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On the Extension of High Polymer Molecules

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First we examined the distribution of chain elements of high polymer molecules and arrived at the conclusion that the distribution must be such that the mean square end-to-end distance of high polymer molecule calculated from this distribution is expressed, within a narrow range of the degree of polymerization N , by

$$\langle r^2 \rangle = CN^r$$

with r which satisfies the relation

$$\frac{dr}{dT} \approx 0,$$

where C is an appropriate constant and T the temperature. Next we inquired into the methods of obtaining the extension of high polymer from empirical data by making use of such a distribution of elements, and, following one of those methods, we determined experimentally the extension of high polymer in various solutions.

Finally, we carried out the theoretical treatment of the extension of high polymer in solution. It has been found that there is a critical value of mixing heat ΔU between the chain elements and solvent molecules, which corresponds to the precipitation of the high polymer from the solution. This critical value of ΔU is inversely proportional to the degree of polymerization of the high polymer.

Chapter I. Introduction

§ 1. Developments of the Theory as to the Extension of High Polymer Molecules

The problem pertaining to the extension of high polymer molecules received its first theoretical treatment at the same time as the first success in theory of rubber elasticity was attained. Since both theories were based upon the same distribution function of the chain elements of high polymer, it was a natural consequence that they were developed keeping step with each other. In the following we shall briefly retrace the progress in the theory of extension of high polymer molecules.

I. Free Rotation, Arbitrary Bond Angle

In the theory of rubber elasticity one assumes as the simplest model of a rubber molecule a chain consisting of C-atoms, in which free rotation about C-C bond can take place and the angles between neighboring C-C bonds are arbitrarily distributed. It is further taken for granted that the chain elements constituting the high

polymer molecule have no volume and there exist neither inter- nor intramolecular interaction between them. As in this model no element other than those of rubber molecules are taken into account, the properties of the molecule deduced therefrom are nothing but those to be expected in vacuum. The initial theory as to the extension of high polymer molecules was founded likewise on this model, so that the results obtained must be considered to hold only in vacuum. (The model consisting of volumeless elements will be called in the following a mathematical model.)

For this model the mean square end-to-end distance of the chain is given by

$$\langle r^2 \rangle = b_0^2 N, \quad (1.1)$$

where b_0 is the bond length of chain elements and N the number of elements.

II. Free Rotation, Constant Bond Angle

If one assumes that while the rotation about C-C bonds is free, the angle between neighboring C-C bonds is not arbitrary but has a definite value which represents a tetrahedral angle θ , then after a simple calculation the mean square end-to-end distance of chains comes out to be

$$\langle r^2 \rangle = b_0^2 \frac{1 + \cos \theta}{1 - \cos \theta} N. \quad (1.2)$$

III. Hindered Rotation, Constant Bond Angle

Assume that the rotation about C-C bond is hindered and the angle between neighboring C-C bonds is a constant equal to θ . The theoretical formula for $\langle r^2 \rangle$ can then be written as

$$\langle r^2 \rangle = b_0^2 \frac{1 + \cos \theta}{1 - \cos \theta} \frac{1 - \langle \cos \phi \rangle}{1 + \langle \cos \phi \rangle} N, \quad (1.3)$$

where ϕ is the rotation angle about C-C bond.

It is to be noted that all the above formulas can be represented in the form

$$\langle r^2 \rangle \propto N. \quad (1.4)$$

IV. Consideration of Excluded Volume

Since the constituent elements of high polymer have their own volume and cannot be regarded as mathematical point, it was naturally required to introduce a correction ensuing from the volume-exclusion effect into the theory of extension. Later developments of the theory in which this effect was taken into account were achieved by a number of authors independently of the theory of rubber elasticity. The results, however, differ with the authors: Some authors gave for the mean square end-to-end distance of chains

$$\langle r^2 \rangle \propto N \quad (1.5)$$

which coincides with that for the mathematical model, as far as the proportionality is concerned; the others obtained the formulas having one or more additional terms, all of which reduce, within a narrow range of N , to

$$\langle r^2 \rangle \propto N^r \quad (r > 1). \quad (1.6)$$

It is therefore particularly interesting from the theoretical point of view to determine whether the formula for $\langle r^2 \rangle$ is actually given by (1.5) or by (1.6) and, in case (1.6) holds, to find out the value of r .

