 \left(1 - \frac{\Theta}{T}\right) N^{\frac{1}{2}}, \quad (1.20)$$

$$\Theta = \left[\left(\frac{\pi}{\delta}\right)^{\frac{1}{2}} \left(\frac{d}{b}\right)^3 - 1 \right] \left(\frac{u_0}{k}\right). \quad (1.21)$$

Θ has the dimension of temperature and it is expected from Eq. (1.18) to have the same sign as u_0 . If we could consider higher terms than the second of u_0/kT , $[1 - (\Theta/T)]$ in z would be replaced by a power series in Θ/T in general.

Calculating the remaining integrals in Eq. (1.14) by the similar procedure as mentioned above, eventually we obtain

* See Appendix I.

** This expression for z is identical to that by Zimm et al.⁹⁾ The substitution of the following into Eq. (1.3) gives Eq. (1.20).

$$\beta = - \int_0^\infty [\exp(-u/kT) - 1] 4\pi r^2 dr \simeq (4\pi b^3/3)[1 - (\Theta/T)].$$

$$\Omega_2^{(1)}(R_{kl}, N) = \sum_{i < j} \left[-z / N^{\frac{1}{2}} (j-i)^{\frac{3}{2}} \right] \\ \times (4\pi a^2)^N (\gamma_{kl}^3 / \pi^{\frac{3}{2}}) \exp(-\gamma_{kl}^2 R_{kl}^2),$$

$$\gamma_{kl}^2 = 3/2 \gamma_{kl} a^2,$$

$$\gamma_{kl} = \begin{cases} l-k & \text{if } 0 \leq i < j \leq k \text{ or } l \leq i < j \leq N, \\ (l-k) - (j-i) & \text{if } k \leq i < j \leq l, \\ (l-k) - [(j-k)^2 / (j-i)] & \text{if } 0 \leq i \leq k, k < j \leq l, \\ (l-k) - [(l-i)^2 / (j-i)] & \text{if } k \leq i \leq l, l < j \leq N, \\ (l-k) - [(l-k)^2 / (j-i)] & \text{if } 0 \leq i \leq k, l < j \leq N. \end{cases} \quad (1.22)$$

The calculation of $\Omega_2^{(n)}(R_{kl}, N)$'s higher than $\Omega_2^{(1)}(R_{kl}, N)$ is not given here, but their contribution to $\Omega_2(R_{kl}, N)$ should be proportional to higher powers than the second of z . Thus, it is concluded that the combination of Eq. (1.13) with Eqs. (1.9) and (1.22) — hereafter, call it the single contact approximation — gives correctly $\Omega_2(R_{kl}, N)$ up to the first power of z and enables one to calculate the initial dependence of average chain configurations on z .

The probability $p_n \{n\} d\{n\}$ of observing a particular set of n segments in $d\{n\}$ at $\{n\}$, irrespective of the coordinates of the remaining segments, is given by

$$p_n\{n\}d\{n\} = C \times \Omega_n(\{n\}, N) d\{n\},$$

$$\Omega_n(\{n\}, N) = \int \exp(-\sum u_{ij}/kT) d\{N+1\}/d\{n\}, \quad (1.23)$$

$$\begin{aligned} C^{-1} &= \frac{1}{V} \int \Omega_n(\{n\}, N) d\{n\} \\ &= \int \exp(-\sum u_{ij}/kT) d\{N+1\}/d(k), \end{aligned}$$

where V is the volume of the system. We shall call the function $p_n\{n\}$ "reduced segment distribution function." Using Eq. (1.13) with (1.9) and (1.22), and remembering the definition of $\Omega_2(|R_{kl}|, N)$, Eq. (1.7), we can obtain

$$\begin{aligned} C^{-1} &= \int_0^\infty \Omega_2(R_{kl}, N) 4\pi R_{kl}^2 dR_{kl} \\ &= (4\pi a^2)^N \left[1 - \sum N^{-\frac{1}{2}} \sum_{i < j} (j-i)^{-\frac{3}{2}} + \dots \right] \quad (1.24) \\ &= (4\pi a^2)^N \left\{ 1 - \sqrt{2} (N^{\frac{1}{2}} - 2\sqrt{2}) \sum + \dots \right\} \text{ for large } N. \end{aligned}$$

In addition, the radial distribution function for unspecified segment $g_2(r)$, which is used in the next chapter, may be written as

$$g_2(r) = 2N^{-2} \sum_{k < l} p_2(k, l; |R_{kl}| = r). \quad (1.25)$$

§ 1. 3. Average Chain Configurations

Our aim in this section is to derive the various average chain configurations which characterize the statistical properties of a single polymer chain present in dilute solution. More generally than in the earlier works, we begin with the calculation of the $2m$ -th moment of the distribution function of the distance between segments k and l , from which the mean square end-to-end distance, the mean square radius of gyration, etc. are immediately derived.

(a) Distance between segments k and l .

It is clear that $\langle R_{kl}^{2m} \rangle$ is given by

$$\begin{aligned} \langle R_{kl}^{2m} \rangle &= \int R_{kl}^{2m} p_2(k, l) 4\pi R_{kl}^2 dR_{kl} \\ &= \int R_{kl}^{2m+2} \Omega_2(R_{kl}, N) dR_{kl} / \int R_{kl}^2 \Omega_2(R_{kl}, N) dR_{kl}. \end{aligned} \quad (1.26)$$

Substituting Eqs. (1.13) with (1.9) and (1.22) into Eq. (1.26), we obtain

$$\begin{aligned} \langle R_{kl}^{2m} \rangle &= \frac{(2m+1)!}{6^m m!} (l-k)^m a^{2m} [1 + I_m(N, k, l) z], \\ I_m(N, k, l) &= N^{-\frac{1}{2}} \sum_{i < j} \{1 - [\gamma_{kl}/(l-k)]^m\} (j-i)^{-\frac{3}{2}}. \end{aligned} \quad (1.27)$$

The sums may be converted to integrals, and the integrations proceed in terms of elementary functions. The result is (for $N^{1/2} \gg 1$),

$$\begin{aligned}
 I_m(N, k, \ell) = & \frac{4}{N^{\frac{1}{2}}} \sum_{p=1}^m \frac{(-1)^{p+1}}{p + \frac{1}{2}} \binom{m}{p} \left\{ \frac{p}{p^2 - \frac{1}{4}} (\ell - k)^{\frac{1}{2}} \right. \\
 & + \frac{1}{p - \frac{1}{2}} [N^{-p+\frac{1}{2}} - \ell^{-p+\frac{1}{2}} - (N-k)^{-p+\frac{1}{2}}] (\ell - k)^p \\
 & + \sum_{q=0}^{2p} \frac{(-1)^{q+1}}{p - q + \frac{1}{2}} \binom{2p}{q} \{ k^q (\ell^{p-q+\frac{1}{2}} - k^{p-q+\frac{1}{2}}) \\
 & \left. + (N-\ell)^q ((N-k)^{p-q+\frac{1}{2}} - (N-\ell)^{p-q+\frac{1}{2}}) \} (\ell - k)^{-p} \right\}. \quad (1.28)
 \end{aligned}$$

When $m = 1$, we obtain immediately the mean square distance $\langle R_{kl}^2 \rangle$ between segments k and l :

$$\langle R_{kl}^2 \rangle = (\ell - k) a^2 [1 + I_1(N, k, \ell)],$$

$$\begin{aligned}
 I_1(N, k, \ell) = & (4/3) N^{-\frac{1}{2}} \left\{ (8/3) (\ell - k)^{\frac{1}{2}} - 4 (N - k)^{\frac{1}{2}} \right. \\
 & - 4 \ell^{\frac{1}{2}} + N^{-\frac{1}{2}} (\ell - k) - (8/3) (\ell - k)^{-1} \\
 & \left. \times \left[(N - \ell)^{\frac{3}{2}} - (N - k)^{\frac{3}{2}} - \ell^{\frac{3}{2}} + k^{\frac{3}{2}} \right] \right\}. \quad (1.29)
 \end{aligned}$$

(b) Distance between the End Segments.

In the case of $k = 0$ and $l = N$, from Eq. (1.27), we obtain for the $2m$ -th moment of the distribution function of the end-to-end distance

$$\begin{aligned} \langle R^{2m} \rangle \equiv \langle R_{ON}^{2m} \rangle &= [(2m+1)! / 6^m m!] N^m a^{2m} \\ &\times \left\{ 1 + \left[\sum_{p=1}^m \frac{(-1)^{p+1}}{p^2 - \frac{1}{4}} \binom{m}{p} \right] z \right\}. \end{aligned} \quad (1.30)$$

The above equation, when $m = 1$, gives the mean square end-to-end distance,

$$\langle R^2 \rangle = N a^2 \left[1 + (4/3) z \right], \quad (1.31)$$

which has been derived by many authors.^{3) - 9)}

(c) Distance between Segment and the Molecular Center of Mass.

As is well known, the mean square radius of gyration $\langle S^2 \rangle$ is given by

$$\langle S^2 \rangle = \frac{1}{N} \sum_k \langle S_k^2 \rangle = \frac{1}{N^2} \sum_{k < l} \langle R_{kl}^2 \rangle, \quad (1.32)$$

where S_k is the distance between segment k and the molecular center of mass. Therefore substituting Eq. (1.29) into Eq. (1.32), and replacing summation by integration, we find

$$\langle S^2 \rangle = \frac{1}{6} N a^2 [1 + (134/105) Z], \quad (1.33)$$

which is just the equation (1.4) already given by Zimm et al.⁹⁾

In addition, $\langle S_k^2 \rangle$ can be easily shown to have the expression*

$$\langle S_k^2 \rangle = \frac{1}{N} \left[\sum_{\ell=0}^{k-2} \langle R_{\ell k}^2 \rangle + \sum_{\ell=k+2}^N \langle R_{k\ell}^2 \rangle \right] - \langle S^2 \rangle, \quad (1.34)$$

where $\langle R_{lk}^2 \rangle$ is obtained by exchanging k for l in $\langle R_{kl}^2 \rangle$, Eq. (1.29), and vice versa. Eventually we find

$$\begin{aligned} \langle S_k^2 \rangle &= \frac{1}{3} N a^2 \{ [1 - 3(k/N) + 3(k/N)^2] + J(N, k) Z \}, \\ J(N, k) &= (121/21) - (32/3) N^{-\frac{3}{2}} [k^{\frac{3}{2}} + (N-k)^{\frac{3}{2}}] \\ &\quad + (24/5) N^{-\frac{5}{2}} [k^{\frac{5}{2}} + (N-k)^{\frac{5}{2}}] \\ &\quad + (4/3) N^{-3} [k^3 + (N-k)^3]. \end{aligned} \quad (1.35)$$

Eq. (1.27) will be used to calculate the angular distribution of scattered lights in the next chapter, and Eqs. (1.29) and (1.35) will be used to calculate the intrinsic

* See Appendix II.

viscosity in Chapter IV.

Eqs. (1.31) and (1.33) show that a polymer chain, owing to the repulsive interaction (volume effect), will expand more largely than a Gaussian case and, in good solvents, the energetical interactions between solvent and segment force the chain to expand more and more, whereas in poor solvents they work to shrink it. Therefore, when $T = \Theta$, the volume effect counteracts the energetical interaction so that the polymer chain apparently behaves like a Gaussian chain. Accordingly the Θ defined by Eq. (1.21) is nothing but the Flory temperature and becomes higher as U_0 is large, namely in the poorer solvents.

§ 1.4. General Remarks on Statistical Properties

Although many studies have been proposed on the excluded volume effect of a polymer chain, most of them have been dealing with the asymptotic behavior of $\langle R^2 \rangle / N$ for large N , which has already been discussed out. Here our attentions are focused on a few other statistical properties of a polymer chain in dilute solution which are easily deduced from the results obtained in the previous section.

(a) Shape of Distribution Function of R .

Suppose a Gaussian distribution function, the second moment of which is just given by Eq. (1.31). Denoting the

2m-th moment of this function by $\langle R^{2m} \rangle_G$, we obtain

$$\langle R^{2m} \rangle_G = \frac{(2m+1)!}{6^m m!} N^m a^{2m} \left(1 + \frac{4}{3} m z \right). \quad (1.36)$$

Comparing this with Eq. (1.30), we immediately find that $\langle R^{2m} \rangle_G$ is always larger than $\langle R^{2m} \rangle$, if z is positive. This is to be compared with the experimental result of Teramoto, Kurata and their coworkers¹²⁾ in Fig. 3, where is shown the distribution function of R for a short lattice chain obtained by direct enumeration of all possible configurations. In the figure, the Gaussian distribution function approaches zero slowly in the range of larger R than that corresponding to its maximum, while the distribution function of R for a real polymer chain (lattice chain) increases gradually to its maximum, and then falls down to zero suddenly; or in other words, $\langle R^{2m} \rangle < \langle R^{2m} \rangle_G$.

$$(b) \quad \langle R^2 \rangle / \langle S^2 \rangle.$$

Eqs. (1.31) and (1.33) lead us to

$$\langle R^2 \rangle / \langle S^2 \rangle = 6 \left(1 + \frac{2}{35} z \right). \quad (1.37)$$

The ratio $\langle R^2 \rangle / \langle S^2 \rangle$ starts at six for $z = 0$, and increases with increasing z . In this connection, it is noted here that, in the case of two-dimensional lattice chain, the

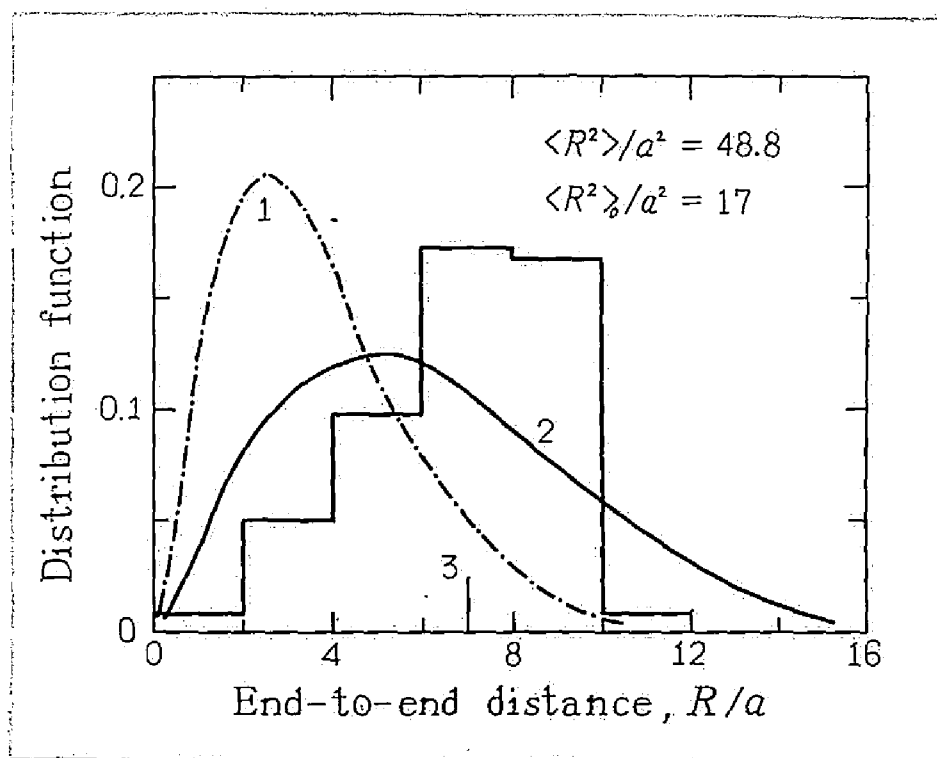


Fig. 3. Shape of the distribution function for end-to-end distance R of two-dimensional square lattice chain with $N=17$. Histogram: Teramoto and Kurata's experiment.¹²⁾ Chain curve 1: random flight. Full curve 2: Gaussian function with the same value of $\langle R^2 \rangle$ as the histogram's. Short line 3 indicates the root-mean-square end-to-end distance $\langle R^2 \rangle^{\frac{1}{2}}$.

ratio arrives indeed at 7.41 for $N = 17$.¹²⁾

$$(c) \quad \langle S_k^2 \rangle .$$

According to Eq. (1.35), we obtain

$$\langle S_k^2 \rangle^{\frac{1}{2}} = \begin{cases} (N/3)^{\frac{1}{2}} a (1 + 0.61 z) & \text{if } k = 0, N \\ \frac{1}{2} (N/3)^{\frac{1}{2}} a (1 + 0.50 z) & \text{if } k = \frac{1}{2} N. \end{cases} \quad (1.38)$$

This equation indicates that the excluded volume effect has the larger influence on the segments near the ends than that on the intermediate segments; those are located, on the average, in the "skin" part of polymer coil and these in the "core" part. Accordingly, the expansion of polymer chain does not occur uniformly, but more largely in the skin part than in the core part. This behavior contributes an unnegligible effect to the intrinsic viscosity as will be shown in Chapter IV.

These results can not be obtained by the Flory theory,¹⁾ for complete account is not taken of the connection of segments and thereby the anisotropic nature of a polymer chain is lost in his theory.*

* According to the Flory theory,¹⁾ the expansion of polymer coil occurs uniformly, and hence $\langle R^2 \rangle / \langle S^2 \rangle = 6$ irrespective of the excluded volume effect.

Chapter II. LIGHT SCATTERING

§ 2. 1. Introduction

As is well known, the light scattering measurement of polymer solutions is a direct and powerful method of determining the molecular size and shape of solute polymer. There are two representative methods of experiment and analysis; one is the angular variation method and the other is the dissymmetry method. The former yields the mean square radius of gyration $\langle S^2 \rangle$ itself. On the other hand, the polymer dimension obtained in the latter is strictly equivalent to neither the mean square end-to-end distance $\langle R^2 \rangle$ nor $\langle S^2 \rangle$ at non-Flory temperatures, since the angular distribution of scattered lights, upon which the analysis is based, has not yet been derived except for a Gaussian chain. Accordingly, it appears necessary to make a more detailed consideration for the dissymmetry method. Thus, in this chapter, we calculate the angular distribution of scattered lights using the same model as before, and examine the excluded volume effect on it somewhat in detail.

§ 2. 2. Expansion of the Angular Distribution

It is already known that the intensity I of light scattered from polymer solution is generally related to the con-

centration c and scattering angle θ by the equation,

$$Kc/I = 1/M P(\theta) + 2A_2 c + \dots, \quad (2.1)$$

where K is the constant, M the polymer molecular weight, and A_2 the osmotic second virial coefficient, which is treated in the next chapter. $P(\theta)$ is the so-called angular distribution of scattered light, which represents the correction for the interference of lights scattered from small elements of large particle (polymer segments) and, just as for X-ray and electron scattering, is expressed in the form,¹³⁾

$$P(\theta) = \int_{-\infty}^{+\infty} \rho_2(r) \exp(2\pi i \Delta \cdot r / \lambda) dr. \quad (2.2)$$

Here λ is the wave length of light in medium and $\rho_2(r)$ is the radial distribution function for segments of the same polymer chain, which is defined by Eq. (1.25). Δ represents the vector difference between unit vectors in the directions of incident and scattered lights, and its magnitude is

$$\Delta = |\Delta| = 2 \sin(\theta/2). \quad (2.3)$$

Since it is difficult to perform straight-forwardly the integration in Eq. (2.2), which extends over all directions as well as magnitudes of r at constant ϕ , we expand the integrand and then integrate term-by-term. The result is

$$P(\theta) = 1 - \delta_1 [2 \sin(\theta/2)]^2 + \dots + (-1)^m \delta_m [2 \sin(\theta/2)]^{2m} + \dots, \quad (2.4)$$

$$\delta_m = \frac{2}{(2m+1)! N^2} \left(\frac{2\pi}{\lambda}\right)^{2m} \sum_{k < l} \langle R_{kl}^{2m} \rangle.$$

Substituting Eq. (1.27) into Eq. (2.4), and replacing summation by integration over k and l , we obtain after tedious calculations,

$$P(\theta) = \frac{2}{v^2} (e^{-v} - 1 + v) + z \sum_{m=1}^{\infty} \frac{(-1)^m}{m!} C_m v^m, \quad (2.5)$$

where $v = (8\pi^2 N a^2 / 3\lambda^2) \sin^2(\theta/2), \quad (2.6)$

$$C_m = 2 \sum_{p=1}^m \frac{(-1)^p}{p^2 - \frac{1}{4}} \binom{m}{p} \left\{ \frac{m+2p+\frac{3}{2}}{(m+p+1)(m+p+2)(m+\frac{5}{2})} \right. \\ \left. - \frac{4p}{(m+\frac{3}{2})(m+\frac{5}{2})(p+\frac{1}{2})} + (2p-1) \sum_{q=0}^{2p} \frac{(-1)^q}{p-q+\frac{1}{2}} \binom{2p}{q} \right. \\ \left. \times \left[\frac{1}{m+\frac{5}{2}} \sum_{\lambda=0}^{m-p} \frac{(-1)^\lambda}{q+\lambda+1} \binom{m-p}{\lambda} - \frac{1}{m-p+1} \sum_{t=0}^{m-p+1} \frac{(-1)^t}{p+t+\frac{3}{2}} \binom{m-p+1}{t} \right] \right\}, \quad (2.7)$$

and z is given by Eq. (1.20). The numerical values of C_m ($m \leq 7$) are shown in Table I, which were calculated by

Table I. Numerical values of the respective coefficients

C_m and D_m in Eqs. (2.5) and (2.9).

m	1	2	3	4	5	6	7
C_m	0.4254	0.3889	0.3240	0.2699	0.2279	0.1953	0.173
$D_m \times 10^2$	0	3.65	5.89	7.04	7.60	7.83	7.51
$D_m \times 10^2/m !$	0	1.825	0.982	0.252	0.063	0.011	0.001

Eq. (2.7). It is noted here that the first term in Eq. (2.5) has already been derived for a Gaussian chain.