§2. Peculiarity of the Problem of Extension

If we wish to work out a physical solution for the problem of extension of high polymer, we are driven to have recourse to experiments. In view of the impossibility of vaporizing a high polymer without causing any decomposition of molecules, however, a state in which separate high polymer molecules exist in vacuum cannot be the object of experimental study. The feasible experiments are confined to systems consisting of high polymer in solid state or in solution, so that, in order to treat about high polymer molecules in separate state, which is of importance to theoretical treatment, the only measure to be taken is to experiment with a system of sufficiently dilute solution. In this lies the peculiarity of the problem of extension. Needless to say, it is necessary along with the experiment to establish a theory as to the extension of high polymer in dilute solution, which is to be compared with

experiment. (The various theories hitherto advanced concerning the extension of high polymers in vacuum possesses by themselves nothing beyond mathematical interest.) The investigation along this line has been performed by the present author as will be fully described in the following.

Chapter II. Determination of the Extension

§ 1. Consistent* Distribution of Chain Elements

For determining the extension of high polymer we have to assume, as a working basis, a function representing the distribution of chain elements which should naturally be compatible with experiment.

To begin with, let us examine whether or not the distribution function hitherto employed for obtaining the extension is consistent. It has usually been assumed that the distribution of chain elements is such that it gives the probability of finding the mean square end-to-end distance $\langle r^2 \rangle$ of a chain between r and $r+dr$ expressed by

$$W(r)dr = \left(\frac{3}{2\pi b^2 N}\right)^{\frac{3}{2}} \exp\left(-\frac{3r^2}{2b^2 N}\right) 4\pi r^2 dr,^{**} \quad (2.1)$$

by aid of which the extension is to be obtained from the measurement of intrinsic viscosity $[\eta]$ or angular intensity distribution of scattered light $I(\theta)$ of high polymer solution.¹⁾²⁾³⁾ In this expression b is the effective bond length given by

$$b^2 = b_0 \frac{1 + \cos \theta}{1 - \cos \theta} \frac{1 - \langle \cos \phi \rangle}{1 + \langle \cos \phi \rangle}, \quad (2.2)$$

θ being the bond angle and $\langle \cos \phi \rangle$ the mean cosine of the angle between two neighboring bond planes. For this distribution it holds that

$$\langle r^2 \rangle = \int_0^\infty r^2 W(r) dr = b^2 N, \quad (2.3)$$

* By "consistent" is meant here "in accord with the experimental result".

** It is to be noticed that here the effects of volume exclusion and of the existence of solvent molecules are disregarded.

or

$$\bar{r} = bN^{1/2}, \quad (2.4)$$

r being defined by

$$\bar{r} = (\langle r^2 \rangle)^{1/2}. \quad (2.5)$$

Taking logarithm of Eq. (2.4) and differentiating it with respect to temperature T , one get the thermal expansion coefficient of $\bar{r}$:

$$\frac{d}{dT} \log \bar{r} = \frac{d}{dT} \log b, \quad (2.6)$$

which is independent of N .

Thus, if $\langle r^2 \rangle$ be experimentally proved to be proportional to N and its expansion coefficient to be independent of N , the distribution function (2.1) is to be regarded as significant and consistent. In case, on the contrary, Eq. (2.6) proves to be invalid, we must conclude that the distribution function (2.1) is inconsistent and should be discarded. We carried out the investigation to see if the Eq. (2.6) holds for several solutions of high polymer, the procedure and the results of which will be discribed below.

§ 2. Decision as Regards the Consistency of a Distribution Function

As the criterion upon which to test the consistency of a distribution function of chain elements, it is convenient to examine the N -dependency of the thermal expansion coefficient β of $\bar{r}$, inasmuch as, as will be shown below, β can easily be derived from the measurement of intrinsic viscosity $[\eta]$, whilst the procedure of obtaining $\bar{r}$ from $[\eta]$ is somewhat too complicated. For the intrinsic viscosity we assume the formula given by DEBYE and BUECHE¹⁾:

$$[\eta] = \frac{4\pi R^3}{3M} \phi(\sigma), \quad (2.7)$$

where R is the radius of a sphere equivalent to the high polymer molecule, M is the molecular weight, and $\phi(\sigma)$ is a function of the shielding ratio σ :

$$\phi(\sigma) = \frac{5}{2} \frac{1 + 3/\sigma^2 - (3/\sigma) \coth \sigma}{1 + (10/\sigma^2) \{1 + 3/\sigma^2 - (3/\sigma) \coth \sigma\}} . \quad (2.8)$$

This formula was deduced by summing up the contributions from each chain element to viscosity with due consideration for the condition that when a high polymer molecule is put in a solvent having velocity gradient, the velocity of the solvent through the high polymer diminishes from surface toward inside of the high polymer.

It is true, the function $\phi(\sigma)$ must come out different according as different distribution of the chain elements is assumed. But, since the above formula is in accord with the experimental facts, we may use it, as an approximation, for any kind of distribution of elements.

Between σ and the shielding length L there holds the relation

$$\sigma = R/L , \quad (2.9)$$

with

$$1/L = \sqrt{\frac{\nu f}{\eta_0}} , \quad (2.10)$$

where f is the frictional constant of chain elements, η_0 the viscosity of the solvent, and ν the mean density of the chain element, i. e.

$$\nu = \frac{3N}{4\pi R^3} . \quad (2.11)$$

Substitution of Eqs. (2.10) and (2.11) in Eq. (2.9) yields

$$\sigma = \sqrt{\frac{3fN}{4\pi\eta_0 R}} . \quad (2.12)$$

For a narrow range of N where σ varies only insignificantly, $\phi(\sigma)$ which is otherwise a complicated function can be expressed in a simple form:

$$\phi(\sigma) = \phi_0 \sigma^x , \quad (2.13)$$

in which ϕ_0 is the proportionality constant.

Since, as can be inferred from Eqs. (2.9), (2.10) and (2.11), σ is

independent of temperature T , x is a constant likewise independent of T . Substituting Eqs. (2.12) and (2.13) in Eq. (2.7), there results

$$[\eta] = \frac{4\pi}{3M} \phi_0 \left(\frac{3fN}{4\pi\eta_0} \right)^{x/2} R^{3-x/2}, \quad (2.14)$$

and further by taking logarithm of Eq. (2.14) and differentiating it with respect to T , we obtain the equation for the thermal expansion coefficient of R :

$$\frac{1}{R} \frac{dR}{dT} = \frac{1}{3-x/2} \frac{d}{dT} \log [\eta]. \quad (2.15)$$

$\bar{r}$ is a function of R , a function which does not explicitly involve N , so that in order to examine whether $(d/dT) \log \bar{r}$ depends on N or not it is sufficient to inquire into the N -dependency of $(d/dT) \log R$, or of $(d/dT) \log [\eta]$ as can be seen from Eq. (2.15). Thus we have studied the N -dependency of $(d/dT) \log [\eta]$ experimentally for several solutions of high polymer.

§ 3. Experimental Results

The temperature dependency of intrinsic viscosity was measured for benzene- and toluene-solutions of fractionated polystyrenes (whose molecular weights were 930,000 for fraction I, 543,000 for fraction II and 342,000 for fraction III) by the use of a rotary type of viscometer kept in a thermostat. Each solution was subjected to heat treatment over six hours. Experimental values of intrinsic viscosity $[\eta]$ and calculated values of $(d/dT) \log [\eta]$ are given in Tables 1-3.

TABLE 1. Intrinsic Viscosity of Polystyrene-Benzene Solutions

M. W.	$[\eta] \text{ g}^{-1} \text{ cm}^3$			
	20°C	30°C	40°C	50°C
930,000	244.7	240.0	234.0	225.3
543,000	171.6	169.0	165.7	162.1
342,000	126.5	125.1	123.4	122.1

TABLE 2. Intrinsic Viscosity of Polystyrene-Toluene Solutions

M. W.	$[\eta] \text{ g}^{-1} \text{ cm}^3$			
	20°C	30°C	40°C	50°C
930,000	317.5	303.4	287.0	278.0
543,000	220.0	210.0	201.0	195.0
342,000	160.0	153.0	148.4	143.8