§ 2.3. Excluded Volume Effect on the Angular Distribution.

Remembering Eq. (1.32), the first coefficient δ_1 in Eq. (2.4) can be written as

$$\delta_1 = (4\pi^2/3\lambda^2) \langle S^2 \rangle. \quad (2.8)$$

Hence, the angular variation method yields true $\langle S^2 \rangle$ irrespective of the volume effect.

On the contrary, it appears necessary to make a more detailed consideration for the dissymmetry method. Eq. (2.5) may be rewritten as

$$P(\theta) = P'(\theta) + z \sum_{m=1}^{\infty} \frac{(-1)^{m+1}}{m!} D_m v'^m, \quad (2.9)$$

$$P'(\theta) = (2/v'^2)(e^{-v'} - 1 + v'),$$

$$v' = (16\pi^2/\lambda^2) \langle S^2 \rangle \sin^2(\theta/2),$$

$$D_m = \frac{2m}{(m+1)(m+2)} \cdot \frac{134}{105} - C_m.$$

In Table I are given the numerical values of D_m . From Eq. (2.9), it is obvious that the angular distribution function

$P'(\theta)$ currently in use deviates from the true function $P(\theta)$, as a result of the excluded volume effect. However, the numerical calculations show that, if $z \leq 0.1$ and $v \leq 1.0$, the deviation of $P'(\theta)$ from $P(\theta)$ is of order 0.1 %, being within experimental error of present measurement. Similarly, the dissymmetry ratio z'_{45} obtained from $P'(\theta)$ shows only minor deviation from its rigorous value, if the ratio $(6 \langle S^2 \rangle)^{1/2} / \lambda$ does not exceed about 0.2. Accordingly, we may conclude that, in such a range, the usual dissymmetry method also provides reliable data of $\langle S^2 \rangle$.

Next, we propose an attempt to evaluate $\langle S^2 \rangle$ by the dissymmetry method, when the value of $(6 \langle S^2 \rangle)^{1/2} / \lambda$ exceed the range mentioned above. Fig. 4 gives the z_{45} vs. $(Na^2)^{1/2} / \lambda$ curves for various values of z , which were drawn taking account of the terms up to $m = 7$ in Eq. (2.5) with the values of C_m in Table I. We first read the value of Na^2 from the observed value of z_{45} at the Flory temperature and the curve for $z = 0$ in the figure, and next determine z from the observed value of z_{45} at the other temperature and from the value of Na^2 obtained above. Inserting these values of Na^2 and z in Eq. (1.33), we obtain $\langle S^2 \rangle$. This method, of course, is not applicable to a good solvent system, for the equations obtained here are derived only for small z . The agreement between the value of $\langle S^2 \rangle$ determined by this

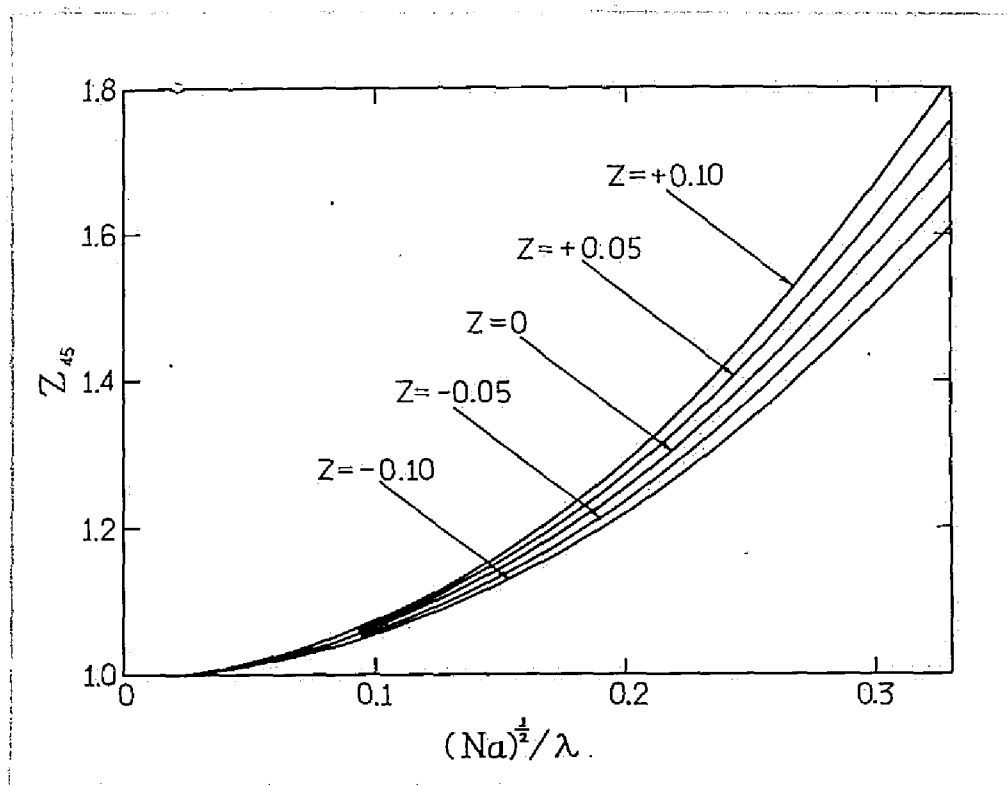


Fig. 4. Dissymmetry ratio z_{45} plotted against $(Na^2)^{1/2}/\lambda$ for various values of the excluded volume parameter z .

method and that by the angular variation method has to be checked experimentally. This is an interesting problem, but we will leave it untouched in the present article.

Chapter III. OSMOTIC PRESSURE

§ 3. 1. Introduction

In the preceding chapters, we have developed a statistical theory of the excluded volume effect of a polymer chain present in dilute solution and made clear its detailed nature. Let us now proceed to other problems of importance related to the excluded volume effect; one of these is of osmotic second virial coefficient A_2 .

According to recent measurements,¹⁴⁾ the second virial coefficient A_2 of osmotic pressure of polymer solutions can be represented over limited ranges of polymer molecular weight M in the form CM^ϵ with a negative exponent ϵ varying from -0.1 to -0.3 . This dependence of A_2 on M has not yet been explained by the lattice theories,¹⁵⁾ in spite of various improvements recently made.^{16) - 18)} On the other hand, the method of imperfect gas-like model which is based on the McMillan and Mayer theory of general solutions¹⁹⁾ offers a more convenient approach to the problem, though the theories indicating a quantitative agreement with the experimental results have not yet been presented.^{20) - 24)} For instance, Flory and Krigbaum²¹⁾ developed a theory of dilute polymer solutions by introducing the Gaussian approximation for the spatial distribution of segments around the mole-

cular center of mass, and derived an expression for A_2 which indicates a gradual decrease of A_2 with increasing M . This is a significant result of their theory, but the agreement with the experimental data is no more than semi-quantitative.²⁵⁾ Very recently, Isihara and Koyama,²³⁾ and Orofino and Flory,²⁴⁾ respectively, improved the Flory and Krigbaum theory with respect to the assumptions for the spatial distribution of segments and for the thermodynamic interaction between segments, but they have still assumed the Gaussian character of polymer chain. Since the excluded volume effect generally introduces a non-Gaussian character into the chain configurations as was shown in Chapter I, we find it necessary to reexamine the theory of A_2 with respect to this point. Furthermore, in the theories cited above, the n -segment distribution function around the molecular center of mass is approximated by the product of one-segment distribution functions for the sake of mathematical convenience.ⁿ But this factorization approximation also requires a further investigation, for it probably leads to the underestimation in the molecular weight dependence of A_2 we believe.

Thus, in this chapter, we will develop a more exact evaluation of A_2 taking account of the intra- and inter-molecular interactions, and attempt to explore the nature of the approximations mentioned above. Albrecht²⁶⁾ has independently presented a theory similar in nature to ours.

However, his treatment of the intramolecular excluded volume effect is based on a more rough approximation, namely the uniform expansion approximation for the polymer coil; accordingly, the overlap between his theory and ours seems not to be so serious.

§ 3. 2. Formulation

We consider the same model of chain polymer as before. That is, a polymer molecule consists of $N + 1$ segments of diameter b , which are linearly connected by N links of a constant length a and are numbered from 0 to N . Using the Greek alphabet to specify each polymer molecule, we denote the coordinate of molecule α by the symbol (α) , the coordinate of segment i of the molecule by the symbol (i_α) and the total coordinates of a particular set of n segments, say $i_\alpha, j_\alpha, \dots, t_\alpha$, by the symbol $\{n_\alpha\}$. Hence,

$$(\alpha) \equiv \{N_\alpha + 1\} = (0_\alpha), (1_\alpha), \dots, (N_\alpha), \quad (3.1)$$

$$d(\alpha) \equiv d\{N_\alpha + 1\} = d(0_\alpha) d(1_\alpha) \dots d(N_\alpha).$$

The total potential energy of the solution is assumed to be additive over segment pairs, for which we assume the following interaction potential:

$$u_{ij} \equiv u(R_{ij}) = \begin{cases} \infty & \text{if } 0 \leq R_{ij} \leq b, \\ -u_0 \exp(-3R_{ij}^2/2d^2) & \text{if } R_{ij} > b, \end{cases} \quad (3.2)$$

where R_{ij} represents the distance between segments i and j . u_0 and d are constants. We then introduce a function $\chi(R_{ij})$ defined by

$$\chi_{ij} \equiv \chi(R_{ij}) = \exp(-u_{ij}/kT) - 1, \quad (3.3)$$

and write it as

$$\chi(R_{ij}) = \begin{cases} -1 & \text{if } 0 \leq R_{ij} \leq b, \\ (u_0/kT) \exp(-3R_{ij}^2/2d^2) & \text{if } R_{ij} > b, \end{cases} \quad (3.4)$$

neglecting terms of higher order in (u_0/kT) . Here k is the Boltzmann constant and T the absolute temperature.

According to the general theory of solutions developed by McMillan and Mayer,¹⁹⁾ the osmotic pressure π is expanded in powers of the concentration c as follows,

$$\pi = RT \left(\frac{1}{M} C + A_2 C^2 + A_3 C^3 + \dots \right), \quad (3.5)$$

where R is the gas constant, M the polymer molecular weight, and A_n the n -th virial coefficient. In particular, the second virial coefficient A_2 , which is here concerned, can be written in the form,

$$A_2 = - \frac{N}{2VM^2} \int [f_2(\alpha, \beta) - f_1(\alpha) f_1(\beta)] d(\alpha) d(\beta), \quad (3.6)$$

where V is the volume of the solution, and N the Avogadro number. $f_1(\alpha)$ and $f_1(\beta)$ represent the distribution functions of single polymer molecules α and β , respectively, and are normalized as *

$$\frac{1}{V} \int f_1(\alpha) d(\alpha) = \int f_1 \{N_\alpha + 1\} d\{N_\alpha + 1\} / d(k_\alpha) = 1. \quad (3.7)$$

$f_2(\alpha, \beta)$ represents the pair distribution function of two polymer molecules in configurations specified by (α) and (β) . These distribution functions all take the values at zero concentration.

* The symbol $d\{N_\alpha + 1\} / d(k_\alpha)$ indicates that the integration goes over all the coordinates except that of the specified segment k .

Now, remembering the assumption of pairwise additivity for the interaction potential of the system, we write the distribution functions as

$$f_1(\alpha) = C \exp(-\sum_{i_\alpha < j_\alpha} u_{i_\alpha, j_\alpha} / kT), \quad (3.8)$$

$$f_2(\alpha, \beta) = f_1(\alpha) f_1(\beta) \exp(-\sum_{k_\alpha, k_\beta} u_{k_\alpha, k_\beta} / kT),$$

where C denotes the normalization constant,

$$C^{-1} = \int \exp(-\sum_{i_\alpha < j_\alpha} u_{i_\alpha, j_\alpha} / kT) d\{N_\alpha + 1\} / d\{k_\alpha\}. \quad (3.9)$$

Then, we expand Eq. (3.8) in the form,

$$f_1(\alpha) = C (1 + \sum \chi_{i_\alpha, j_\alpha} + \sum \sum \chi_{i_\alpha, j_\alpha} \chi_{s_\alpha, t_\alpha} + \dots),$$

$$f_2(\alpha, \beta) = f_1(\alpha) f_1(\beta) \quad (3.10)$$

$$\times (1 + \sum \chi_{k_\alpha, k_\beta} + \sum \sum \chi_{k_\alpha, k_\beta} \chi_{l_\alpha, l_\beta} + \dots),$$

and substitute them into Eq. (3.6). The result is

$$A_2 = -\frac{N}{2VM^2} (B_1 + B_2 + \dots) \quad (3.11)$$

with

$$B_1 = \sum_{k_\alpha, k_\beta} \int \chi_{k_\alpha, k_\beta} f_1(\alpha) f_1(\beta) d(\alpha) d(\beta), \quad (3.12)$$

$$B_2 = \sum_{k_\alpha, k_\beta, l_\alpha, l_\beta} \int \chi_{k_\alpha, k_\beta} \chi_{l_\alpha, l_\beta} f_1(\alpha) f_1(\beta) d(\alpha) d(\beta),$$

$$B_n = \sum \int \left[\prod_{n \text{ pairs}} \chi_{k_\alpha, k_\beta} \right] f_1(\alpha) f_1(\beta) d(\alpha) d(\beta),$$

where the symbol $\prod$ represents a product of n different χ_{k_α, k_β} 's and the summation goes over all distinguishable configurations. On performing the integration with respect to all coordinates of segments except (k_α) , (k_β) , etc., Eq. (3.12) turns into*

* In Eq. (3.12), there are many terms with a degenerate set of indices, e.g., $l_\alpha = k_\alpha$. For such terms, we have

$$\begin{aligned} \int \chi_{k_\alpha, k_\beta} \chi_{k_\alpha, l_\beta} f_1(\alpha) f_1(\beta) d(\alpha) d(\beta) \\ = \int \chi_{k_\alpha, k_\beta} \chi_{k_\alpha, l_\beta} p_1(k_\alpha) p_2(k_\beta, l_\beta) d(k_\alpha) d(k_\beta) d(l_\beta). \end{aligned}$$

However, if N is sufficiently large, the number of degenerate terms does not exceed over one N th of the number of terms with non-degenerate indices; accordingly, neglecting a minor contribution of the former to B_n , one may arrive at Eq. (3.13).

$$B_n = \sum \int \left\{ \prod_{n \text{ pairs}} \chi_{k_\alpha, k_\beta} \right\} p_n \{n_\alpha\} p_n \{n_\beta\} d\{n_\alpha\} d\{n_\beta\}, \quad (3.13)$$

where $p_n \{n_\alpha\}$ denotes the reduced segment distribution function defined by Eq. (1.23):

$$p_n \{n_\alpha\} = \int f_1(\alpha) d\{N_\alpha + 1\} / d\{n_\alpha\}. \quad (3.14)$$

From the normalization condition (3.7), it is clear that

$$p_1(k_\alpha) = 1. \quad (3.15)$$

For the sake of convenience, we hereafter call B_n the n -pl intermolecular contact term.

§ 3. 3. Expansion of A_2 in Powers of z

Now we proceed to quantitative evaluation of B_n defined by Eq. (3.12) or (3.13), though the calculation is carried out up to the triple contact term.

(a) The Single Contact Term B_1 .

For B_1 , we can easily obtain by using Eqs. (3.4) and (3.15)

$$\begin{aligned}
B_1 &= V \sum_{k_\alpha, k_\beta} \int_0^\infty \chi(R_{k_\alpha, k_\beta}) 4\pi R_{k_\alpha, k_\beta}^2 dR_{k_\alpha, k_\beta} \\
&= -VN^2(4\pi b^3/3)[1+(\Theta/T)],
\end{aligned}
\tag{3.16}$$

in which the symbol Θ represents the Flory temperature,*

$$\Theta = [(\pi/6)^{\frac{1}{2}}(d/b)^3 - 1](u_0/k).
\tag{3.17}$$

(b) The Double Contact Term B_2 .

For $P_2(k, l)$, we in Chapter I have already derived an expression expanded in powers of the excluded volume parameter z , which may be written in the form,

$$P_2(k, l) = P_2^{(0)}(k, l) + P_2^{(1)}(k, l) + \dots
\tag{3.18}$$

with

$$\begin{aligned}
P_2^{(0)}(k, l) &= (\beta_{kl}^3/\pi^{\frac{3}{2}}) \exp(-\beta_{kl}^2 R_{kl}^2), \\
\beta_{kl}^2 &= 3/2(l-k) a^2,
\end{aligned}
\tag{3.19}$$

* See Eq. (1.21).

$$p_2^{(1)}(k, l) = (Z/N^{\frac{1}{2}}) \sum_{i < j} (j-i)^{-\frac{3}{2}} \left[1 - (\gamma_{kl}^3 / \pi^{\frac{3}{2}}) \exp(-\gamma_{kl}^2 R_{kl}^2) \right],$$

$$\gamma_{kl}^2 = 3/2 \gamma_{kl} a^2,$$

$$\gamma_{kl} = \begin{cases} l-k & \text{if } 0 \leq i < j \leq k \text{ or } l \leq i < j \leq N, \\ (l-k) - (j-i) & \text{if } k \leq i < j \leq l, \\ (l-k) - [(j-k)^2 / (j-i)] & \text{if } 0 \leq i \leq k, k < j \leq l, \\ (l-k) - [(l-i)^2 / (j-i)] & \text{if } k \leq i \leq l, l < j \leq N, \\ (l-k) - [(l-k)^2 / (j-i)] & \text{if } 0 \leq i \leq k, l \leq j \leq N, \end{cases} \quad (3.20)$$

and

$$Z = (6/\pi)^{\frac{1}{2}} (b/a)^3 [1 - (\Theta/T)] N^{\frac{1}{2}}. \quad (3.21)$$

In these expressions the terms higher than $p_2^{(1)}(k, l)$ represent the contributions of intramolecular contact; the indices i and j specify the segments participating in such contact. Now, substituting Eq. (3.18) into Eq. (3.13), and taking account of the symmetry condition that

$$p_2^{(1)}(k_\alpha, l_\alpha) p_2^{(0)}(k_\beta, l_\beta) = p_2^{(0)}(k_\alpha, l_\alpha) p_2^{(1)}(k_\beta, l_\beta),$$

we obtain

$$B_2 = B_{20} + B_{21} + \dots,$$

$$B_{20} = \sum \int \chi_{k_\alpha, k_\beta} \chi_{l_\alpha, l_\beta} p_2^{(0)}(k_\alpha, l_\alpha) \times p_2^{(0)}(k_\beta, l_\beta) d(k_\alpha) \dots d(l_\beta), \quad (3.22)$$

$$B_{21} = 2 \sum \int \chi_{k_\alpha, k_\beta} \chi_{l_\alpha, l_\beta} p_2^{(1)}(k_\alpha; l_\alpha) \times p_2^{(0)}(k_\beta, l_\beta) d(k_\alpha) \dots d(l_\beta).$$

Here the first subscript attached to B specifies the number of intermolecular contacts and the second subscript the number of intramolecular contacts.