TABLE 3. Differential Coefficient of $\log [\eta]$ of Polystyrene Solutions

M. W.	$(d/dT) \log [\eta]$	
	Polystyrene-Benzene	Polystyrene-Toluene
930,000	- 0.0028	- 0.0044
543,000	- 0.0019	- 0.0040
342,000	- 0.0012	- 0.0038

From the experimental results described above it is evident that the values of $(d/dT) \log [\eta]$, which is proportional to the thermal expansion coefficient of high polymer in solution, do depend on the number of elements N . This means that Eq. (2.6) proves to be invalid, so that the hitherto used distribution function (2.1) of chain elements, which gives Eq. (2.3) as an expression for $\langle r^2 \rangle$, is inadequate for the purpose of obtaining the extension of high polymer.

Now the question arises what sort of distribution function is compatible with the experimental results. It is not easy to treat the problem in a general way, but now that, as we have seen, the N -dependency of $\langle r^2 \rangle$ serves as a criterion for the reliability of the function, we are now in a position to be able to set up a distribution function which conforms at least to the observational facts with respect to the N -dependency of $\langle r^2 \rangle$.

Assume that when we calculate $\langle r^2 \rangle$ theoretically we obtain an equation

$$\bar{r} = (\langle r^2 \rangle)^{1/2} = F(N). \quad (2.16)$$

For a narrow range of N this can be rewritten, with a proper choice of C and r , in the form

$$\bar{r} = (CN^r)^{1/2}, \quad (2.17)$$

where r is a function of T in general. We take logarithm of Eq. (2.17) and differentiate it with respect to T , obtaining

$$(d/dT) \log \bar{r} = \frac{1}{2} \left\{ (d/dT) \log C + \log N \cdot \frac{dr}{dT} \right\}. \quad (2.18)$$

Thus we arrive at a conclusion that $(d/dT) \log \bar{r}$, which represents the thermal expansion coefficient, depends on N , in so far as r is a function of T , or

$$\frac{dr}{dT} \neq 0. \quad (2.19)$$

In other words, if r in the formula for $\langle r^2 \rangle$ represented by Eq. (2.17) satisfies Eq. (2.19), the distribution function of chain elements from which the formula can be derived must be consistent one.

§ 4. Method of Determining the Extension of High Polymer Corresponding to the Consistent Distribution of Chain elements.

In the preceding section we have seen that the consistent distribution must be such that $\bar{r} = (\langle r^2 \rangle)^{1/2}$ calculated from this distribution is expressed, within a narrow range of N , by

$$\bar{r} = (CN^r)^{1/2} \quad (2.17)$$

with r that satisfies the relation

$$\frac{dr}{dT} \neq 0. \quad (2.19)$$

Now it is intended to consider a method of obtaining the extension of high polymer by making use of such a consistent distribution of elements.

Assumption: The consistent distribution is of Gaussian type such as to give $\langle r^2 \rangle$ that satisfies Eqs. (2.17) and (2.19).

As such a distribution function we may take the expression for the probability of finding the end-to-end distance between r and

$r+dr$ given by

$$W(r) dr = \left(\frac{3}{2\pi CN^r} \right)^{3/2} \exp\left(-\frac{3r^2}{2CN^r} \right) 4\pi r^2 dr. \quad (2.20)$$

By making use of this distribution function we are able to obtain the extension of high polymer from the measurement of intrinsic viscosity $[\eta]$ or of angular intensity distribution of scattered light $I(\theta)$.

The quantities C and r can be determined in the process of experimental determination of $\langle r^2 \rangle$; if the value of r , which can for the moment be either

$$r \geq 1 \quad \text{or} \quad r = 1, \quad (2.21)$$

comes out equal to unity, it will correspond to the mathematical model, which however has been rejected as was evidenced in §2 and §3.

§5. Method of Determining the Extension of High Polymer from $[\eta]$

The determination of the extension of high polymer from $[\eta]$ calls for a relation connecting the extension and $[\eta]$.

For this we use the relation given by DEBYE and BUECHE¹¹:

$$[\eta] = \frac{4\pi R^3}{3M} \phi(\sigma), \quad (2.7)$$

with

$$\phi(\sigma) = \frac{5}{2} \frac{1 + 3/\sigma^2 - (3/\sigma) \coth \sigma}{1 - (10/\sigma^2) \{1 + 3/\sigma^3 - (3/\sigma) \coth \sigma\}}. \quad (2.8)$$

Eq. (2.7) is based on the assumption that the high polymer molecule considered as a sphere has a uniform distribution of chain elements. To apply this equation to our case involves taking for granted that the relation (2.7) remains approximately valid for R and $\phi(\sigma)$ to be expected from the distribution (2.20), notwithstanding that these quantities ought to be different from those expected from uniform distribution of elements.

For the distribution function (2.20) R is related to r by

$$\langle R^2 \rangle = \frac{1}{6} \langle r^2 \rangle, \quad (2.22)$$

so that the value of R obtained from $[\eta]$ gives the required extension. The procedure of obtaining R from $[\eta]$ will be described in the next section.

(I) Determination of R from $[\eta]$:—

Eq. (2.17) can be rewritten as

$$\bar{r} = \alpha b N^{1/2}$$

where b is the effective bond length represented by the relation

$$b^2 = b_0^2 \frac{1 + \cos \theta}{1 - \cos \theta} \frac{1 - \langle \cos \phi \rangle}{1 + \langle \cos \phi \rangle} \quad (2.2)$$

and α is a function of N and T :

$$\alpha = \alpha(N, T) \quad (2.24)$$

meaning the ratio of the extension of a real high polymer molecule to that corresponding to an ideal distribution of mathematical elements having no volume. From Eqs. (2.7), (2.22) and (2.23) we have

$$[\eta] = K_0 \phi M^{1/2} \alpha^3 \quad (2.25)$$

with

$$K_0 = \frac{4\pi b^3}{3(6m)^{3/2}}, \quad (2.26)$$

where m is the mass of element. Provided the value of $K_0 \phi$ is known, α can be obtained by the help of Eq. (2.25). In order to obtain $K_0 \phi$, a relation⁽⁴⁾ which holds thermodynamically is used, namely,

$$\alpha^5 - \alpha^3 = C' (1 - \mu/T) M^{1/2}. \quad (2.27)$$

Here C' is the proportionality constant depending on the kind of solvent, and μ is a function of B , a measure of the interaction energy between a high polymer molecule and the solvent and v , the molar volume of solvent :

$$\mu = \frac{2Bv}{R}, \quad (2.28)$$

where R is the gas constant.

Thus we get, from Eqs. (2.25) and (2.27),

$$\frac{1}{(K_0\phi)^{5/3}} \frac{[\eta]^{5/3}}{M^{4/3}} - \frac{1}{K_0\phi} \frac{[\eta]}{M} = C'(1-\mu/T). \quad (2.29)$$

If $K_0\phi$ is not sharply dependent on M , remaining nearly constant within a narrow range of M , then we obtain

$$\frac{d}{d([\eta]/M)} \{[\eta]^{5/3}/M^{4/3}\} = (K_0\phi)^{2/3}, \quad (2.30)$$

whereby to determine $K_0\phi$. As will be seen later from the experimental results, $K_0\phi$ actually proves to be a constant independent of M , so that substitution of $K_0\phi$ thus determined in Eq. (2.25) yields significant value of α .

Within a narrow range of N , the N -dependency of α can be expressed in the form

$$\alpha = \alpha_0 N^a, \quad (2.31)$$

and accordingly r is given by

$$r/2 = 1/2 + a. \quad (2.32)$$

Since from Eqs. (2.17) and (2.22) R appearing in Eq. (2.7) can be written as

$$R = C'' N^{r/2}, \quad (2.33)$$

Eq. (2.7) turns out to be

$$[\eta] = C''' N^{3r/2-1} \phi(\sigma). \quad (2.34)$$

C'' and C''' are suitably selected proportionality constants, and σ is, according to Eqs. (2.12) and (2.33), given by

$$\sigma = \sqrt{\frac{3f}{4\pi\eta}} \frac{N^{1/2-r/4}}{\sqrt{C''}}. \quad (2.35)$$

An empirical formula for $[\eta]$ can be written in the form

$$[\eta] = AN^\epsilon, \quad (2.36)$$

so that, by aid of Eqs. (2.34) and (2.35), we obtain

$$\epsilon = \frac{d \log [\eta]}{d \log N} = \left(\frac{3r}{2} - 1\right) + \left(\frac{1}{2} - \frac{r}{4}\right) \frac{\sigma}{\phi} \frac{d\phi}{d\sigma}. \quad (2.37)$$

This equation enables one to determine the value of $(\sigma/\phi) \times (d\phi/d\sigma)$ for given values of ϵ and r , hence the corresponding value of ϕ

from Eq. (2.8), and finally the required extension R from Eq. (2.7).