The integrations in Eq. (3.22) can be easily performed by the Fourier and inverse transformations.¹¹⁾ An example is taken of B_{20} below. Remembering that, although the products of χ 's in the integrand of B_{20} are $\chi_{k_\alpha, k_\beta} \chi_{l_\alpha, l_\beta}$ for $k_\alpha < l_\alpha, k_\beta < l_\beta$ and that for $k_\alpha < l_\alpha, k_\beta > l_\beta$, these make the same contribution to B_{20} , we can calculate B_{20} as follows:

$$B_{20} = 2V \sum_{k_\alpha < l_\alpha} \sum_{k_\beta < l_\beta} \int_0^\infty J(l_\alpha - k_\alpha, l_\beta - k_\beta; R_{k_\alpha, k_\beta}) \times \chi(R_{k_\alpha, k_\beta}) 4\pi R_{k_\alpha, k_\beta}^2 dR_{k_\alpha, k_\beta}, \quad (3.23)$$

$$\text{where } J(l_\alpha - k_\alpha, l_\beta - k_\beta; R_{k_\alpha, k_\beta}) = \frac{1}{8\pi^3} \int \exp(-i\mathbf{q} \cdot \mathbf{R}_{k_\alpha, k_\beta}) H(\mathbf{q}) d\mathbf{q}, \quad (3.24)$$

$$H(\mathbf{q}) = h_1(\mathbf{q}) h_2(\mathbf{q}) h_3(\mathbf{q}),$$

$$h_1(\mathbf{q}) = \int p_2^{(0)}(k_\alpha, l_\alpha) \exp(i\mathbf{q} \cdot \mathbf{R}_{k_\alpha, l_\alpha}) d\mathbf{R}_{k_\alpha, l_\alpha}, \quad (3.25)$$

$$h_2(\mathbf{q}) = \int \chi(R_{l_\alpha, l_\beta}) \exp(i\mathbf{q} \cdot \mathbf{R}_{l_\alpha, l_\beta}) d\mathbf{R}_{l_\alpha, l_\beta},$$

$$h_3(\mathbf{q}) = \int p_2^{(0)}(k_\beta, l_\beta) \exp(i\mathbf{q} \cdot \mathbf{R}_{k_\beta, l_\beta}) d\mathbf{R}_{k_\beta, l_\beta}.$$

After laborious but straight-forward calculations, we obtain *

$$J(l_\alpha - k_\alpha, l_\beta - k_\beta; R_{k_\alpha, k_\beta}) = -(\mathbf{z}/N^{\frac{1}{2}}) [(\ell_\alpha - k_\alpha) + (\ell_\beta - k_\beta)]^{-\frac{3}{2}} \quad (3.26)$$

$$\times \exp\left\{-3 R_{k_\alpha, k_\beta}^2 / 2 [(\ell_\alpha - k_\alpha) + (\ell_\beta - k_\beta)] a^2\right\},$$

$$B_{20} = -2 B_1 \mathbf{z} N^{-\frac{3}{2}} \sum_{k_\alpha < l_\alpha} \sum_{k_\beta < l_\beta} [(\ell_\alpha - k_\alpha) + (\ell_\beta - k_\beta)]^{-\frac{3}{2}} \quad (3.27)$$

$$= -(32/15)(7 - 4\sqrt{2}) B_1 \mathbf{z} = -2.865 B_1 \mathbf{z}.$$

* Although B_{20} has already been calculated by Zimm²⁰⁾ using another method, his evaluation is half smaller than Eq. (3.27) because of miscounting of the summation.

The second term B_{21} also can be calculated by the similar way as above. The result is

$$B_{21} = 4B_1 z^2 N^{-3} \sum_{k_\alpha < l_\alpha} \sum_{k_\beta < l_\beta} \sum_{i_\alpha < j_\alpha} (j_\alpha - i_\alpha)^{-\frac{3}{2}} \times \left\{ \left[\nu_{k_\alpha, l_\alpha} + (l_\beta - k_\beta) \right]^{-\frac{3}{2}} - \left[(l_\alpha - k_\alpha) + (l_\beta - k_\beta) \right]^{-\frac{3}{2}} \right\}. \quad (3.28)$$

Here the summation extends over all the distinguishable configurations, which are classified into six types according to order of magnitude of four indices k_α , l_α , i_α and j_α . Fig. 5 gives a diagrammatic representation of these six types of contact. From Eqs. (3.20) and (3.28), it is easily seen that the $B_{21}(a)$ and $B_{21}(c)$ types of contact in the figure make no contribution to the sum B_{21} . Furthermore, in the case of single polymer chain, we can show that the effect of excluded volume is mainly produced by the contacts corresponding to the $B_{21}(b)$ type. Thus, if the contributions from the $B_{21}(d)$, (e) , and (f) types are assumed negligible, we obtain

$$B_{21} = 8 \left[(304/45) - (11\sqrt{2}/3) + 3\ln(1+\sqrt{2}) - \pi \right] B_1 z^2 \quad (3.29)$$

$$= 8.78 B_1 z^2.$$

The combination of Eq. (3.22) with Eqs. (3.27) and (3.29)

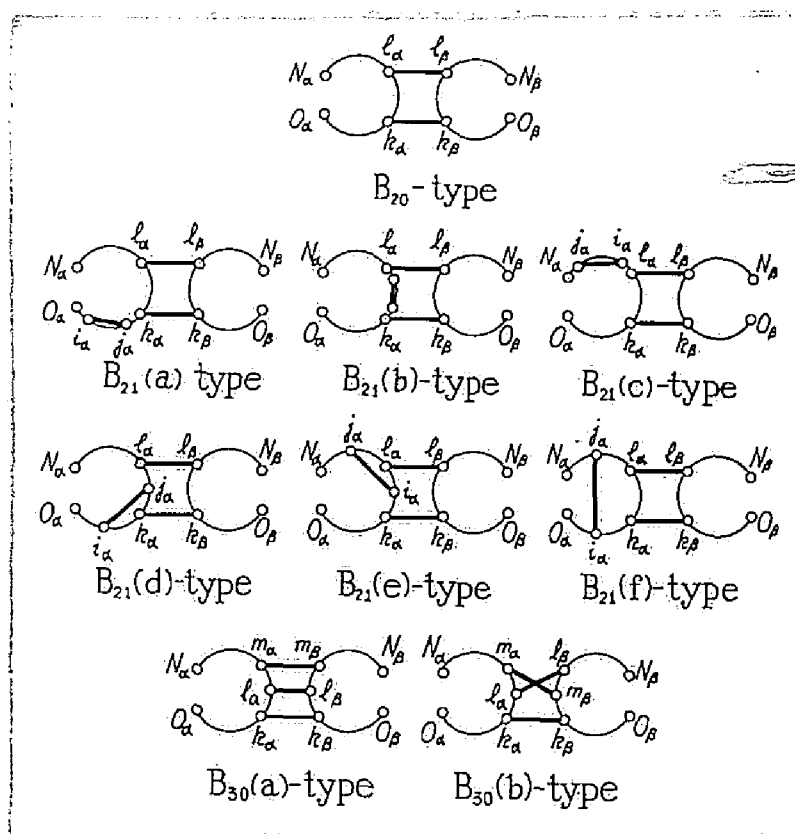


Fig. 5. Cluster diagrams for double and triple intermolecular contact types. The heavy lines connect the contact segments.

yields

$$B_2 = B_1(-2.865 z + 8.78 z^2 - \dots). \quad (3.30)$$

(c) The Triple Contact Term B_3 .

The triple intermolecular contact term B_3 may be expanded in the form,

$$B_3 = B_{30} + (\text{higher terms than } z^3, \quad (3.31) \\ \text{including intramolecular} \\ \text{contacts}),$$

and the leading term B_{30} is written as

$$B_{30} = \sum \int \chi_{k_\alpha, k_\beta} \chi_{l_\alpha, l_\beta} \chi_{m_\alpha, m_\beta} p_3^{(0)}(k_\alpha, l_\alpha, m_\alpha) \quad (3.32) \\ \times p_3^{(0)}(k_\beta, l_\beta, m_\beta) d(k_\alpha) d(l_\alpha) \dots d(m_\beta).$$

Here $p_3^{(0)}(k_\alpha, l_\alpha, m_\alpha)$ denotes the three-segment distribution function for the unperturbed (ideal) chain. Therefore we can write it as

$$p_3^{(0)}(k_\alpha, l_\alpha, m_\alpha) = p_2^{(0)}(k_\alpha, l_\alpha) p_2^{(0)}(l_\alpha, m_\alpha),$$

if $k_\alpha < l_\alpha < m_\alpha$. Furthermore, if it is remembered that there exist six types of products of χ 's in the integrand

of B_{30} which reduce to two $\chi_{k_\alpha, k_\beta} \chi_{l_\alpha, l_\beta} \chi_{m_\alpha, m_\beta}$ for $k_\alpha < l_\alpha < m_\alpha$, $k_\beta < l_\beta < m_\beta$ and four for $k_\alpha < l_\alpha < m_\alpha$, $k_\beta < m_\beta < l_\beta$, Eq. (3.32) can be rewritten as

$$\begin{aligned}
 B_{30} = & 2 \sum_{\text{Type}(a)} \int \chi_{k_\alpha, k_\beta} \chi_{l_\alpha, l_\beta} \chi_{m_\alpha, m_\beta} p_2^{(0)}(k_\alpha, l_\alpha) p_2^{(0)}(l_\alpha, m_\alpha) \\
 & \times p_2^{(0)}(k_\beta, l_\beta) p_2^{(0)}(l_\beta, m_\beta) d(k_\alpha) \dots d(m_\beta) \\
 & + 4 \sum_{\text{Type}(b)} \int \chi_{k_\alpha, k_\beta} \chi_{l_\alpha, l_\beta} \chi_{m_\alpha, m_\beta} p_2^{(0)}(k_\alpha, l_\alpha) p_2^{(0)}(l_\alpha, m_\beta) \\
 & \times p_2^{(0)}(k_\beta, m_\beta) p_2^{(0)}(m_\beta, l_\beta) d(k_\alpha) \dots d(m_\beta).
 \end{aligned} \quad (3.33)$$

The integrations in Eq. (3.33) can be easily performed by using the function $J(R)$ given by Eq. (3.26) as follows:

$$\begin{aligned}
 B_{30} = & 2V \sum_{\text{Type}(a)} \int_0^\infty J(l_\alpha - k_\alpha, l_\beta - k_\beta; R_{l_\alpha, l_\beta}) J(m_\alpha - l_\alpha, m_\beta - l_\beta; R_{l_\alpha, l_\beta}) \\
 & \times \chi(R_{l_\alpha, l_\beta}) 4\pi R_{l_\alpha, l_\beta}^2 dR_{l_\alpha, l_\beta} \\
 & + 4V \sum_{\text{Type}(b)} \int_0^\infty J(l_\alpha - k_\alpha, m_\beta - k_\beta; R_{l_\alpha, m_\beta}) J(m_\alpha - l_\alpha, 0; R_{l_\alpha, m_\beta}) \\
 & \times J(0, l_\beta - m_\beta; R_{l_\alpha, m_\beta}) 4\pi R_{l_\alpha, m_\beta}^2 dR_{l_\alpha, m_\beta} \\
 = & 2B_1 \bar{z}^2 N^{-3} \left\{ \sum_{\text{Type}(a)} [(m_\alpha - l_\alpha) + (m_\beta - l_\beta)]^{-\frac{3}{2}} \right. \\
 & \times [(l_\alpha - k_\alpha) + (l_\beta - k_\beta)]^{-\frac{3}{2}} + 2 \sum_{\text{Type}(b)} [(m_\alpha - l_\alpha + l_\beta - m_\beta) \\
 & \times (l_\alpha - k_\alpha + m_\beta - k_\beta) + (m_\alpha - l_\alpha) \times (l_\beta - m_\beta)]^{-\frac{3}{2}} \left. \right\} \\
 = & 9.73 B_1 \bar{z}^2.
 \end{aligned} \quad (3.34)$$

It is noted here that the B_{30} (a) type of contact in Fig. 5 contributes $8[\pi - (8/3)] B_1 z^2 = 3.80 B_1 z^2$ and the B_{30} (b) type contributes $5.93 B_1 z^2$, respectively.

Thus, substituting Eqs. (3.16), (3.30), and (3.34) into Eq. (3.11), we obtain the final expression for the osmotic second virial coefficient:

$$A_2 = \frac{2\pi N b^3}{3 M_0^2} \left(1 - \frac{\Phi}{T}\right) h(z), \quad (3.35)$$

$$h(z) = 1 - 2.865 z + 18.51 z^2 - \dots,$$

where M_0 is the molar weight of a segment. The correct value of the coefficient of z^2 is expected to be somewhat larger than ours.

§ 3.4. Comparison with Other Theories

The calculation of A_2 presented indicates that the influence of intramolecular interactions is unexpectedly large. For example, assuming a uniform expansion of polymer coil, let us write the distribution function of segments in the form,

$$p'_2(k, \ell) = (\beta'_{k\ell}{}^3 / \pi^{\frac{3}{2}}) \exp(-\beta'_{k\ell}{}^2 R_{k\ell}{}^2),$$

$$p'_3(k, \ell, m) = p'_2(k, \ell) p'_2(\ell, m), \quad (3.36)$$

$$\beta'_{k\ell}{}^2 \equiv 3/2(\ell - k) \alpha^2 a^2.$$

If we represent the expansion factor in linear dimension of polymer coil by

$$\alpha = (\langle R^2 \rangle / Na^2)^{1/2} = 1 + \frac{2}{3} z - \dots, \quad (3.37)$$

the distribution functions given by Eq. (3.36) lead to the following expression for $h(z)$,

$$h(z) = 1 - 2.865 (z/\alpha^3) + 9.73 (z/\alpha^3)^2 - \dots \quad (3.38a)$$

$$= 1 - 2.865 z + 15.46 z^2 - \dots \quad (3.38b)$$

By comparing this with Eq. (3.35), we find that the uniform expansion model introduces an underestimation in the coefficient of higher terms of $h(z)$, rather contrary to Albrecht's presumption.²⁶⁾ This discrepancy might be attributed to a non-Gaussian character of polymer chain.

Next, the function h derived by Flory and Krigbaum (FK)²¹⁾ is given by

$$h(X)_{FK} = 1 - \frac{X}{2! 2^{3/2}} + \frac{X^2}{3! 3^{3/2}} - \dots, \quad (3.39)$$

$$X = 2(\alpha^2 - 1).$$

On the other hand, according to the Flory theory¹⁾ of the excluded volume effect, α satisfies the relation:

$$\alpha^5 - \alpha^3 = (3^{3/2}/2) z \quad (3.40)$$

in our notation. Therefore, Eq. (3.39) can be rewritten as

$$h(z)_{FK} = 1 - 0.919 (z/\alpha^3) + 0.866 (z/\alpha^3)^2 - \dots \quad (3.41)$$

Furthermore, according to the Isihara and Koyama theory (IK),²³⁾ the function h is given by *

$$h(z)_{IK} = 1 - 1.024 (z/\alpha^3) + 1.134 (z/\alpha^3)^2 - \dots \quad (3.42)$$

By comparing Eqs. (3.41) and (3.42) with Eq. (3.38a), we find again the coefficients are appreciably underestimated in their theories. This undoubtedly indicates a disadvantage of the factorization approximation for the segment distribution function with reference to the molecular center of mass or the neglect of pairwise correlation between segments, though this is not the case for the segment distribu-

* The intramolecular excluded volume effect has been ignored in the IK theory. However, if we assume the uniform expansion model, the argument of $h(X)_{IK}$ may be written as $X = 3^{3/2} z / \alpha^3$.

tion function with reference to a segment. As the parameter z is an increasing function of polymer molecular weight M , it would be expected that both FK and IK theories lead to an underestimation in the molecular weight dependence of A_2 , though, in the IK theory, slightly larger coefficients than in the FK theory have been obtained with taking account of the distinguishability between segments i and j .

In conclusion, it must be remarked that the factorization approximation is more seriously open to question than the uniform expansion approximation is, and that an interesting refinement of the former has recently been proposed by Casassa.²⁷⁾

Chapter IV INTRINSIC VISCOSITY

§ 4. 1. Introduction

There remains another problem of importance related to the excluded volume effect; this is of frictional properties, namely intrinsic viscosity $[\eta]$ and frictional coefficient ζ . In this chapter, we shall concern ourselves with the former.

Theories of the intrinsic viscosity $[\eta]$ of chain polymer solutions have already been developed by Debye and Bueche,²⁸⁾ Kirkwood and Riseman,²⁹⁾ and Flory and Fox.³⁰⁾ The former two theories^{28), 29)} have the apparent difference in their mathematical analyses, but equivalent are the physical meanings involved by them: the dependence of $[\eta]$ on the polymer molecular weight is uniquely related to the variation of the velocity gradient of fluids in the polymer coil which is subjected to the hydrodynamic interactions between segments, or the draining effect. Combining with Stokes' law, these theories render us the smaller diameter of a segment than that to be expected. This would take its rise in their Gaussian model, or in the neglect of the excluded volume effect. On the other hand, Flory and Fox³⁰⁾ have presented a view that the molecular weight dependence of $[\eta]$ arises from the excluded volume effect rather than the draining

effect. The essential correctness of this view is now widely accepted, but there remain several deviations of the theory from experiments unsolved. One of the most significant examples is found in the recent measurement carried out by Krigbaum and Carpenter³¹⁾ who have indicated that, in contradiction to the Flory and Fox theory,³⁰⁾ the hydrodynamic radius of a polymer coil increases less rapidly than the statistical radius as the excluded volume increases.

Thus, in this chapter, we develop a theory of $[\eta]$ taking account of the influence of the excluded volume effect on the chain configurations as well as the draining effect, on the basis of the Kirkwood and Riseman scheme²⁹⁾ rather than the Debye and Bueche,²⁸⁾ for the former theory seems to be superior to the latter in their model and formulations in so far as linear polymers are concerned. And we re-examine the relation between the hydrodynamic and statistical radii of polymer coil from a more rigorous standpoint.

§ 4. 2. Integral Equation for the Viscosity Function

The pearl-necklace model and the continuous medium approximation are adopted as before. According to Kirkwood and Riseman,²⁹⁾ the intrinsic viscosity $[\eta]$ of the polymer solution is given by

$$\begin{aligned}
[\eta] &= \lim_{c \rightarrow 0} (\eta - \eta_0) / \eta_0 c \\
&= - \frac{1N}{100 M \eta_0 \dot{\epsilon}} \sum_{i=0}^N \langle (S_i \cdot e_x)(F_i \cdot e_y) \rangle, \quad (4.1)
\end{aligned}$$

$$F_i = - \frac{\zeta \dot{\epsilon}}{2} [e_x (S_i \cdot e_y) + e_y (S_i \cdot e_x)] - \zeta \sum_{s=0}^N T_{is} \cdot F_s, \quad (4.2)$$

$$T_{is} = \frac{1}{8 \pi \eta_0 R_{is}} \left(1 + \frac{R_{is} R_{is}}{R_{is}^2} \right). \quad (4.3)$$

Here η and η_0 represent the viscosity coefficient of the solution and the solvent, respectively, c is the concentration in grams per 100 ml solution, M is the polymer molecular weight, N is the Avogadro number, $\dot{\epsilon}$ is the velocity gradient between parallel plane boundaries, and ζ is a friction constant characteristic of the fluid and the segment. e_x , e_y , and e_z are unit vectors defining a coordinate system with origin in the molecular center of mass, e_x being parallel to the stream lines and e_y perpendicular to the plane boundaries. F_i denotes the force of frictional resistance exerted on the fluid by segment i which is located at a distance S_i from the origin, and T_{is} denotes the Oseen

tensor determined by the vector distance R_{is} between the indicated segments i and s .

Now if we define $\mathcal{Y}_{ij}$ by the relation,

$$\langle (S_j \cdot e_x)(F_i \cdot e_y) \rangle = -(N\alpha^2 \zeta \dot{\epsilon} / 18) \mathcal{Y}_{ij}, \quad (4.4)$$

from Eqs. (4.1) and (4.4), $[\eta]$ may be expressed in the form,

$$[\eta] = (N \zeta \alpha^2 M / 3600 \eta_0 M_0^2) F, \quad (4.5a)$$

$$F = \frac{2}{N} \sum_{i=0}^N \mathcal{Y}_{ii}, \quad (4.5b)$$

where M_0 is the molar weight of a segment. If we introduce the approximation,

$$\langle (e_x \cdot S_i)(e_y \cdot \pi_{is} \cdot F_s) \rangle = \langle (e_x \cdot S_i)(e_y \cdot \langle \pi_{is} \rangle \cdot F_s) \rangle, \quad (4.6)$$

$$\langle \pi_{is} \rangle = (1/6\pi\eta_0) \langle 1/R_{is} \rangle,$$

ignoring the fluctuation of π_{is} , then $\mathcal{Y}_{ij}$ defined by Eq. (4.4) could be determined as the solutions of the following simultaneous equation,

$$\varphi_{ij} = \frac{3}{Na^2} \langle S_i \cdot S_j \rangle - \frac{\zeta}{6\pi\eta_0} \sum_{s=0}^N \left\langle \frac{1}{R_{is}} \right\rangle \varphi_{sj}. \quad (4.7)$$

Here, according to the theory of excluded volume effect developed in Chapter I, we obtain*

$$\langle R_{ij}^2 \rangle = (j-i)a^2 (1 + I_{ij} z - \dots), \quad \text{if } i < j, \quad (4.8)$$

$$I_{ij} = (4/3) N^{-\frac{1}{2}} \left\{ (8/3)(j-i)^{\frac{1}{2}} - 4(N-i)^{\frac{1}{2}} - 4j^{\frac{1}{2}} + N^{-\frac{1}{2}}(j-i) - (8/3)(j-i)^{-1} \times [(N-j)^{\frac{3}{2}} - (N-i)^{\frac{3}{2}} - j^{\frac{3}{2}} + i^{\frac{3}{2}}] \right\},$$

$$\langle S_i^2 \rangle = \frac{1}{3} Na^2 \{ [1 - 3(i/N) + 3(i/N)^2] + J_i z - \dots \}, \quad (4.9)$$

$$J_i = (121/21) - (32/3) N^{-\frac{3}{2}} [i^{\frac{3}{2}} + (N-i)^{\frac{3}{2}}] + (24/5) N^{-\frac{5}{2}} [i^{\frac{5}{2}} + (N-i)^{\frac{5}{2}}] + (4/3) N^{-3} [i^3 + (N-i)^3],$$

* Eqs. (4.8) and (4.9) are identical to Eqs. (1.29) and (1.35), respectively. It is also obvious that, if $i=j$, Eq. (4.10) reduces to Eq. (1.35) or (4.9).

$$\begin{aligned}
\langle S_i \cdot S_j \rangle &= \frac{1}{2} \{ \langle S_i^2 \rangle + \langle S_j^2 \rangle - \langle R_{ij}^2 \rangle \} \\
&= \frac{1}{3} N a^2 \{ [1 - (3/2N)(j-i+j+l) \\
&\quad + (3/2N^2)(j^2 + i^2)] + K_{ij} \bar{z} - \dots \}, \text{ if } l < j, \\
K_{ij} &= (121/21) - (32/3) N^{-\frac{3}{2}} \{ j^{\frac{3}{2}} + (N-l)^{\frac{3}{2}} \\
&\quad + \frac{1}{2}(j-l)^{\frac{3}{2}} - (3/4)(j-l) [j^{\frac{1}{2}} + (N-l)^{\frac{1}{2}}] \} \\
&\quad - 2N^{-2}(j-l)^2 + (12/5) N^{-\frac{5}{2}} [j^{\frac{5}{2}} + i^{\frac{5}{2}} + (N-j)^{\frac{5}{2}} \\
&\quad + (N-l)^{\frac{5}{2}}] + \frac{2}{3} N^{-3} [j^3 + i^3 + (N-j)^3 + (N-l)^3], \quad (4.10)
\end{aligned}$$

$$\bar{z} = (6/\pi)^{\frac{1}{2}} (b/a)^3 [1 - (\Theta/T)] N^{\frac{1}{2}}. \quad (4.11)$$

Similarly, we can also derive the expression for $\langle 1/R_{ij} \rangle$, making use of the segment distribution function $p_2(i, j)$ given by Eqs. (3.18) to (3.20). The result, however, is so complicated, as is shown in Appendix III, that we are obliged to introduce an approximation. That is, replacing the ratio between $\langle 1/R_{ij} \rangle$ and the corresponding quantity $\langle 1/R_{ij} \rangle_0$

for the ideal chain by an average value, we put*

$$\frac{1}{\tilde{\alpha}} = \frac{\langle 1/R_{ij} \rangle}{\langle 1/R_{ij} \rangle_0} = \frac{\sum_{i < j} \langle 1/R_{ij} \rangle}{\sum_{i < j} \langle 1/R_{ij} \rangle_0} ; \quad (4.12)$$

otherwise, the integral equation which follows must become formidable in form. Then we assume

$$\tilde{\alpha}^{-1} = \frac{\sum_{i < j} \alpha_{ij}^{-1} \langle 1/R_{ij} \rangle_0}{\sum_{i < j} \langle 1/R_{ij} \rangle_0} , \quad (4.13)$$

$$\alpha_{ij}^2 = \langle R_{ij}^2 \rangle / \langle R_{ij}^2 \rangle_0$$

which, together with Eq. (4.8), yield

$$\begin{aligned} \langle \frac{1}{R_{ij}} \rangle &= \langle \frac{1}{R_{ij}} \rangle_0 \left[1 - 2\left(\pi - \frac{44}{15}\right) \bar{z} + \dots \right] \\ &= \left(\frac{6}{\pi}\right)^{\frac{1}{2}} \frac{1}{(j-i)^{\frac{1}{2}} a} (1 - 0.416 \bar{z} + \dots) . \end{aligned} \quad (4.14)$$

The estimation of accuracy of this approximation (4.14) is a difficult problem; nevertheless, in view of averaging, we believe the approximation to be more favorable than the follow-

* $\tilde{\alpha}^{-1}$ is a correction factor which would represent the amount by which the average quantity of $\langle 1/R_{ij} \rangle$ over i and j deviates from the corresponding quantity for the ideal chain.

ing approximation:*

$$\left\langle \frac{1}{R_{ij}} \right\rangle = \left\langle \frac{1}{R_{ij}} \right\rangle_0 \alpha_s^{-1} \quad (4.15a)$$

$$\begin{aligned} \alpha_s &= (\langle S^2 \rangle / \langle S^2 \rangle_0)^{\frac{1}{2}} = 1 + (67/105) \bar{z} - \dots \\ &= 1 + 0.638 \bar{z} - \dots \end{aligned} \quad (4.15b)$$

This prediction may be supported also by the fact that α_s is very close in its magnitude to $\alpha (\equiv \alpha_{ON})$ given by Eq. (3.37); the substitution of α_{ON} for $\tilde{\alpha}$ of course must lead to an overcorrection.

Now if we replace the sum defining F by the integral

$$F = \int_{-1}^{+1} \mathcal{F}(x, x) dx, \quad (4.16)$$

$$\mathcal{F}(x, y) = \mathcal{F}_{ij}, \quad x = (2i/N) - 1, \quad y = (2j/N) - 1,$$

and furthermore replace the summation in Eq. (4.7) by integration, then Eq. (4.7) reduces to the integral equation,

$$\mathcal{F}(x, y) = f(x, y) - (X/\sqrt{2})(1 - 0.416 \bar{z} + \dots) \int_{-1}^{+1} \frac{\mathcal{F}(t, y)}{|x - t|^{\frac{1}{2}}} dt, \quad (4.17a)$$

* See Eq. (1.33).

with

$$f(x, y) = f^{(0)}(x, y) + f^{(1)}(x, y)z - \dots,$$

$$f^{(0)}(x, y) = \frac{1}{8} [3(x^2 + y^2) - 6|x - y| + 2],$$

$$f^{(1)}(x, y) = \begin{cases} K(x, y) & \text{if } y \geq x, \\ K(y, x) & \text{if } y < x, \end{cases}$$

$$\begin{aligned} K(x, y) = & (121/21) - (8\sqrt{2}/3) \left\{ (1+y)^{\frac{3}{2}} + (1-x)^{\frac{3}{2}} \right. \\ & + \frac{1}{2}(y-x)^{\frac{3}{2}} - \frac{3}{4}(y-x) \left[(1+y)^{\frac{1}{2}} + (1-x)^{\frac{1}{2}} \right] \} \\ & - \frac{1}{2}(y-x)^2 - (3\sqrt{2}/10) \left\{ (1+y)^{\frac{5}{2}} + (1+x)^{\frac{5}{2}} \right. \\ & + (1-y)^{\frac{5}{2}} + (1-x)^{\frac{5}{2}} \} + \frac{1}{12} \left\{ (1+y)^3 + (1+x)^3 \right. \\ & \left. + (1-y)^3 + (1-x)^3 \right\}. \end{aligned} \quad (4.17b)$$

Here X represents the draining parameter defined by

$$X = \zeta N^{\frac{1}{2}} / 6^{\frac{1}{2}} \pi^{\frac{3}{2}} a \eta_0. \quad (4.18)$$

If the integral equation (4.17a) is solved with respect to $\mathcal{F}(x, y)$, $[\eta]$ is obtained by Eqs. (4.5a) and (4.16). Although, when $z = 0$, Eq. (4.17a) is nothing but the Kirkwood and Riseman (KR) integral equation for ideal chain, it is clear

that Eq. (4.17a) is of the same type as the KR's irrespective of the value of z . But, as has been pointed out by Zimm³²⁾ and Kirkwood et al.,^{33), 34)} the integral equation of this type can not analytically be solved.

§ 4. 3. Solution of the Integral Equation and Intrinsic Viscosity

The integral equation (4.17a) can be solved approximately. If $\mathcal{Y}(x, y)$ and $f(x, y)$ are expanded in Fourier series of the forms

$$\mathcal{Y}(x, y) = \sum_{k=-\infty}^{+\infty} \mathcal{Y}_k(y) e^{i\pi k x}, \quad (4.19)$$

$$f(x, y) = \sum_{k=-\infty}^{+\infty} f_k(y) e^{i\pi k x},$$

respectively, then Eq. (4.17a) is transformed into the following set of linear equations for the Fourier coefficients,

$$\mathcal{Y}_k(y) + (X/\sqrt{2})(1 - 0.416z + \dots) \sum_{l=-\infty}^{+\infty} a_{kl} \mathcal{Y}_l(y) = f_k(y). \quad (4.20)$$

When the matrix elements a_{kl} are approximated by the values

which are asymptotically valid for large k and l , a_{kl} become

$$a_{kl} = \begin{cases} 8\sqrt{2}/3 & \text{if } k = l = 0, \\ (2/|k|)^{\frac{1}{2}} \delta_{kl} & \text{if } k \neq 0, \end{cases} \quad (4.21)$$

where δ_{kl} is Kronecker's delta. Substituting the solutions of Eq. (4.20) to the approximation (4.21) into Eq. (4.19), we find

$$\begin{aligned} \varphi(x, y) = & \frac{f_0(y)}{1 + (8/3)X(1 - 0.416z + \dots)} \\ & + \sum_{\substack{k=-\infty \\ k \neq 0}}^{+\infty} \frac{f_k(y)}{1 + X(1 - 0.416z + \dots)|k|^{-\frac{1}{2}}} \cdot e^{i\pi kx} \end{aligned} \quad (4.22)$$

Since it can be easily shown that $f_0(y) \equiv 0$, $\varphi(x, y)$ given by Eq. (4.22), when $z = 0$, reduces to the approximate solution obtained by Kirkwood and Riseman.²⁹⁾ Now adopting the above solution (4.22), we obtain after laborious calculations,

$$\begin{aligned} F(x) = & \frac{6}{\pi^2} \sum_{k=1}^{\infty} \frac{1}{k^2} \frac{1}{1 + (1 - 0.416z + \dots)(X/k^{\frac{1}{2}})} \\ & \times \left\{ 1 + \frac{2}{3} \left[1 + 2\pi^{\frac{1}{2}} \frac{C(2\pi k)}{(\pi k)^{\frac{1}{2}}} + \frac{3}{2}\pi^{\frac{1}{2}} \frac{S(2\pi k)}{(\pi k)^{\frac{3}{2}}} \right] z - \dots \right\}, \end{aligned} \quad (4.23)$$

where $C(y)$ and $S(y)$ represent the Fresnel integrals defined by

$$C(y) = \int_0^y \frac{\cos t}{(2\pi t)^{\frac{1}{2}}} dt,$$

$$S(y) = \int_0^y \frac{\sin t}{(2\pi t)^{\frac{1}{2}}} dt. \quad (4.24)$$

Expanding the $F(X)$ in powers of z as for the average chain configurations and osmotic second virial coefficient, we obtain the final expression for the intrinsic viscosity:

$$[\eta] = \frac{N \zeta a^2}{3600 \eta_0 M_0} N F(X) = \frac{\pi^{\frac{3}{2}} N}{100} [X F(X)] \frac{\langle S^2 \rangle_0^{\frac{3}{2}}}{M}, \quad [\quad] ?$$

$$F(X) = F_0(X) [1 + p(X)z - \dots],$$

$$F_0(X) = \frac{6}{\pi^2} \sum_{k=1}^{\infty} \frac{1}{k^2} \frac{1}{1 + (X/k^{\frac{1}{2}})} \quad (4.25)$$

$$p(X) = [F_1'(X) + F_1''(X)] / F_0(X),$$

$$F_1'(X) = \frac{4}{\pi^2} \sum_{k=1}^{\infty} \frac{1}{k^2} \frac{1}{1 + (X/k^{\frac{1}{2}})} \\ \times \left[1 + 2\pi^{\frac{1}{2}} \frac{C(2\pi k)}{(\pi k)^{\frac{1}{2}}} + \frac{3}{2} \pi^{\frac{1}{2}} \frac{S(2\pi k)}{(\pi k)^{\frac{3}{2}}} \right],$$

$$F_1''(X) = 0.416 \times \frac{6}{\pi^2} \sum_{k=1}^{\infty} \frac{1}{k^{5/2}} \frac{X}{[1 + (X/k^{\frac{1}{2}})]^2},$$

Table II gives the numerical values of the viscosity functions $F_0(X)$, $p(X)$, etc. There are also given the values of $\nu(X)$:

$$\nu(X) = \frac{1}{2} [d \log X F_0(X) / d \log X]. \quad (4.26)$$

The explanation of this table will be given in the next section.

Now, if the Stokes law is applied to the friction constant ζ of segment, we have

$$\zeta = 3\pi\eta_0 b. \quad (4.27)$$

Then, Eq. (4.18) can be rewritten as

$$X = \frac{1}{2} (6/\pi)^{\frac{1}{2}} (b/a) N^{\frac{1}{2}}. \quad (4.28)$$

It is noted here that the application of Stokes' law to the molecular scale, of course, requires careful investigations. However, as is well known, Flory and Fox's theory³⁰⁾ of $[\eta]$ in the beginning has been proposed to bring the Stokes radius $(1/2)b$ of segment to a reasonable order, which was evaluated as unreasonably small by Kirkwood and Riseman's theory.²⁹⁾

Table II. Numerical values of the viscosity functions.

X	$\chi F_0(X)$			$\nu(X)$	$\frac{F_1'(X)}{F_0(X)}$	$\frac{F_1''(X)}{F_0(X)}$	$p(X)$	$n(X)$	$\Phi_0(X) \times 10^{-21}$
	KR	KZF	Revised						
0	0	0	0	0.500	1.276	0	1.276	2.00	0
0.1	0.092	0.09	0.073	0.463	1.27	0.04	1.31	2.05	0.17
0.2	0.172	0.17	0.136	0.432	1.27	0.06	1.33	2.08	0.31
0.3	0.242	0.24	0.192	0.405	1.26	0.08	1.34	2.10	0.44
0.4	0.304	0.30	0.241	0.382	1.26	0.10	1.36	2.13	0.55
0.5	0.358	0.35	0.284	0.362	1.26	0.11	1.37	2.14	0.65
1.0	0.564	0.54	0.447	0.291	1.25	0.16	1.41	2.20	1.02
2.0	0.800	0.75	0.634	0.215	1.23	0.22	1.45	2.26	1.45
3.0	0.936	0.88	0.742	0.174	1.21	0.25	1.46	2.29	1.69
4.0	1.024	0.96	0.812	0.147	1.21	0.27	1.47	2.31	1.85
5.0	1.090	1.02	0.864	0.132	1.20	0.28	1.48	2.32	1.97
10.0	1.260	1.17	0.999	0.083	1.18	0.32	1.50	2.34	2.28
20.0	1.400	1.31	1.110	0.052	1.16	0.34	1.51	2.36	2.53
50.0	1.486	—	1.178	0.024	1.15	0.37	1.52	2.38	2.69
100.0	1.528	—	1.212	0.010	1.14	0.38	1.53	2.39	2.77
∞	1.588	1.48	1.259	0	1.135	0.416	1.55	2.43	2.87

In this connection, the interpretation of shear viscosity for liquid argon developed by Kirkwood et al.³⁵⁾ is of great interest, in which the Stokes radius of an argon molecule was evaluated to be 2.0 Å at 89°K in good agreement with its actual radius 1.9 Å.

§ 4.4. Discussions

As is shown in Appendix IV, in the limit for $X = 0$ corresponding to the free-draining molecule, we obtain

$$\lim_{X \rightarrow 0} p(X) = 134/105 = 1.276. \quad (4.29)$$

Thus, remembering Eq. (4.15b) for the mean square radius of gyration $\langle S^2 \rangle$, we find

$$[\eta]_{X=0} = \frac{N \zeta}{600 \eta_0 M_0} \langle S^2 \rangle = \frac{N \zeta}{600 \eta_0 M_0} \langle S^2 \rangle_0 \alpha_s^2, \quad (4.30)$$

which is identical to Debye's expression.³⁶⁾

Another case of interest is the asymptotic limit for $X = \infty$ corresponding to the impermeable molecule. In this case, Eq. (4.25) yields

$$\{\eta\}_{X=\infty} = \frac{\pi^{\frac{3}{2}} N}{100} [X F_0(X)]_{X=\infty} \frac{\langle S^2 \rangle_0^{\frac{3}{2}}}{M} (1 + 1.55 z - \dots), \quad (4.31a)$$

which may be rewritten in a closed form by using Eq. (4.15b):

$$\{\eta\}_{X=\infty} = \frac{\pi^{\frac{3}{2}} N}{100} [X F_0(X)]_{X=\infty} \frac{\langle S^2 \rangle_0^{\frac{3}{2}}}{M} \alpha_s^{2.43} \quad (4.31b)$$

Similarly, in the case of intermediate X , the intrinsic viscosity appears to be proportional to α_s^n with

$$\eta(X) = (105/67) \rho(X) \quad (\text{for small } z), \quad (4.32)$$

the values of n being also given in Table II as functions of X . It appears very interesting that, in contradiction to the existing theories, the intrinsic viscosity is not proportional to $\langle S^2 \rangle^{3/2}$ or the spherical volume occupied by the polymer coil even in the limiting case for impermeable molecule.

We now turn to discussions on the approximations employed in the present theory. According to Kirkwood, Zwanzig and Plock (KZP),³⁴⁾ their improved solution of the integral equation in the case of ideal chain yields the KZP values of

$XF_0(X)$ given in the third column of Table II, which are to be compared with the KR values in the second column. There is a fortunate but excellent constancy in the ratio between KZP and KR values. Furthermore, the correct asymptotic value of $XF_0(X)$ as X approaches infinity has been evaluated to be 1.259 by Auer and Gardner.³⁷⁾ From these facts, we may obtain revised values of $XF_0(X)$ by multiplying the KR values by the factor 0.793 ($= 1.259/1.588$), which seem to be more suitable for practical use than the KR or KZP values themselves. The boldface numbers in Table II represent the revised values thus obtained.

Similarly, some corrections for $F_1(X)$ are also required in a rigorous sense. However, we do not touch the values of $p(X)$, taking an optimistic view that the corrections for $F_0(X)$ and $F_1(X)$ might be cancelled out one another in the ratio.

For the sake of comparison, let us now consider the uniform expansion model and assume that

$$\langle S_i \cdot S_j \rangle = \alpha_s^2 \langle S_i \cdot S_j \rangle_0, \quad (4.33a)$$

$$\left\langle \frac{1}{R_{ij}} \right\rangle = \alpha_s^{-1} \left\langle \frac{1}{R_{ij}} \right\rangle_0. \quad (4.33b)$$

Substituting these relations into Eq. (4.7), we obtain the integral equation,

$$\varphi(x, y) = \alpha_s^2 f^{(0)}(x, y) - \frac{X}{\sqrt{2} \alpha_s} \int_{-1}^{+1} \frac{\varphi(t, y)}{|x-t|^{\frac{1}{2}}} dt, \quad (4.34)$$

which leads to the results:

$$F(X) = \frac{6}{\pi^2} \sum_{k=1}^{\infty} \frac{1}{k^2} \frac{\alpha_s^2}{1 + (X/\alpha_s k^{\frac{1}{2}})}, \quad (4.35)$$

$$[\eta]_{X=\infty} = \frac{\pi^{\frac{3}{2}} N}{100} [X F_0(X)]_{X=\infty} \frac{\langle S^2 \rangle_0^{\frac{3}{2}}}{M} \alpha_s^3. \quad (4.36)$$

This Eq. (4.36) is identical to the Flory and Fox (FF) equation³⁰⁾ currently in use.

The difference 0.57 between the exponents of α_s of our Eq. (4.31b) and FF's (4.36) consists of two parts, 0.22 and 0.35. The first part 0.22 arises from the difference between our asymptotic value 1.135 and FF's value 1.276 for $F_1'(X)/F_0(X)$ and illustrates the disadvantage of the uniform expansion approximation (4.33a) for $\langle S_1 \cdot S_j \rangle$. Similarly, the second part 0.35 arises from the difference between our asymptotic value 0.416 and FF's value 0.638 for $F_1''(X)/F_0(X)$ and again illustrates the disadvantage of the approximation

(4.33b), for which we have already pointed out that employment of α_s must introduce an overcorrection into $\langle 1/R_{ij} \rangle$. We accordingly may conclude that the decrease of n ($X = \infty$) from 3.00 to 2.43 in the present theory is not fictitious, though the quantitative estimation of its accuracy is not given here.

As was pointed out in Chapter I,^{*} the expansion of a polymer coil due to the volume effect does not occur uniformly, but more largely in the skin part than in the core part. This predicts that the greater expansion of the polymer chain is followed by the deeper penetration of the solvent molecules, or, in other words, the hydrodynamic radius S_η of the polymer coil increases less rapidly than the statistical radius $\langle S^2 \rangle^{1/2}$ as the parameter z increases.

Thus, according to Eq. (4.31b), we find

$$S_\eta = \langle S^2 \rangle_0^{1/2} \alpha_s^{1/3} n(X) \quad (4.37)$$

Similarly, for Flory's universal constant Φ defined by

$$[\eta] = 6^{3/2} \Phi (\langle S^2 \rangle_0^{3/2} / M) \alpha_s^3, \quad (4.38)$$

* See Eq. (1.38).

we find

$$\begin{aligned}\Phi(X) &= \Phi_0(X) \alpha_s^{-[3-\eta(X)]} \\ &= \Phi_0(X) [1 - (1.91 - \eta(X)) \alpha + \dots],\end{aligned}\quad (4.39)$$

$$\Phi_0(X) = (\pi^{\frac{3}{2}} N / 6^{\frac{3}{2}} \cdot 100) [X F_0(X)] = 2.283 \times 10^{21} [X F_0(X)].$$

This relationship implies that the constant Φ may be a decreasing function of the temperature in poor solvent systems. The last column of Table II gives the values of $\Phi_0(X)$ as functions of X .^{*} The general behavior of Φ predicted by Eq. (4.39) will be discussed somewhat in detail by comparison with experiment (Chapter VI).

* KR's original value 1.588 for $[X F_0(X)]_{X=\infty}$ yields

$$\Phi_0(X=\infty) = 3.62 \times 10^{21}$$

instead of 2.87×10^{21} given in Table I.

Chapter V. FRICTIONAL COEFFICIENT

§ 5. 1. Introduction

In the previous chapter, we have developed a theory of the intrinsic viscosity of chain polymer solution. Another problem of frictional properties is of frictional coefficient ζ , which is the essential quantity in diffusion and sedimentation experiments. In the case of the intrinsic viscosity, the molecular center of mass of polymer molecule acquires a mean velocity equal to the local velocity of the solvent in which the polymer molecule is immersed. To the contrary, in the case of the diffusion and sedimentation, the molecular center of mass is in motion with mean velocity relative to the solvent. This is the only difference between these two problems. Therefore, we can easily extend our theory of the intrinsic viscosity to the frictional coefficient.

Thus, in this chapter, we calculate the dependence of the frictional coefficient on the excluded volume parameter z , and again discuss the relation between the hydrodynamic radius S_z of polymer coil and the statistical radius $\langle s^2 \rangle^{1/2}$. *

* In the course of preparation of this article, Stockmayer and Albrecht³⁸⁾ have presented a theory similar in nature to ours.

§ 5. 2. z-Dependence of Frictional Coefficient

If the translational diffusion constant and the sedimentation constant are denoted by D and s respectively, we may write

$$D = kT/\xi \quad \text{and} \quad s = M(1 - \bar{v}_p \rho_0)/\xi, \quad (5.1)$$

where $\bar{v}_p$ is the partial specific volume of the polymer, and ρ_0 the density of the solvent.

According to Kirkwood and Riseman,²⁹⁾ the frictional coefficient ξ of a chain polymer molecule is expressed as

$$\xi \mathcal{U} = - \sum_{i=0}^N \langle F_i \rangle, \quad (5.2)$$

$$\langle F_i \rangle = -\zeta \mathcal{U} - \zeta \sum_{s=0}^N \langle T_{is} \cdot F_s \rangle, \quad (5.3)$$

where $\mathcal{U}$ represents the mean translational velocity of the polymer molecule, relative to the solvent, and F_i represents the frictional force exerted on the fluid by segment i . If the fluctuation of T_{is} is again ignored, Eqs. (5.2) and (5.3) become

$$\Xi = \frac{1}{2} \zeta N G, \quad (5.4a)$$

$$G = \frac{2}{N} \sum_{i=0}^N \psi_i, \quad (5.4b)$$

$$\psi_i u \equiv -\frac{1}{\zeta} \langle F_i \rangle = u - \frac{\zeta}{6\pi\eta_0} \sum_{s=0}^N \left\langle \frac{1}{R_{is}} \right\rangle \psi_s u. \quad (5.4c)$$

Now, substituting Eq. (4.14) into Eq. (5.4c), and then replacing summations by integrations, we obtain

$$G(X) = \int_{-1}^{+1} \psi(x) dx, \quad (5.5a)$$

$$\alpha = (2L/N) - 1,$$

$$\psi(x) = 1 - \frac{X}{\sqrt{2}} (1 - 0.416z + \dots) \int_{-1}^{+1} \frac{\psi(t)}{|x-t|^{\frac{1}{2}}} dt. \quad (5.5b)$$

where X represents the draining parameter defined by Eq. (4.18) or (4.28). As the integral equation (5.5b) is the same in form as Kirkwood and Riseman's²⁹⁾ except for the extra factor $(1 - 0.416z)$, we can easily obtain its approximate solution by the Fourier expansion method employed in the previous chapter. That is, putting $\varphi(x, y) = \psi(x)$,

$f_0(y) = 1$, and $f_k(y) = 0$ for $k \neq 0$ in Eqs. (4.19) and (4.22), we find

$$\psi(x) = \frac{1}{1 + (8/3)X(1 - 0.416Z + \dots)} \quad (5.6)$$

which leads to

$$\begin{aligned} E &= \frac{1}{2} \zeta N G(X) = 3\pi^{\frac{3}{2}} \eta_0 [X G(X)] \langle S^2 \rangle_0^{\frac{1}{2}}, \\ G(X) &= G_0(X) [1 + q(X)Z - \dots], \\ G_0(X) &= 2/[1 + (8X/3)], \\ q(X) &= 0.416 [8X/(3 + 8X)]. \end{aligned} \quad (5.7)$$

In Table III are given the numerical values of the diffusion functions $G_0(X)$, $q(X)$, etc., together with the values of $\mu(X)$,

$$\mu(X) = \frac{1}{2} [d \log X G_0(X) / d \log X], \quad (5.8)$$

For a sufficiently small value of X , Eq. (5.7) asymptotically reduces to

$$E_{X=0} = \zeta N. \quad (5.9)$$

Table III. Numerical values of the diffusion functions.

X	$XG_o(X)$		$\mu(X)$	$q(X)$	$m(X)$	$P_o(X)$	$\Phi_o^{1/3} P_o^{-1} \times 10^{-7}$
	KR	Revised					
0	0	0	0.500	0	0	0	
0.1	0.158	0.161	0.395	0.087	0.137	1.10	5.01
0.2	0.261	0.265	0.326	0.145	0.227	1.81	3.74
0.3	0.333	0.338	0.278	0.185	0.290	2.31	3.29
0.4	0.387	0.393	0.242	0.214	0.335	2.68	3.06
0.5	0.429	0.436	0.214	0.238	0.373	2.97	2.91
1.0	0.545	0.554	0.136	0.303	0.476	3.78	2.67
2.0	0.632	0.642	0.079	0.349	0.547	4.38	2.58
3.0	0.667	0.678	0.056	0.369	0.578	4.62	2.58
4.0	0.686	0.697	0.043	0.380	0.596	4.75	2.58
5.0	0.698	0.709	0.035	0.387	0.607	4.84	2.59
10.0	0.723	0.735	0.018	0.400	0.627	5.01	2.63
20.0	0.736	0.748	0.009	0.408	0.639	5.10	2.67
50.0	0.744	0.756	0.004	0.413	0.647	5.16	2.70
100.0	0.747	0.759	0.002	0.415	0.650	5.18	2.71
∞	0.750	0.762	0	0.416	0.652	5.20	2.73

On the other hand, for a sufficiently large value of X , we obtain

$$\begin{aligned} \Sigma_{X=\infty} &= 3\pi^{\frac{3}{2}} \eta_0 [X G_0(X)]_{X=\infty} \langle S^2 \rangle_0^{\frac{1}{2}} (1 + 0.416 Z - \dots) \\ &= 3\pi^{\frac{3}{2}} \eta_0 [X G_0(X)]_{X=\infty} \langle S^2 \rangle_0^{\frac{1}{2}} \alpha_s^{0.652} \end{aligned} \quad (5.10)$$

This again indicates that even in the case of impermeable molecule, the effective hydrodynamic radius S_E varies with varying the excluded volume more slowly than the statistical radius does. Thus, in general, we may write

$$S_E = \langle S^2 \rangle_0^{\frac{1}{2}} \alpha_s^{m(X)} \quad (5.11)$$

with $m(X) = (105/67) Z(X), \quad (5.12)$

The values of $m(X)$ are also given in Table III.

As given in Appendix V, by using the Gegenbauer polynomial, the correct asymptotic value of

$$[X G_0(X)]_{X=\infty}$$

can be evaluated to be 0.7622 instead of the Kirkwood and Riseman (KR) value 0.7500 ($=6/8$), but the difference is

quite insignificant in comparison with the experimental accuracy of $\bar{Z}$. This explains why the Kirkwood and Riseman theory agrees very well with experiment in the case of frictional coefficient but not in the case of intrinsic viscosity.³⁹⁾ We however make a slight revision in the values of $XG_0(X)$, multiplying the KR values by 1.016 ($= 0.7622/0.7500$); the revised values are given in Table III by boldface numbers.

According to Mandelkern and Flory,⁴⁰⁾ the frictional coefficient is expressed in the form,

$$\bar{Z}/\eta_0 = 6^{\frac{1}{2}} P \langle s^2 \rangle_0^{\frac{1}{2}} \alpha_s \quad (5.13)$$

where P represents a universal constant analogous to Φ of the viscosity theory. Making a comparison of Eq. (5.7) with Eq. (5.13), we find*

$$\begin{aligned} P(X) &= P_0(X) \alpha_s^{-[1-m(X)]} \\ &= P_0(X) [1 - (0.638 - \bar{z}(X)) \bar{z} + \dots], \end{aligned} \quad (5.14)$$

$$P_0(X) = (3\pi^3/2)^{\frac{1}{2}} [XG_0(X)] = 6.820 [XG_0(X)].$$

* The KR value for $XG_0(X)$ lead to

$$P_0(X = \infty) = 5.11$$

instead of 5.20 in Table III.

The combination of Eq. (5.14) with (4.39) yields

$$\begin{aligned}\Phi^{\frac{1}{3}} P^{-1} &= \Phi_0^{\frac{1}{3}} P_0^{-1} \alpha_s^{\frac{1}{3} n(X) - m(X)} \\ &= \Phi_0^{\frac{1}{3}} P_0^{-1} \{ 1 + [\frac{1}{3} p(X) - q(X)] z - \dots \}.\end{aligned}\tag{5.15}$$

The last two columns of Table III give the values of P_0 and $\Phi_0^{\frac{1}{3}} P_0^{-1}$ as functions of X . Eq. (5.15) will be discussed by comparison with experiment somewhat in detail in Chapter VI.

Chapter VI: COMPARISON WITH EXPERIMENT

§ 6. 1. Introduction

In the preceding chapters, we have developed the theories of dilute polymer solution, and derived the expressions for various measurable solution-properties related to the excluded volume effect. The present theories have been proposed to improve the theories developed by Flory and others and to interpret the recent experimental results, and have been treated more rigorously than their theories. Moreover, our theories are systematically described by the molecular or model constants such as the segment size b , its link length a , etc., without including the phenomenological parameters. Therefore, it seems to be worth while to compare the theory with experiment at this stage and to estimate the model constants. To do this, the measurement carried out in the vicinity of the Flory temperature appears to offer the most suitable data, for the expressions presented here all are expressed in a power series in the excluded volume parameter z which becomes zero at the Flory temperature.

Thus, in this chapter, a thorough comparison of the present theories with experimental data is made, taking solutions of polystyrene in cyclohexane as an example. The results will prove that the theories are in excellent accord

with the experiments at least in the vicinity of the Flory temperature, and are very fitted for structural interpretation of experimental data.

§ 6. 2. Summary of the Theories

Before proceeding to a comparison of theory and experiment, it would be convenient for readers to summarize the important notations and equations proposed in this article.

In our model, the potential of mean force between two segments is assumed to be of short-range nature:

$$u(R) = \begin{cases} \infty & \text{if } 0 \leq R \leq b, \\ -u_0 \exp(-3R^2/2d^2) & \text{if } R > b, \end{cases} \quad (6.1)$$

where R represents the distance between the segments, b the diameter of segment, u_0 the energy parameter positive in endothermic solutions and negative in exothermic solutions, and d a constant approximately equal to the link length a . When $u_0 \ll kT$ and $d = a$, the Flory temperature Θ and the excluded volume parameter z , respectively, are expressed as

$$\Theta = [(\pi/6)^{\frac{1}{2}}(a/b)^3 - 1](u_0/k), \quad (6.2)$$

$$z = (6/\pi)^{\frac{1}{2}} (b_0/a_0)^3 [1 - (\Theta/T)] M^{\frac{1}{2}} \quad (6.3)$$

$$\text{with} \quad a_0 = a/M_0^{\frac{1}{2}}, \quad b_0 = b/M_0^{\frac{2}{3}}, \quad (6.4)$$

where M and M_0 are the respective molecular weight of polymer and segment.

Our expressions for the measurable solution-properties all are expressed in a power series in z as follows.

(a) Mean Square Radius of Gyration, $\langle S^2 \rangle$

$$\begin{aligned} \langle S^2 \rangle &= \langle S^2 \rangle_0 (1 + 1.276 z - \dots), \\ \langle S^2 \rangle_0 &= \frac{1}{6} M a_0^2. \end{aligned} \quad (6.5)$$

(b) Osmotic Second Virial Coefficient, A_2

$$\begin{aligned} A_2 &= \frac{2}{3} \pi N b_0^3 [1 - (\Theta/T)] (1 - 2.865 z + 18.51 z^2 - \dots) \\ &= 4\pi^{\frac{3}{2}} N (\langle S^2 \rangle_0^{\frac{3}{2}} / M^2) z (1 - 2.865 z + 18.51 z^2 - \dots), \end{aligned} \quad (6.6)$$

where N is the Avogadro number, $-2.865 z$ represents the double contact term, and $18.51 z^2$ the triple contact term.

(c) Intrinsic Viscosity, $[\eta]$

$$[\eta] = [\eta]_0 [1 + p(X)z - \dots],$$

$$\begin{aligned} [\eta]_0 &= (\pi^{\frac{3}{2}} N / 6^{\frac{3}{2}} \cdot 100) [X F_0(X)] a_0^3 M^{\frac{1}{2}} \\ &= (\pi^{\frac{3}{2}} N / 100) [X F_0(X)] (\langle S^2 \rangle_0^{\frac{3}{2}} / M), \end{aligned} \quad (6.7)$$

where $[\eta]_0$ represents the intrinsic viscosity at the Flory temperature, and X represents the draining parameter defined by

$$X = (3/2\pi)^{\frac{1}{2}} (b_0 / a_0 M_0^{\frac{1}{3}}) M^{\frac{1}{2}}. \quad (6.8)$$

The values of $X F_0(X)$ and $p(X)$ are given in Table II by boldface numbers.

(d) Frictional Coefficient, Ξ

$$\Xi = 3\pi^{\frac{3}{2}} \eta_0 [X G_0(X)] \langle S^2 \rangle_0^{\frac{1}{2}} [1 + q(X)z - \dots]. \quad (6.9)$$

Here η_0 is the viscosity coefficient of solvent, and the values of $X G_0(X)$ and $q(X)$ are given in Table III by boldface numbers.

§ 6. 3. Radius of Gyration

As has already been mentioned in Chapter II, the light scattering measurement carried out in the vicinity of the Flory temperature provides the most available data for the experimental test of $\langle S^2 \rangle$.

Table IV gives the experimental values of $S (= \langle S^2 \rangle^{1/2})$ for the system polystyrene-cyclohexane, which are obtained by Outer, Carr and Zimm⁴¹⁾ by using the angular variation method. The weight average molecular weight M_w of this sample is 1.61×10^6 , and the Θ temperature of this system has been evaluated to be 307.4°K by Krigbaum.⁴²⁾ Now, using the linear expansion factor α_s defined by Eq. (4.15b):

$$\alpha_s^2 = \langle S^2 \rangle / \langle S^2 \rangle_0$$

Eq. (6.5) may be rewritten as

$$\frac{\alpha_s^2 - 1}{1 - (\Theta/T)} = 1.276 \left(\frac{6}{\pi}\right)^{1/2} \left(\frac{b_0}{a_0}\right)^3 M^{1/2}. \quad (6.10)$$

Assigning $S_0 (= \langle S^2 \rangle_0^{1/2})$ to be $379 \text{ \AA}$ by the interpolation of experimental data, we can find that the ratio in the left hand side of Eq. (6.10) is indeed constant within experimental error (see Table IV). Thus, from two obtained values of this ratio and S_0 , we get

Table IV. Radius of gyration S_w of polystyrene
in cyclohexane. I.^a

T [°K]	obs. ^b	S_w [Å] Eq.(6.5)	Flory ^c	$\frac{\alpha_s^2 - 1}{1 - (\Theta/T)}$	$\frac{\alpha_s^5 - \alpha_s^3}{1 - (\Theta/T)}$
300.2	347	348	335	6.7	5.1
304.2	365	366	363	6.6	5.9
307.4	(379)	(379)	(379)	—	—
308.2	382	382	382	5.9	6.0
312.2	394	397	395	5.3	5.9
314.7	406	406	402	6.4	7.9

^a $M_w = 1.61 \times 10^6$ and $\Theta = 30.4^\circ\text{K}$. S_w represents the root of the weight average of $\langle S^2 \rangle$.

^b Data are obtained by Outer, Carr and Zimm, Ref. 41).

^c C_F in Eq. (6.12) is assigned to be 6.50.

$$a_o = 0.731 \text{ \AA} , \quad b_o = 0.1037 \text{ \AA} , \quad (6.11a)$$

which lead to the model constants a and b of a reasonable order:

$$\begin{aligned} a = 7.5 \text{ \AA} , \quad b = 2.3 \text{ \AA} , \quad \text{if } M_o = 104 \text{ (monomer weight)}, \\ a = 5.3 \text{ \AA} , \quad b = 1.4 \text{ \AA} , \quad \text{if } M_o = 52 \text{ (average weight of} \\ \text{-CH(C}_6\text{H}_5\text{)- and -CH}_2\text{-)}. \end{aligned} \quad (6.11b)$$

In Table IV are also given the values of S calculated by Eq. (6.5) and by Flory's equation:

$$\alpha_s^5 - \alpha_s^3 = C_F [1 - (\Theta/T)] , \quad (6.12)$$

where C_F is a constant proportional to $M^{1/2}$. It appears from the result that, at least in the vicinity of the Θ point, the temperature dependence of S is better represented by Eq. (6.5) than by Flory's equation (6.12), though a final decision must await a more extensive test.*

* In this respect, Krigbaum's theory⁴²⁾ recently developed has just given the same conclusion as ours.

Table V gives another experimental test of Eq. (6.5) for the same system as above; the observed values of S are by Krigbaum and Carpenter.³¹⁾ The molecular weight M_w of this material is 3.20×10^6 , and Θ is described as 308.4°K. The similar calculation as before leads to the results shown in Table V, and to the following values of a_0 and b_0 :

$$a_0 = 0.672 \text{ \AA}^3, \quad b_0 = 0.1178 \text{ \AA}^3, \quad (6.13a)$$

Hence,

$$a = 6.9 \text{ \AA}^3, \quad b = 2.6 \text{ \AA}^3, \quad \text{if } M_0 = 104, \quad (6.13b)$$

$$a = 4.8 \text{ \AA}^3, \quad b = 1.6 \text{ \AA}^3, \quad \text{if } M_0 = 52,$$

which are fairly in agreement with those in Eq. (6.11b). In this case, however, the ratio $(\alpha_s^2 - 1)/[1 - (\Theta/T)]$ becomes appreciably dependent on T at the temperature higher than about 311°K. In other words, Eq. (6.5) seems to be applicable only within a very limited range of temperature, $\Theta \pm 5^\circ\text{K}$ at most. Fig. 6 is a graphic representation of these statements.

In this connection, it is a matter of interest to examine the contribution of higher terms neglected in Eq. (6.5). Fixman⁹⁾ has recently derived the following expression for

Table v. Radius of gyration S_w of polystyrene
in cyclohexane. II.^a

T [°K]	obs. ^b	S_w [Å]		$\frac{\alpha_s^2 - 1}{1 - (\Theta/T)}$	$\frac{\alpha_s^5 - \alpha_s^3}{1 - (\Theta/T)}$
		Eq.(6.5)	Flory ^c		
305.7	451	452	428	17.3	13.5
307.2	474	474	472	17.3	15.6
308.4	(491)	(491)	(491)	—	—
311.2	526	527	521	16.8	20.7
318.2	571	606	568	11.5	18.2
328.2	607	699	607	8.9	16.9
333.2	630	737	623	8.9	18.9

^a $M_w \approx 3.20 \times 10^6$ and $\Theta \approx 308.4^\circ \text{K}$.

^b Data are obtained from S_z obs. by using the relation,
 $S_w = [(h+1)/(h+2)]^{\frac{1}{2}} S_z$ with $h=4$, where S_z
represents the root of the z average of $\langle S^2 \rangle$ (see
Krigbaum and Carpenter, Ref. 31)).

^c C_F in Eq. (6.12) is assigned to be 17.0.

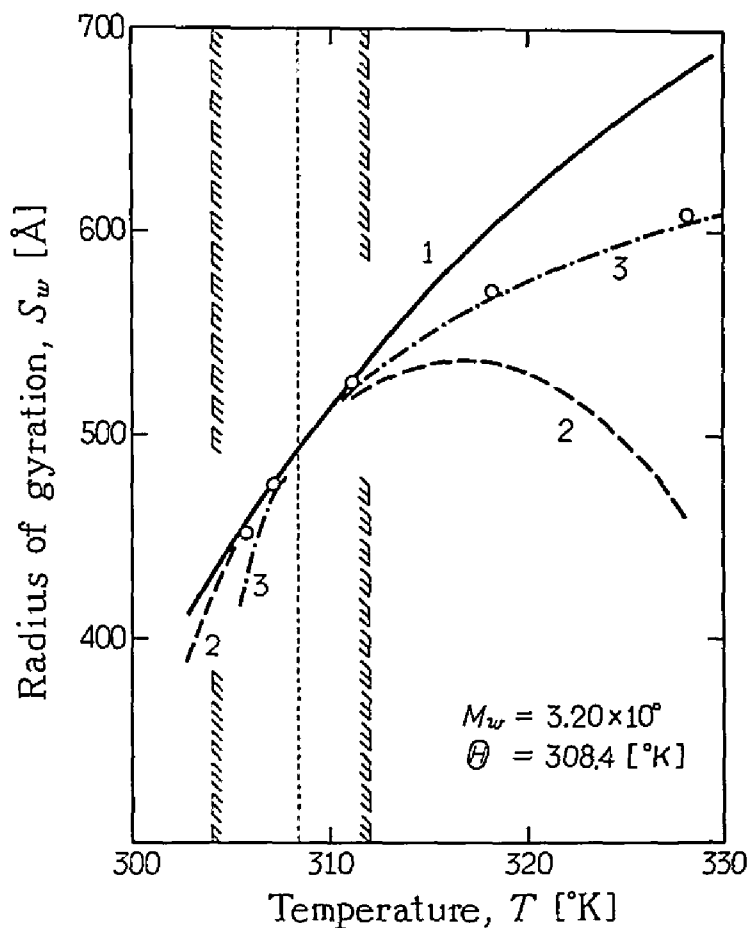


Fig. 6. Experimental test of the theoretical expressions for the radius of gyration S_w . Open circles: experimental values of S_w for polystyrene in cyclohexane obtained by Krigbaum and Carpenter.³¹⁾ Heavy curve 1: present theory to the single contact approximation, Eq. (6.5). Broken curve 2: present theory to the double contact approximation, Eq. (6.15). Chain curve 3: Flory equation (6.12) with $C_F = 17.0$. Shaded area: range of applicability of z -series ($|z| \leq 0.15$).

$\langle R^2 \rangle$,

$$\langle R^2 \rangle = \langle R^2 \rangle_0 [1 + (4/3)z - (6.23/3)z^2 + \dots], \quad (6.14)$$

but the corresponding expression for $\langle S^2 \rangle$ has not yet been obtained. Hence, let us resort to the following makeshift;

$$\langle S^2 \rangle = \langle S^2 \rangle_0 (1 + 1.276z - 2.077z^2 + \dots). \quad (6.15)$$

The broken curve in Fig. 6 is the values obtained by this equation. From the figure, we find that the introduction of the Fixman term, the double contact term, does not utterly contribute to improving the deviation of Eq. (6.5) from the experimental data. This implies the deviation is resulted from the divergence of z-series rather than the neglect of higher terms. Thus, we can estimate the range of applicability of the z-expansion method, which is enclosed in Fig. 6 by two shaded lines, each corresponding to $z = \pm 0.15$. In the next section, the condition for convergence of z-series will be ascertained by a more extensive test. Both in Table V and Fig. 6 are also given the results obtained by Flory's equation, Eq. (6.12), for the sake of comparison. The results illustrate that, in the very vicinity of the Θ temperature,

the present theory is again in better agreement with experiment than the Flory's, but the latter is of very wide application.

For the foregoing comment, the system polystyrene-butanone offers an illustrative example, for which the Φ -value is assigned to be almost zero by Flory and others.⁴³⁾ In this case, if the constants a and b have still the values of Eq. (6.11), three equations (6.5), (6.15), and (6.12) give the narrow curves in Fig. 7, all of them being far from the experimental points.⁴¹⁾ However, this is not a surprising result, for both a and b , in general, must depend on the nature of solvent as well as that of polymer. Then, assuming that a and b themselves change their values by solvent nature but the ratio b_0/a_0 remains unchanged,* we obtain the heavy curves in Fig. 7.

Although such a rough calculation as above can furnish no quantitative information, we may suggest that, in the system of this kind, the interpretation of experimental data should be developed on the basis of such formula closed in form as Flory's, so far as the molecular weight is not smaller than about four hundreds. The value, four hundreds, is not of polymer. Therefore, the present theory can not

* This assumption corresponds to shifting of the curves by a factor, which is evaluated to be 2.

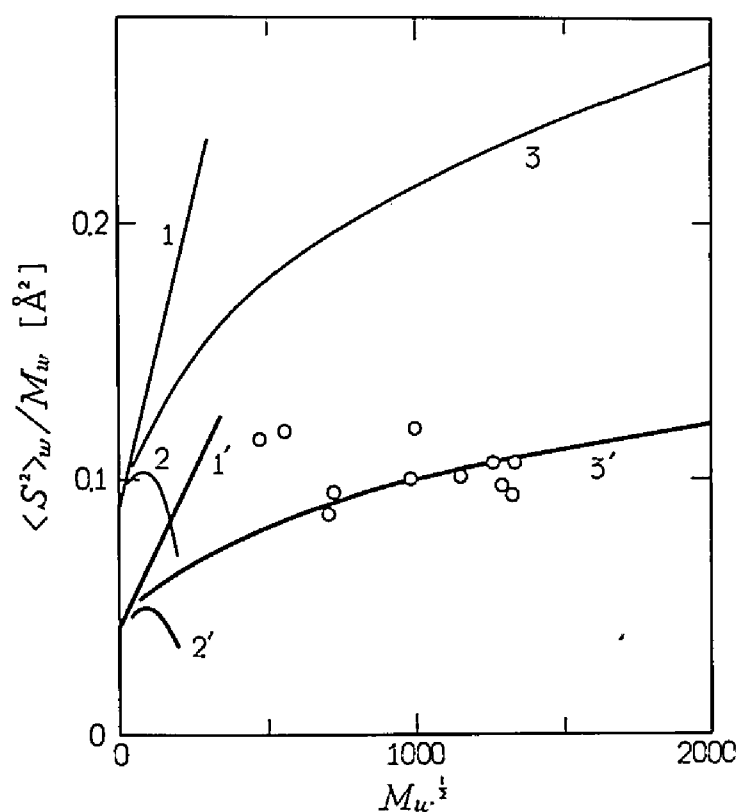


Fig. 7. Radius of gyration S_w of polystyrene in butanone at 25°C obtained by Outer, Carr and Zimm.⁴¹⁾ Open circles: experimental data. Curves 1 and 1': present theory to the single contact approximation, Eq. (6.5). Curves 2 and 2': present theory to the double contact approximation, Eq. (6.15). Curves 3 and 3': Flory equation (6.12).

utterly be applied to the good solvent systems with negative Θ .

§ 6. 4. Second Virial Coefficient

The first example is the light scattering experiment of Outer, Carr and Zimm,⁴¹⁾ cited in the previous section, in which $\langle S^2 \rangle$ and A_2 are obtained for polystyrene in cyclohexane. The weight average molecular weight M_w and the Θ -temperature of this system are

$$M_w = 1.61 \times 10^6 \quad \text{and} \quad \Theta = 307.4^\circ \text{K}.$$

We have already shown that the assignments,

$$a_o = 0.731 \text{ \AA} \quad \text{and} \quad b_o = 0.1037 \text{ \AA},$$

bring Eq. (6.5) into an excellent accord with the observed values of S_w .^{*} Now substituting the values of M_w , Θ , a_o , and b_o cited above into Eq. (6.6) of A_2 , we obtain the full curve 1 corresponding to the double contact approximation and the broken curve 2 corresponding to the triple contact approximation, respectively, in Fig. 8. Both are favorably compared with the observed values which are shown

* S_w represents the root of the weight average of $\langle S^2 \rangle$.

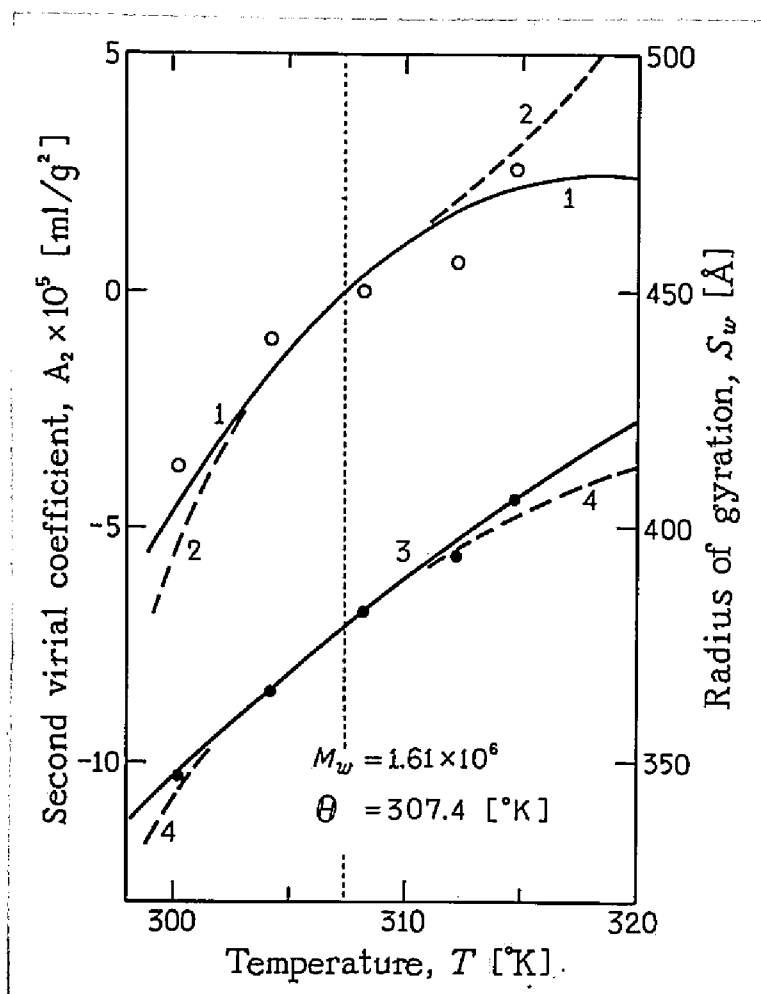


Fig. 8. Experimental test of the theoretical expression (6.6) for the osmotic second virial coefficient A_2 . Open circles: experimental values of A_2 for polystyrene in cyclohexane obtained by Outer, Carr and Zimm.⁴¹⁾ Full curve 1: double contact approximation for A_2 . Broken curve 2: triple contact approximation for A_2 . Closed circles, curves 3 and 4, respectively, represent the observed values of the radius of gyration S_w , and its single and double contact approximations (see Table IV).

by the open circles. For the sake of comparison, the experimental test of S_w is also given in the figure, where the filled circles represent the observed values, and the curves 3 and 4 the calculated values corresponding to the single and double contact approximations, respectively.

The second example is the light scattering experiment of Krigbaum and Carpenter³¹⁾ for the same system as the foregoing, but the values of M_w and Θ in this case are

$$M_w = 3.20 \times 10^6 \quad \text{and} \quad \Theta = 308.4^\circ \text{K}.$$

From the experimental data of $\langle S^2 \rangle$ for this material, we have determined in the previous section the range of applicability of the z-expansion method, which is indicated in Figs. 6 and 9 by two shaded lines, each corresponding to $z = \pm 0.15$, and evaluated as

$$a_0 = 0.672 \text{ \AA} \quad \text{and} \quad b_0 = 0.1178 \text{ \AA}.$$

Now again substituting these values into Eq. (5.6), we obtain the results shown in Fig. 9, where the open circles represent the observed values of A_2 , and the curves 1 and 2 represent its calculated values corresponding to the double and triple contact approximations, respectively. In the figure, the chain curve 3 represents the values obtained by Orofino and Flory's formulae,²⁴⁾

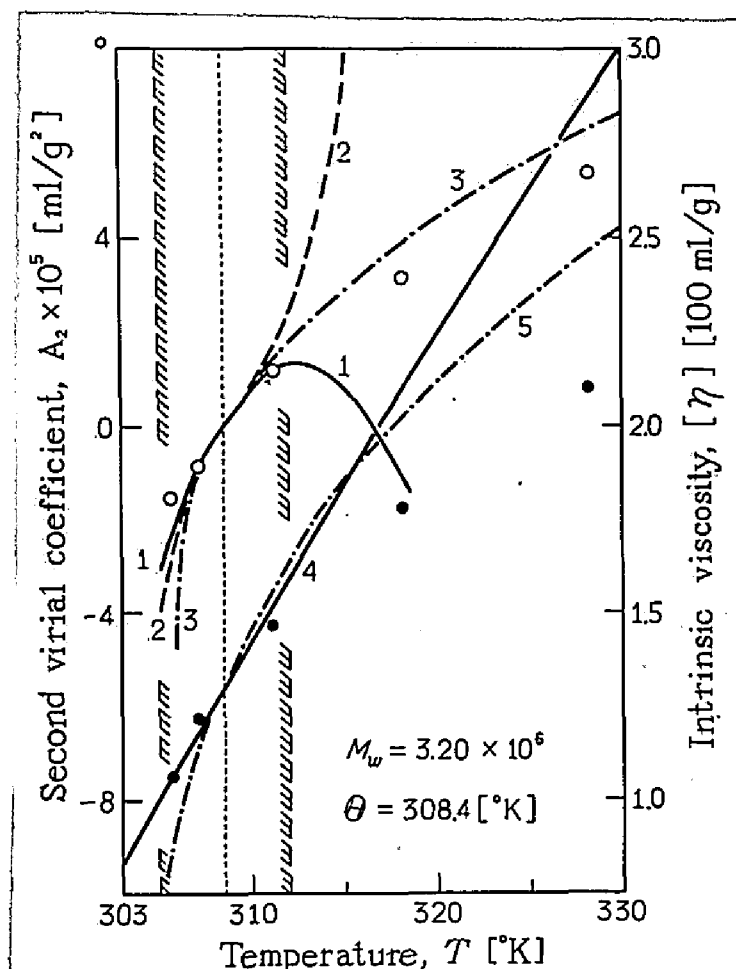


Fig. 9. Experimental test of the theoretical expressions (6.6) and (6.7) for the osmotic second virial coefficient A_2 for polystyrene in cyclohexane obtained by Krigbaum and Carpenter.³¹⁾ Full curve 1: double contact approximation for A_2 . Broken curve 2: triple contact approximation for A_2 . Chain curve 3: Orofino and Flory's equation (6.16). Closed circles: experimental values of $[\eta]$ for the same material. Full curve 4: present theory, Eq. (6.7), with $[\eta]_0 = 1.31$. Chain curve 5: Flory and Fox's equation (4.36) with Eq. (6.17). Shaded area: range of applicability of the theory ($|z| \leq 0.15$).

$$A_2 = \frac{2}{3} \pi N b_0^3 \left(1 - \frac{\Theta}{T}\right) \frac{\ln(1 + C_0 z \alpha_s^{-3})}{C_0 z \alpha_s^{-3}}, \quad (6.16)$$

$$\alpha_s^5 - \alpha_s^3 = C_s z \quad (6.17)$$

with $C_0 = 5.73^*$ and $C_s = 1.276$. The essential behavior of Fig. 9 is quite analogous to that of Fig. 6, though the deviation of the broken curve 2 from the full curve 1 is appreciably amplified in the former than in the latter, and we can find that, in the very vicinity of the Θ temperature, Eq. (6.6) is fitted for quantitative interpretation of experiment. In addition, the condition for convergence of the z -series (6.6) may be written as

$$z < 2.865 / 18.51 = 0.155 \quad \text{if } z > 0, \quad (6.18)$$

* Orofino and Flory have evaluated as $C_0 = 2.30$ from a wide variety of data; however for small z , we consider $C_0 = 5.73$ to be more appropriate, as has already been pointed out by Albrecht.²⁶⁾

though the exact condition is unknown due to the lack of knowledge of the higher coefficients. This condition (6.18) is consistent with $|z| \leq 0.15$ for the application of Eq. (6.5).

As easily seen from the definition (6.3) of z , the decrease of the molecular weight extends the application range of our theory in temperature scale (compare the first example with the second). Therefore, to make a more thorough comparison of the theory with experiment, the data for materials with a lower M are desired. In this meaning, the osmotic pressure measurement carried out by Krigbaum⁴⁴⁾

offers an illustrative example, though the Θ value, 305.6°K , of his material is a little lower, but beyond the experimental error, than those of two examples cited above.* Fig. 10 shows his data, together with the theoretical curves which are obtained by combining Eq. (6.6) with

$$a_0 = 0.962 \text{ \AA} \quad \text{and} \quad b_0 = 0.1283 \text{ \AA}. \quad (6.19)$$

In this plot of A_2 against $M^{1/2}$ the double contact approximation gives a line for each given temperature. Although

* This difference is probably due to impurities, or, in Krigbaum's words, "traces of moisture."

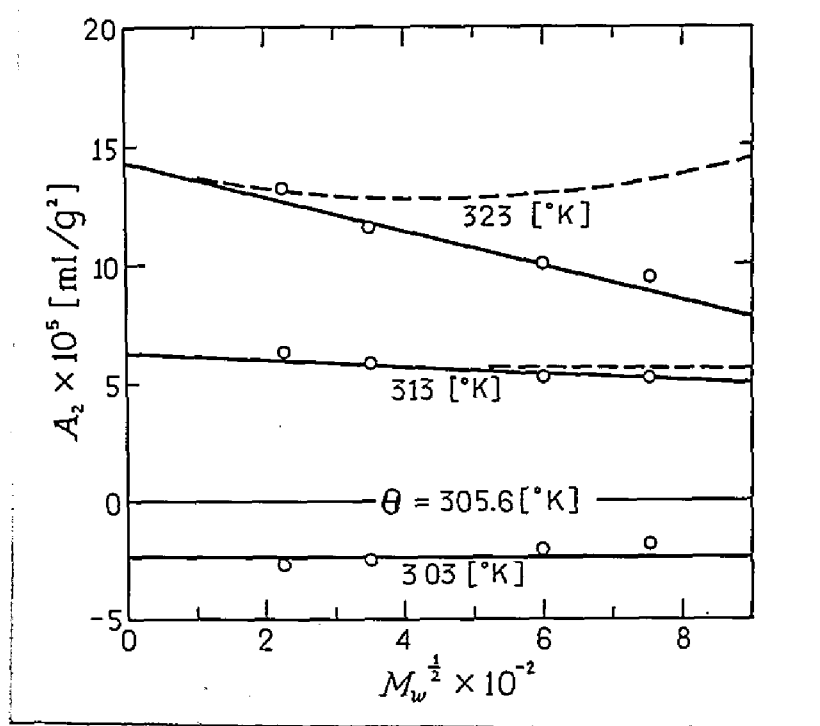


Fig. 10. Experimental test of the theoretical expression (6.6) for A_2 . Open circles: experimental values for polystyrene in cyclohexane obtained by Krigbaum.⁴⁴⁾ Full lines: present theory (double contact approximation). Broken curves: present theory (triple contact approximation).

the values (6.19) are somewhat different from those given in Eqs. (6.11a) and (6.13a), we have no doubt that this third example also supports our theory.

§ 6. 5. Frictional Properties

So far as we know, the intrinsic viscosity data of polystyrene in cyclohexane solution given by Krigbaum and Carpenter³¹⁾ appear to offer the most illustrative example for testing our Eq. (6.7). The filled circles in Fig. 9 represent their data. Now if we remember the values of M_w , a_0 , and b_0 of this system, we obtain by using Eq. (6.8) and Table II *

$$X \approx 30 \sim 50, \quad X F_0(X) = 1.14 \sim 1.18, \quad \text{and} \quad p(X) = 1.52. \quad (6.20)$$

The substitution of these values into Eq. (6.7) yields

* The detailed value of X is $217 \times M_0^{-1/3}$; hence

$$\begin{aligned} X &= 58, \quad \text{if } M_0 = 52 \quad (\text{average weight of } -CH(C_6H_5)- \\ &\quad \text{and } -CH_2-), \\ &= 46, \quad \text{if } M_0 = 104 \quad (\text{monomer weight}), \\ &= 27, \quad \text{if } M_0 = 520 \quad (\text{preferred statistical segment} \\ &\quad \text{weight; see the next section}). \end{aligned}$$

$$[\eta]_0 = 1.41 \sim 1.46, \quad (6.21)$$

which is tolerably in agreement with the observed value, 1.31 (100 ml/g), obtained by the interpolation of experimental data.

Furthermore, representing the molecular weight distribution by

$$g_w(M) = (y^{h+1}/h!) M^h \exp(-yM) \quad (6.22)$$

with $y = (h+1)/M_w = (h+2)/M_z$, (6.23)

we can easily show that for the heterogeneous polymer, Eq. (6.7) becomes^{13),30),45),46)}

$$[\eta]_0 = (1/g_w)(N/100)(\pi/6)^{\frac{3}{2}} [X F_0(X)] a_0^3 M_w^{\frac{1}{2}}, \quad (6.24a)$$

$$g_w = (h+1)^{\frac{1}{2}} [\Gamma(h+1)/\Gamma(h+1.5)], \quad (6.24b)$$

or
$$[\eta]_0 = \frac{1}{g_z} \cdot \frac{\pi^{\frac{3}{2}} N}{100} [X F_0(X)] \frac{\langle S^2 \rangle_0^{\frac{3}{2}}}{M_w}, \quad (6.25a)$$

$$\varphi_z = [(\hbar+2)^{\frac{3}{2}}/(\hbar+1)] [\Gamma(\hbar+1)/\Gamma(\hbar+1.5)], \quad (6.25b)$$

Here the subscript z attached to M and $\langle S^2 \rangle_0$ indicates the so-called z average. Now, if we set $\hbar = 4$ according to the indication of the original authors,³¹⁾ we obtain

$$\varphi_w = 1.03, \quad \varphi_z = 1.35, \quad \text{and} \quad [\eta]_\theta = 1.37 \sim 1.42, \quad (6.26)$$

instead of Eq. (6.21), and then the full curve 4 in Fig. 9. In the vicinity of the Flory temperature, this theoretical curve agrees very well with the experimental data. For the sake of comparison, we show by a chain curve the results obtained by Flory and Fox's equation.

As was noted in Chapter IV, we can write Eq. (6.7) in a closed form,

$$[\eta] = [\eta]_\theta \alpha_s^{n(x)}, \quad (6.27a)$$

or more explicitly in the form,

$$[\eta] = K_z \cdot \langle S^2 \rangle_z^{\frac{1}{2}n(x)}, \quad (6.27b)$$

$$K_z = (\pi^{\frac{3}{2}} N / 100 \varphi_z) [X F_0(x)] M_w^{-1} \langle S^2 \rangle_{0z}^{\frac{1}{2}(3-n)}$$

Fig. 11 illustrates a test for the correctness of these relations. As is expected, the intrinsic viscosity data plotted against S_z in log-log scale fall on a line of slope 2.4,* instead of 3.0. In this connection, we can find that Flory's universal constant Φ decreases with increasing temperature. This observed tendency can be well approximated by

$$\Phi(X) = \Phi_0(X) \alpha_s^{-(3-n)}, \quad (6.28)$$

$$\Phi_0(X) = 2.283 \times 10^{21} [X F_0(X)],$$

as shown in the insert to Fig. 11. It is also noteworthy that Eq. (6.27) or (6.28), although correct in itself only for small z , nevertheless can be used effectively to correlate the volume effect with the intrinsic viscosity over wide ranges of temperature. This fortunate situation is of course due to a mutual cancellation between the higher terms of two z series for $[\eta]$ and $\langle S^2 \rangle$.

In Section 6.3, we have illustrated taking the polystyrene-butanone system as an example that the Flory expression

* If $X = 30 \sim 50$, Table II reads $n(X) = 2.37 \sim 2.38$. On the other hand, the slope of the best fit line for these data has been found to be 2.2 by the original authors.³¹⁾

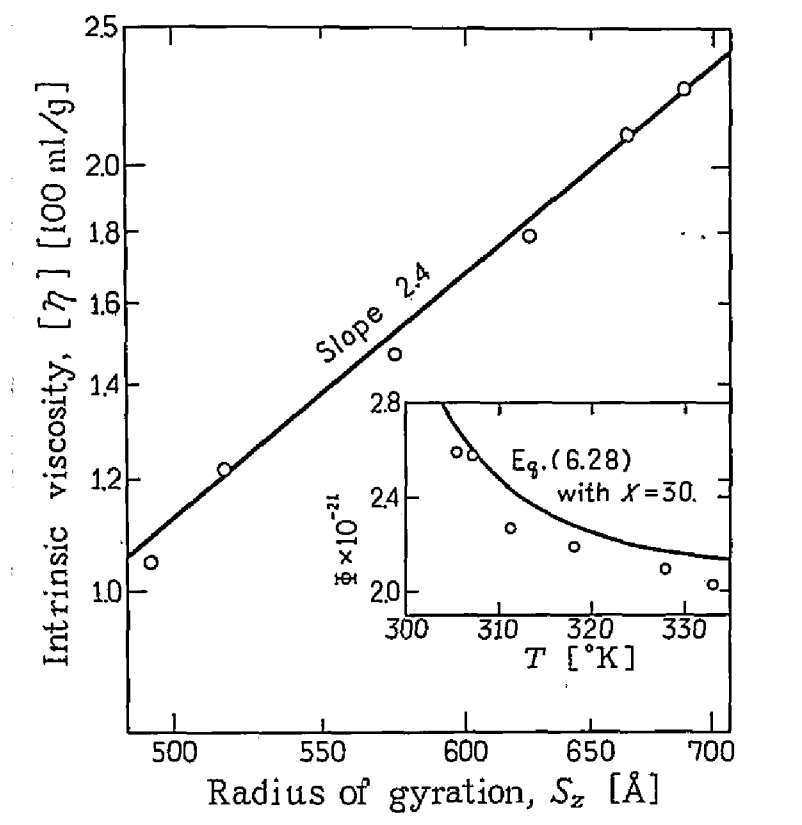


Fig. 11. Intrinsic viscosity $[\eta]$ plotted against the radius of gyration S_z , using log-log plot. Open circles: experimental data for the polystyrene-cyclohexane system ($M_w = 3.20 \times 10^6$, $\Theta = 308.4^\circ\text{K}$) obtained by Krigbaum and Carpenter.³¹⁾ The slope of theoretical line is 2.4. The insert shows the temperature dependence of Flory's constant Φ .

for α_s , Eq. (6.12) or (6.17), shows a good correspondence with experimental data over wide ranges of temperature or solvent power. Now, keeping the foregoing comments in mind, we turn to a discussion on general behaviors of Flory's constant.

As is well known, Fox and Flory⁴⁷⁾ have pointed out that the constant Φ takes a common value, 2.1×10^{21} , not only for sufficiently large values of M , but also down to low values of M . For this behavior, the present Eq. (6.28) appears to give a satisfactory explanation. That is, we may write the solution of Eq. (6.12) in the form,*

$$\alpha_s \propto M^\varepsilon, \quad \varepsilon = 0 \sim 0.1 ; \quad (6.29a)$$

then obtain remembering Eq. (4.26)

$$\Phi \propto M^\gamma, \quad \gamma = \nu(x) - \varepsilon[3 - n(x)]. \quad (6.29b)$$

* In the limit of large z , Eq. (6.17) yields the asymptotic solution,

$$\alpha_s = (C_s z)^{1/5} \propto M^{0.1}.$$

The numerical values of $\nu(X)$ and $n(X)$ are given in Table II. This relation suggests that the counter contributions of the draining effect and the volume effect, $\nu(X)$ and $\epsilon[3 - n(X)]$, make the Φ approximately independent of M over wide ranges insofar as the argument X takes a value larger than about ten. However, as X decreases beyond ten, the balance inclines toward the draining effect,* and a decrease of the Φ values will become significant. Table VI proves these statements, where the Φ values for several polystyrene fractions in butanone solutions are given, together with the experimental data of $[\eta]$ and S_w obtained by Outer, Carr and Zimm.⁴¹⁾ For the sake of comparison, there is also given a rough evaluation of X by using the same value of a/b as that for the polystyrene-cyclohexane system cited before.

Generally speaking, to adjust Eq. (6.28) to the empirical value $\Phi = 2.1 \times 10^{21}$ which was found by Fox and Flory as a mean of many data for a wide variety of polymer-solvent systems, it is only necessary to assume that α_s ranges over

* As shown in Table II, $\epsilon[3 - n(X)]$ does not exceed 0.1 for $\epsilon_{\max} = 0.1$ and $[3 - n(X)]_{\max} = 1$; while $\nu(X)$ exceeds 0.1 when $X \leq 8$.

Table VI. Values of Φ for polystyrene in
butanone solutions at 22°C.

Polymer	$M_w \times 10^{-6}$	S_w [Å] ^a	$[\eta]$ (100ml/g) ^a	$\Phi \times 10^{-21}$	X^b
A-7	0.23	163	0.53	1.90	8~13
A-6	0.52	222	0.77	2.47	12~20
A-3	0.94	306	1.17	2.61	16~27
A-2	1.32	368	1.40	2.53	19~32
B-2	1.63	414	1.61	2.51	21~36
A-1	1.77	437	1.65	2.38	22~37
	(3.20)	—	—	—	(30~50)

^a

Data are obtained by Outer, Carr and Zimm, Ref. 41).

^b

Values of X are obtained by making molecular weight correction of the X values (30~50) for Krigbaum and Carpenter's material ($M_w = 3.20 \times 10^6$). See Eq. (6.20).

1.1 to 1.7 depending on the X values, ten to infinity, of the systems. The values of α_s of this order seem to be very plausible for ordinary good solvent systems.

Our Eq. (6.28) further predicts two kinds of deviations of Φ from the constancy; the one is related to the volume effect and often observed in mixed solvent systems, and the other is related to the draining effect and often observed for relatively short chain or rigid molecule such as the cellulose derivatives. Table VII proves the volume effect on Φ , where the Φ value for the same polystyrene increases as the concentration of cyclohexane is increased (or the solvent power and α_s are decreased). Table VIII proves the draining effect on Φ , where the values of Φ and $\Phi^{1/3}P^{-1}$ for the ethyl hydroxyethyl cellulose in water vary appreciably with increasing M .⁴⁸⁾ These variations undoubtedly correspond to those of Φ_0 and $\Phi_0^{1/3}P_0^{-1}$ for $X = 0.3 \sim 0.6$ in Tables II and III, and indicate that the system is to be characterized by very small X , or in other words a large value of a_0/b_0 (see Eq. (6.8)).

Thus we may arrive at a conclusion that the draining effect is important for quantitative interpretation of intrinsic viscosity data as well as the excluded volume effect.

Table VII. Values of $\bar{\Phi}$ for polystyrene ($M_w = 1.62 \times 10^6$)
in the solvent mixtures of dichloroethane
and cyclohexane.

Solvent			$S_w [\text{\AA}]^a$	$[\eta][100\text{ml/g}]^a$	$\bar{\Phi} \times 10^{-21}$
Dichloroethane: cyclohexane					
6	:	94	408	1.30	2.11
100	:	0	545	2.78	1.89
35	:	65	563	2.80	1.72
65	:	35	645	3.20	1.31

^a

Data are obtained by Outer, Carr and Zimm, Ref. 41).

Table VIII. Values of Φ and $\Phi^{1/3}P^{-1}$ for ethyl
hydroxyethyl cellulose in water.^a

Fraction No.	$M_w \times 10^{-3}$	$\Phi \times 10^{-21}$	$\Phi^{1/3}P^{-1} \times 10^{-7}$
3	160	0.74	3.30
5	250	0.79	3.08
7	400	0.95	3.05
12	570	1.00	2.90

^a

Data are obtained by R. St. J. Manley, Ref. 48),

§ 6. 6. Short Range Interferences

We have evaluated in the preceeding sections the model constants a_0 and b_0 of the random chain representing a polystyrene molecule in cyclohexane solutions. Now we evaluate the structural constants of polystyrene, taking account of the effect of short range interferences.

Letting l be the length of valence bond, m_0 the molar weight of a chain element, θ the valence angle, and ϕ the rotation angle about valence bond, we obtain

$$a_0 M^{\frac{1}{2}} (= a_N^{\frac{1}{2}}) = l \left(\frac{M}{m_0} \right)^{\frac{1}{2}} \left[\frac{1 + \cos \theta}{1 - \cos \theta} \cdot \frac{1 + \langle \cos \phi \rangle}{1 - \langle \cos \phi \rangle} \right]^{\frac{1}{2}} \quad (6.30)$$

In the case of polystyrene, we can put

$$l = 1.54 \text{ \AA} , \quad \cos \theta = \frac{1}{3} , \quad (6.31)$$

$m_0 = 52$ (average weight of
 $-\text{CH}(\text{C}_6\text{H}_5)-$ and $-\text{CH}_2-$).

Hence using the data of a_0 in Table IX, we find $\langle \cos \phi \rangle$ to be about 0.7. As Benoit⁴⁹⁾ has shown, if the steric hindrance due to side chains is represented by a hard potential which is zero for $|\phi| \leq \phi_0$ and infinite for all other positions, we can write $\langle \cos \phi \rangle = \sin \phi_0 / \phi_0$, and find

Table IX. Structural constants for polystyrene
in cyclohexane solutions.

Data	$\langle S^2 \rangle$, A_2 by Outer-Carr- Zimm ^a	$\langle S^2 \rangle$, A_2 , $[\eta]$ by Krigbaum- Carpenter ^b	A_2 by Krigbaum ^c
$M_w \times 10^{-5}$	16.1	32.0	0.505~5.66
Θ [$^{\circ}\text{K}$]	307.4	308.4	305.6
a_0 [$\text{\AA}$]	0.731	0.672	0.962
b_0 [$\text{\AA}$]	0.1037	0.1178	0.1285
$\langle \cos \phi \rangle$	0.710	0.665	0.820
ϕ_0 [degree]	80	86	61
M_0	610	615	1055
a [$\text{\AA}$]	18.1	15.3	31.3
b [$\text{\AA}$]	7.5	7.6	12.0
u_0/k [$^{\circ}\text{K}$]	34	62	26

^a See Ref. 41).

^b See Ref. 31).

^c See Ref. 44).

$\phi_0 \simeq 80^\circ$ in rough agreement with the value 100° obtained by a stereochemical consideration.

The values of a and b depend on the choice of the segment size M_0 . If we put $M_0 = m_0 = 52$, the following values are obtained:

$$a \simeq 5 \text{ \AA} , \quad b \simeq 1.5 \text{ \AA} . \quad (6.32)$$

It is to be noted that both a and b are obtained in angstrom order.

In order to define completely the equivalent chain, it is required to set an additional condition besides Eq. (6.30). An example is Kuhn's condition,⁵⁰⁾

$$a_N = (a_0/M_0^{1/2}) M = l(M/m_0). \quad (6.33)$$

This relation, together with Eq. (6.30), determines the size and length of the so-called preferred statistical segment as

$$M_0 = 520 , \quad a = 16 \text{ \AA} , \quad \text{and} \quad b = 7 \text{ \AA} . \quad (6.34)$$

The values of the structural constants thus obtained are collected in Table IX.

On the other hand, the force constants ϵ and σ for

the Lennard-Jones potential $\phi(r)$ have been evaluated by Hirschfelder et al. as follows:⁵¹⁾

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (6.35)$$

$$\epsilon/k = \begin{cases} 440^\circ K \\ 324^\circ K \end{cases} \quad \sigma = \begin{cases} 5.270 \text{ \AA} & \text{for benzene} \\ 6.093 \text{ \AA} & \text{for cyclohexane.} \end{cases} \quad (6.36)$$

Although we cannot derive conclusive informations from the comparison between these potential for simple molecules and the mean force potential for polymer segments, nevertheless we may say that the preferred statistical chain model is that of giving a segment size b of more reasonable magnitude than the simple equivalent chain model (6.32).

CONCLUSION

In this work, we have been dealing with the theory of dilute polymer solutions from a rigorous and molecular-theoretical standpoint with the aim of describing systematically the various properties of dilute polymer solutions, related to the excluded volume effect, by the molecular or model constants such as the segment size and its link length without including the phenomenological parameters, and of interpreting the recent experimental results which cannot be explained by the published theories. And this aim has almost been attained, we believe. Namely, the theory presented here can be applied very satisfactorily not only to give a completely quantitative interpretation for the experimental data of various properties of dilute polymer solutions such as $\langle S^2 \rangle$, A_2 , and $[\eta]$ but also to explore the nature of various approximate theories. This, of course, results from our rigorous treatment in which complete account is taken of the connection of segments or the spatial correlation between segments. Although the range of applicability of the theory is limited in the vicinity of the Flory temperature, for the expressions all are expressed in a power series in the excluded volume parameter which becomes zero at the Flory temperature, it is to be emphasized that the values of model constants obtained from the light scattering data of $\langle S^2 \rangle$ can be used, without

introducing any makeshift, for quantitative analyses of other quantities such as A_2 and $[\eta]$. Accordingly, it is desired that the theory, which is rigorously developed from a molecular-theoretical standpoint and moreover is expressed in a closed form, will be proposed in near future, so that it may be extended to apply to good solvent systems. In this meaning, the theory of second virial coefficient recently proposed by Casassa and Markovitz²⁷⁾ seems to be a very interesting approach.

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APPENDIX I. $J(R_{kl})$

If we denote the components of vectors $\mathbf{R}$ and $\mathbf{q}$ in the 3-dimensional space by (x, y, z) and (q_1, q_2, q_3) respectively, the integral $h_1(\mathbf{q}, n)$ in Eq. (1.17) can be evaluated as follows,

$$\begin{aligned} h_1(\mathbf{q}, n) &= (4\pi a^2)^n (\beta^3/\pi^{\frac{3}{2}}) \int \exp(-\beta^2 R^2) \exp(i\mathbf{q} \cdot \mathbf{R}) d\mathbf{R} \\ &= (4\pi a^2)^n (\beta^3/\pi^{\frac{3}{2}}) \iiint_{-\infty}^{+\infty} \exp[i(q_1 x + q_2 y + q_3 z) - \beta^2(x^2 + y^2 + z^2)] dx dy dz \\ &= (4\pi a^2)^n \exp[-na^2(q_1^2 + q_2^2 + q_3^2)/6] \\ &= (4\pi a^2)^n \exp(-na^2 q^2/6), \end{aligned} \tag{AI.1}$$

where $\beta^2 = 3/2 na^2$.

Next, using the polar coordinates (R, θ, φ) with the z axis in the direction of vector $\mathbf{q}$, we may rewrite the integral $h_2(\mathbf{q}, n)$ in Eq. (1.17) as

$$\begin{aligned} h_2(\mathbf{q}, n) &= (4\pi a^2)^n (\beta^3/\pi^{\frac{3}{2}}) \int \chi(R) \exp(-\beta^2 R^2) \exp(i\mathbf{q} \cdot \mathbf{R}) d\mathbf{R} \\ &= (4\pi a^2)^n (\beta^3/\pi^{\frac{3}{2}}) \int_0^\infty \int_0^\pi \int_0^{2\pi} \chi(R) \exp(-\beta^2 R^2) \exp(iqR \cos \theta) \\ &\quad \times R^2 \sin \theta dR d\theta d\varphi \\ &= (4\pi a^2)^n (\beta^3/\pi^{\frac{3}{2}}) \int_0^\infty 4\pi R \chi(R) \exp(-\beta^2 R^2) \frac{\sin(qR)}{q} dR, \end{aligned} \tag{AI.2}$$

Substituting Eq. (1.11) for $\chi(R)$ with the neglect of all terms higher than the second of u_0/kT , and splitting the integral in Eq. (AI.2) into two parts 0 to b and b to ∞ , we may rewrite Eq. (AI.2) as

$$\begin{aligned} h_2(q, n) = & -(4\pi a^2)^n (\beta^3/\pi^{\frac{3}{2}}) (4\pi) \left[\int_0^b R \exp(-\beta^2 R^2) \frac{\sin(qR)}{q} dR \right. \\ & \left. - (u_0/kT) \int_b^\infty R \exp(-3R^2/2d^2) \exp(-\beta^2 R^2) \frac{\sin(qR)}{q} dR \right]. \end{aligned} \quad (\text{AI.3})$$

Splitting the second integral in Eq. (AI.3) into two parts 0 to ∞ and b to 0, and using the approximation (1.18), Eq. (AI.3) becomes

$$\begin{aligned} h_2(q, n) \simeq & -(4\pi a^2)^n (\beta^3/\pi^{\frac{3}{2}}) (4\pi) \left\{ \int_0^b R (1 - \beta^2 R^2) \frac{\sin(qR)}{q} dR \right. \\ & - (u_0/kT) \left[\int_0^\infty R \exp(-3R^2/2d^2) \cdot \frac{\sin(qR)}{q} dR \right. \\ & \left. \left. - \int_0^b R (1 - 3R^2/2d^2) \frac{\sin(qR)}{q} dR \right] \right\} \\ \simeq & -(4\pi a^2)^n (\beta^3/\pi^{\frac{3}{2}}) (4\pi b^3/3) \left\{ 1 - \frac{1}{10} (q^2 + q^2/n a^2) b^2 \right. \\ & - (u_0/kT) \left\{ (\pi/6)^{\frac{1}{2}} (d/b)^3 \exp(-d^2 q^2/6) \right. \\ & \left. \left. - 1 + \frac{1}{10} (q^2 + q^2/d^2) b^2 \right\} \right\}. \end{aligned} \quad (\text{AI.4})$$

Therefore, from Eqs. (AI.1) and (AI.4), we obtain for the Fourier transform of the integral $J(R_{kl})$ defined by Eq. (1.15)

$$\begin{aligned}
 H(q) = & -(4\pi a^2)^m (\beta^3/\pi^{\frac{3}{2}}) (4\pi b^3/3) \left\{ 1 - \frac{1}{10} (q^2 + q/na^2) b^2 \right. \\
 & - (u_0/kT) \left[(\pi/6)^{\frac{1}{2}} (d/b)^3 \exp(-d^2 q^2/6) \right. \\
 & \left. \left. - 1 + \frac{1}{10} (q^2 + q/d^2) b^2 \right] \right\} \exp[-(m-n) a^2 q^2/6],
 \end{aligned} \tag{AI.5}$$

where we have replaced $l-k$ and $j-i$ by m and n respectively for the sake of simplicity.

Now the integral $J(R_{kl})$ is given by the inverse transform of $H(q)$ as follows,

$$\begin{aligned}
 J(R_{kl}) = & \frac{1}{8\pi^3} \int \exp(-i q \cdot R_{kl}) \cdot H(q) dq \\
 = & \frac{1}{8\pi^3} \int_{-\infty}^{+\infty} \int \int \exp[-i(q_1 x_{kl} + q_2 y_{kl} + q_3 z_{kl})] \\
 & \times H(q_1, q_2, q_3) dq_1 dq_2 dq_3.
 \end{aligned} \tag{AI.6}$$

Substituting Eq. (AI.5) into Eq. (AI.6) and performing the integration with taking account of the approximation (1.18), we arrive at

$$J(R_{kl}) = -(4\pi a^2)^m (z/N^{\frac{1}{2}} n^{\frac{3}{2}}) [3/2\pi(m-n)a^2]^{\frac{3}{2}} \times \exp[-3R_{kl}^2/2(m-n)a^2], \quad (\text{AI.7})$$

which is just identical to Eq. (1.19).

APPENDIX II. $\langle S_k^2 \rangle$

If S_k and x are the vectors from the molecular center of mass to segment k and from segment 0 to the molecular center of mass respectively,

$$S_k = R_{ok} - x, \quad (\text{AII.1})$$

$$\sum_k S_k = 0. \quad (\text{AII.2})$$

Hence
$$x = \frac{1}{N} \sum_k R_{ok},$$

$$x^2 = x \cdot x = \frac{1}{N^2} \sum_k \sum_\ell R_{ok} \cdot R_{o\ell}. \quad (\text{AII.3})$$

From Eqs. (AII.1) and (AII.2), we find

$$\begin{aligned} S_k^2 &= S_k \cdot S_k \\ &= R_{ok}^2 + \frac{1}{N^2} \sum_k \sum_\ell R_{ok} \cdot R_{o\ell} - \frac{2}{N} \sum_\ell R_{ok} \cdot R_{o\ell}. \end{aligned} \quad (\text{AII.4})$$

On the other hand, it can be easily shown that

$$\sum_k \sum_\ell \langle R_{ok} \cdot R_{o\ell} \rangle = N \sum_k \langle R_{ok}^2 \rangle - \sum_{k < \ell} \langle R_{k\ell}^2 \rangle, \quad (\text{AII.5})$$

$$2 \sum_{\ell} \langle R_{o\ell} \cdot R_{o\ell} \rangle = N \langle R_{ok}^2 \rangle + \sum_k \langle R_{ok}^2 \rangle \quad (\text{AII.6})$$

$$- \sum_{\ell=0}^{k-2} \langle R_{\ell k}^2 \rangle - \sum_{\ell=k+2}^N \langle R_{k\ell}^2 \rangle.$$

Hence, from Eqs. (AII.4) to (AII.6), we obtain

$$\langle S_k^2 \rangle = \frac{1}{N} \left[\sum_{\ell=0}^{k-2} \langle R_{\ell k}^2 \rangle + \sum_{\ell=k+2}^N \langle R_{k\ell}^2 \rangle \right] - \frac{1}{N^2} \sum_{k < \ell} \langle R_{k\ell}^2 \rangle, \quad (\text{AII.7})$$

which is identical to Eq. (1.34).

APPENDIX III. $\langle \frac{1}{R_{1j}} \rangle$

Using the phase integral $\Omega_2(R_{ij}, N)$ given by Eqs. (1.9), (1.13), and (1.22), or the segment distribution function $p_2(i, j)$ given by Eqs. (3.18) to (3.20), we obtain for $\langle 1/R_{1j} \rangle$

$$\begin{aligned} \langle \frac{1}{R_{1j}} \rangle &= \frac{\int_0^\infty R_{ij} \Omega_2(R_{ij}, N) dR_{ij}}{\int_0^\infty R_{ij}^2 \Omega_2(R_{ij}, N) dR_{ij}} \\ &= \int_0^\infty R_{ij}^{-1} p_2(i, j) 4\pi R_{ij}^2 dR_{ij} \quad (\text{AIII.1}) \\ &= \left(\frac{6}{\pi}\right)^{\frac{1}{2}} \frac{1}{(j-i)^{\frac{1}{2}} a} (1 - L_{ij} z + \dots) \quad \text{if } i < j, \end{aligned}$$

where

$$\begin{aligned} L_{ij} &= \frac{1}{N^{\frac{1}{2}}} \sum_{p=1}^{\infty} \frac{C_p}{p + \frac{1}{2}} \left\{ \frac{4p}{p^2 - \frac{1}{4}} (j-i)^{\frac{1}{2}} \right. \\ &\quad + \frac{1}{p - \frac{1}{2}} [N^{-p+\frac{1}{2}} - j^{-p+\frac{1}{2}} - (N-i)^{-p+\frac{1}{2}}] (j-i)^p \\ &\quad + \sum_{q=0}^{2p} \frac{(-1)^{q+1}}{p-q+\frac{1}{2}} \binom{2p}{q} [i^q (j^{p-q+\frac{1}{2}} - i^{p-q+\frac{1}{2}}) \\ &\quad \left. + (N-j)^q ((N-i)^{p-q+\frac{1}{2}} - (N-j)^{p-q+\frac{1}{2}})] (j-i)^{-p} \right\}, \end{aligned}$$

$$C_p = (2p)! / 2^{2p} (p!)^2,$$

APPENDIX IV. $\lim_{x \rightarrow 0} p(x)$

From tables of the Riemann ζ -function, we have

$$\zeta(2) = \sum_{k=1}^{\infty} \frac{1}{k^2} = \frac{\pi^2}{6}. \quad (\text{AIV.1})$$

From Eqs. (4.25) and (AIV.1), it is easy to see that

$$\lim_{x \rightarrow 0} p(x) = \frac{2}{3} + \sum_{k=1}^{\infty} \left[8\pi^{\frac{1}{2}} \frac{C(2\pi k)}{(\pi k)^{5/2}} + 6\pi^{\frac{1}{2}} \frac{S(2\pi k)}{(\pi k)^{3/2}} \right]. \quad (\text{AIV.2})$$

Now, expanding the function $(1+x)^{3/2} + (1-x)^{3/2}$ defined in the range $-1 \leq x \leq 1$ in a Fourier series, we obtain

$$\begin{aligned} (1+x)^{\frac{3}{2}} + (1-x)^{\frac{3}{2}} &= \frac{8\sqrt{2}}{5} + \sum_{\substack{k=-\infty \\ k \neq 0}}^{+\infty} (-1)^k \left\{ \frac{3\sqrt{2}}{2(\pi k)^2} \right. \\ &\quad \left. - \frac{3\sqrt{2}}{4} \pi^{\frac{1}{2}} \frac{C(2\pi|k|)}{(\pi|k|)^{5/2}} \right\} e^{i\pi k x}. \end{aligned} \quad (\text{AIV.3})$$

Putting $x = 1$ in this equation and using Eq.(AIV.1), we obtain

$$\pi^{\frac{1}{2}} \sum_{k=1}^{\infty} \frac{C(2\pi k)}{(\pi k)^{5/2}} = \frac{1}{15}. \quad (\text{AIV.4})$$

Similarly, the function $(1+x)^{5/2} + (1-x)^{5/2}$ leads to

$$\pi^{\frac{1}{2}} \sum_{k=1}^{\infty} \frac{S(2\pi k)}{(\pi k)^{7/2}} = \frac{4}{315}. \quad (\text{AIV.5})$$

Hence, from Eqs. (AIV.2), (AIV.4) and (AIV.5) we arrive at

$$\lim_{x \rightarrow 0} p(X) = \frac{134}{105}. \quad (\text{AIV.6})$$

APPENDIX V. Solution of the Integral Equation
(5.5b) in the Asymptotic Limit of
Large X

If we put $\phi(x) = (X/\sqrt{x})(1-0.416 x)\psi(x)$, (AV.1)

the integral equation (5.5b) in the asymptotic limit of large X turns into

$$f(x) = \int_{-1}^{+1} \frac{\phi(t)}{|x-t|^{\frac{1}{2}}} dt, \quad (\text{AV.2})$$

where $f(x)$ is a known function of x in general. This integral equation can be solved in a relatively simple manner using the Gegenbauer polynomial expansion proposed by Auer and Gardner.³⁷⁾

Let $P_m(x)$ be the Gegenbauer polynomials; we expand the kernel appearing in the integral equation and the function $\phi(x)$ as

$$|x-t|^{-\frac{1}{2}} = \sum_{n=0}^{\infty} a_n P_n(x) P_n(t),$$

$$\phi(x) = \sum_{m=0}^{\infty} \frac{b_m P_m(x)}{N_m (1-x^2)^{1/4}}, \quad (\text{AV.3})$$

where the coefficient a_n and the normalization constant N_n are given by

$$a_n = \pi^{\frac{1}{2}} (2n + \frac{1}{2}) \left[\frac{\Gamma(n + \frac{1}{2})}{\Gamma(\frac{3}{4}) \Gamma(n+1)} \right]^2, \quad (AV.4)$$

$$N_n = \frac{\sqrt{2} \left[\Gamma(\frac{3}{4}) \right]^2 \Gamma(n+1)}{(2n + \frac{1}{2}) \Gamma(n + \frac{1}{2})}.$$

Then, by substituting Eqs. (AV.3) into Eq. (AV.2), we obtain

$$f(x) = \int_{-1}^{+1} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} a_n b_m N_m^{-1} P_n(x) \frac{P_m(t) P_n(t)}{(1-t^2)^{1/4}} dt \quad (AV.5)$$

$$= \sum_{n=0}^{\infty} a_n b_n P_n(x),$$

and

$$\int_{-1}^{+1} \frac{f(x)}{(1-x^2)^{1/4}} P_m(x) dx = a_m b_m N_m = C_m. \quad (AV.6)$$

Hence,

$$\phi(x) = \sum_{m=0}^{\infty} \frac{C_m P_m(x)}{a_m N_m^2 (1-x^2)^{1/4}}. \quad (AV.7)$$

Since we here concern ourselves with the case:

$$f(x) = 1 = P_0(x), \quad (AV.8)$$

Eqs. (AV.6) and (AV.7) yield the results,

$$C_m = \int_{-1}^{+1} \frac{P_0(x) P_m(x)}{(1-x^2)^{1/4}} dx$$

$$= \begin{cases} 0 & \text{for } m \geq 1 \\ N_0 = (2\sqrt{2}/\pi^{1/2}) [P(\frac{3}{4})]^2 & \text{for } m=0, \end{cases} \quad (\text{AV.9})$$

$$\phi(x) = \frac{N_0}{4\pi^{1/2} [P(\frac{3}{4})]^2} \cdot \frac{P_0(x)}{(1-x^2)^{1/4}} \quad \text{for } X=\infty. \quad (\text{AV.10})$$

The frictional coefficient Σ can be calculated by

$$\Sigma = \frac{N\zeta}{2} \int_{-1}^{+1} \psi(x) dx$$

$$= \frac{\sqrt{2} \zeta N}{X} (1 - 0.416 \zeta)^{-1} \left[\frac{1}{2} \int_{-1}^{+1} \phi(x) dx \right]. \quad (\text{AV.11})$$

By using Eq. (AV.10), we obtain

$$\Sigma_{X=\infty} = 0.3811 (\zeta N/X) (1 - 0.416 \zeta)^{-1}, \quad (\text{AV.12})$$

or $[X G_0(X)]_{X=\infty} = 0.7622, \quad (\text{AV.13})$

REFERENCES

- 1) P. J. Flory, J. Chem. Phys., 17, 303 (1949).
- 2) K. Suzuki, Bull. Chem. Soc. Japan, 22, 8 (1949).
- 3) E. Teramoto, Busseiron-Kenkyu (in Japanese), 39, 1 (1951); 40, 18 (1951); 41, 14 (1951); Proceedings of the International Conference of Theoretical Physics, Kyoto and Tokyo, September, 1953, 410. A brief english summary of these papers is given by the courtesy of P. J. Flory, J. Polymer Sci., 14, 1 (1954).
- 4) M. Yamamoto, Busseiron-Kenkyu (in Japanese), 44, 36 (1951).
- 5) T. B. Grimley, J. Chem. Phys., 21, 185 (1953).
- 6) F. Bueche, J. Chem. Phys., 21, 205 (1953).
- 7) H. M. James, J. Chem. Phys., 21, 1628 (1953).
- 8) N. Saito, J. Phys. Soc. Japan, 9, 780 (1954).
- 9) B. H. Zimm, W. H. Stockmayer and M. Fixman, J. Chem. Phys., 21, 1716 (1953); M. Fixman, *ibid.*, 23, 1656 (1955).
- 10) For example, W. R. Krigbaum, J. Polymer Sci., 18, 315 (1955). See also Ref. 8).
- 11) S. Chandrasekhar, Rev. Mod. Phys., 15, 1 (1943).
- 12) E. Teramoto, M. Kurata, R. Chujo, C. Suzuki, K. Tani and T. Kajikawa, J. Phys. Soc. Japan, 10, 953 (1955).
- 13) B. H. Zimm, J. Chem. Phys., 16, 1093, 1099 (1948).
- 14) For example, P. J. Flory, "Principles of Polymer Chemistry" (Cornell University Press, Ithaca, New York, 1953), Chap. XII.

- 15) Earlier theories of polymer solutions are comprehensibly reviewed by H. Tompa, "Polymer Solutions" (Butterworths Scientific Publications, London, 1956), Chap. 4.
- 16) A. Münster, "Statistische Thermodynamik hochmolekularer Lösungen," in "Die Physik der Hochpolymeren" (H. A. Stuart, Springer-Verlag, Berlin, 1953) Bd II.
- 17) G. S. Rushbrooke, H. I. Scoins and A. J. Wakefield, Discussions Faraday Soc., 15, 57 (1953).
- 18) M. Kurata, M. Tamura and T. Watari, J. Chem. Phys., 23, 991 (1955).
- 19) W. G. McMillan and J. E. Mayer, J. Chem. Phys., 13, 276 (1945).
- 20) B. H. Zimm, J. Chem. Phys., 14, 164 (1946).
- 21) P. J. Flory and W. R. Krigbaum, J. Chem. Phys., 18, 1086 (1950).
- 22) T. B. Grimley, Proc. Roy. Soc. (London), A212, 339 (1952).
- 23) A. Ishihara and R. Koyama, J. Chem. Phys., 25, 712 (1956).
- 24) T. A. Orofino and P. J. Flory, J. Chem. Phys., 26, 1067 (1957).
- 25) W. R. Krigbaum and P. J. Flory, J. Am. Chem. Soc., 75, 1775 (1953).
- 26) A. C. Albrecht, J. Chem. Phys., 27, 1002 (1957).
- 27) E. F. Casassa, J. Chem. Phys., 27, 970 (L) (1957); E. F. Casassa and H. Markovitz, *ibid.*, 29, 493 (1958).

- 28) P. Debye and A. M. Bueche, J. Chem. Phys., 16, 573 (1948).
- 29) J. G. Kirkwood and J. Riseman, J. Chem. Phys., 16, 565 (1948).
- 30) P. J. Flory and T. G. Fox, Jr., J. Am. Chem. Soc., 73, 1904 (1951); and their succeeding papers.
- 31) W. R. Krigbaum and D. K. Carpenter, J. Phys. Chem., 59, 1166 (1955).
- 32) B. H. Zimm, J. Chem. Phys., 24, 269 (1956).
- 33) J. G. Kirkwood and J. Riseman, J. Chem. Phys., 22, 1626 (L) (1954).
- 34) J. G. Kirkwood, R. W. Zwanzig and R. J. Plock, J. Chem. Phys., 23, 213 (L) (1955).
- 35) J. G. Kirkwood, F. P. Buff and M. S. Green, J. Chem. Phys., 17, 988 (1949).
- 36) P. Debye, J. Chem. Phys., 14, 636 (1946).
- 37) P. L. Auer and C. S. Gardner, J. Chem. Phys., 23, 1545 (L), 1956 (L) (1955).
- 38) W. H. Stockmayer and A. C. Albrecht, J. Polymer Sci., 32, 215 (1958).
- 39) For example, P. J. Flory, "Principles of Polymer Chemistry" (Cornell University Press, Ithaca, New York, 1953), Chap. XIV.
- 40) L. Mandelkern and P. J. Flory, J. Chem. Phys., 20, 212 (1952).

- 41) P. Outer, C. I. Cas^{yr} and B. H. Zimm, J. Chem. Phys., 18, 830 (1950).
- 42) W. R. Krigbaum, J. Chem. Phys., 23, 2113 (1955).
- 43) P. J. Flory, "Principles of Polymer Chemistry" (Cornell University Press, Ithaca, New York, 1953), p. 625, Table XL I.
- 44) W. R. Krigbaum, J. Am. Chem. Soc., 76, 3758 (1954).
- 45) S. Newman, W. R. Krigbaum, C. Langier and P. J. Flory, J. Polymer Sci., 14, 451 (1954).
- 46) A. R. Shultz, J. Am. Chem. Soc., 76, 3422 (1954).
- 47) T. G. Fox, Jr. and P. J. Flory, J. Am. Chem. Soc., 73, 1909, 1915 (1951). See also Ref. 30).
- 48) R. St. J. Manley, Arkiv Kemi, 9, 519 (1956).
- 49) H. Benoit, J. Polymer Sci., 3, 376 (1948); H. Benoit and C. Sadron, *ibid.*, 4, 473 (1949).
- 50) W. Kuhn, Kolloid-Z., 68, 2 (1934).
- 51) J. O. Hirschfelder, C. F. Curtiss and R. S. Bird, "Molecular Theory of Gases and Liquids" (John Wiley & Sons, Inc., New York, 1954), Appendix, Table I-A.

NOTE

This article was prepared based upon the following papers already published.

(1) Statistical Mechanics of Dilute Polymer Solutions. I.

End-to-end Distance.
. Busseiron-Kenkyu (in Japanese), 96, 93 (1956).

(2) Statistical Mechanics of Dilute Polymer Solutions. II.

Osmotic Second Virial Coefficient (General Theory).
. Busseiron-Kenkyu (in Japanese), 97, 153 (1956).

(3) Statistical Mechanics of Dilute Polymer Solutions. III.

Osmotic Second Virial Coefficient.
. Busseiron-Kenkyu (in Japanese), 98, 175 (1956).

(4) Statistical Mechanics of Dilute Polymer Solutions. IV.

Radius of Gyration.
. Busseiron-Kenkyu (in Japanese), 99, 62 (1956).

(5) Statistical Mechanics of Dilute Polymer Solutions. V.

Comparison with Experiment.
. Busseiron-Kenkyu (in Japanese), 101, 88 (1956).

(6) Excluded Volume Effect on Light Scattering of Polymer Solutions.

. Busseiron-Kenkyu (in Japanese), 104, 55 (1957).

(7) Excluded Volume Effect on Intrinsic Viscosity of Polymer Solutions.

. Busseiron-Kenkyu (in Japanese), 2-1, 311 (1957).

- (8) Statistical Mechanics of Dilute Polymer solutions (Supplementary Remarks).
. Busseiron-Kenkyu (in Japanese), 2-2, 329 (1957).
- (9) Theory of Dilute Polymer Solutions. I. Chain Configuration and Light Scattering.
. J. Phys. Soc. Japan, 13, 78 (1958).
- (10) Theory of Dilute Polymer Solutions. II. Osmotic Pressure.
. J. Phys. Soc. Japan, 13, 87 (1958).
- (11) Theory of Dilute Polymer Solutions. III. Intrinsic Viscosity.
. J. Phys. Soc. Japan, 13, 94 (1958).
- (12) Theory of Dilute Polymer Solution. I. Excluded Volume Effect.
. J. Chem. Phys., 28, 785 (1958).
- (13) Theory of Dilute Polymer Solution. II. Osmotic Pressure and Frictional Properties.
. J. Chem. Phys., 29, 311 (1958).