(II) Determination of $\bar{r}$ from $[\eta]$:—

The values of $K_0\phi$ and ϕ determined by the method described above yield at once the value of K_0 ; we therefore get b by the use of Eq. (2.26):

$$b = \left(\frac{3}{4\pi}\right)^{1/3} K_0^{1/3} (6m)^{1/2}, \quad (2.38)$$

and consequently obtain $\bar{r}$ from Eq. (2.23).

§ 6. Method of Determining the Extension of High Polymers from $I(\theta)$

Recently DEBYE²⁹ showed that the extension of high polymer can be determined from the angular intensity distribution $I(\theta)$ of the scattered light from the high polymer solution irradiated with parallel beam of light. Following this, ZIMM³⁰ developed a more elaborate method to be applied to chain-like high polymers. But, his method has proved to be still unsatisfactory on account of the inconsistency of the underlying distribution function. We now succeeded in establishing a method involving a consistent distribution function.

The basic distribution function is

$$W(r) dr = \left(\frac{3}{2\pi CN^r}\right)^{3/2} \exp\left(-\frac{3r^2}{2CN^r}\right) 4\pi r^2 dr, \quad (2.20)$$

and the mean square end-to-end distance of the chains is given by

$$\langle r^2 \rangle = CN^r, \quad (2.17)$$

so that, in order to determine the extension, it is sufficient to obtain the values of r and C .

We apply the same procedure as adopted by ZIMM³⁰ to our case of consistent distribution:

Consider that a parallel beam of light be incident upon a dilute solution of high polymer, where ν molecules each consisting of N elements are contained in volume V of the solution. We define a distribution function $\rho(r)$ such that for a pair of arbitrarily chosen elements the probability of finding the center of one element

within the volume element $d\tau$ at a distance r from the other is $\rho(r)d\tau$. Further, let the wave-length of light be λ , the unit vector in the directions of incident and scattered light be s_1 , and s_2 respectively, and their difference be $s = s_1 - s_2$, then we have for the intensity of the scattered light

$$I(\theta) = \frac{KN^2\nu}{V^2} \int \rho(r) \exp\left(\frac{2\pi i s \cdot r}{\lambda}\right) d\tau, \quad (2.39)$$

where K is a constant factor. According to ZIMM, this equation can be transformed into

$$I(\theta) = K \{MP(\theta)c - 2A_2M^2P^2(\theta)c^2\}, \quad (2.40)$$

with

$$\left. \begin{aligned} c &= \nu M/V, \\ K &= kN^2/M^2, \\ A_2 &= -N_0N^2X/2M^2, \\ X &= \int \chi(r_{\kappa\lambda}) d\tau. \end{aligned} \right\} \quad (2.41)$$

Here k is Boltzmann's constant, N_0 Avogadro's number, $\chi(r_{\kappa\lambda})$ the function of the potential energy between the κ th and the λ th element and

$$P(\theta) = \frac{1}{N^2} \sum_i \sum_j \int W_{ij}(r) \exp\left(\frac{2\pi i s \cdot r}{\lambda}\right) d\tau, \quad (2.42)$$

where $W_{ij}(r)$ is a function such that $W_{ij}(r)d\tau$ gives the probability of finding j th element within the volume element $d\tau$ at a distance r from i th element.

The function $W_{ij}(r)$ must take a form different from that given by ZIMM, inasmuch as it is to be based upon the consistent distribution of elements. Let the i th and j th elements be taken for the end elements, then $W_{ij}(r)$ which in this case reduces to $W(r)$ comes out, according to Eq. (2.20), to be

$$W_{ij}(r) d\tau = \left\{ \frac{3}{2\pi C|i-j|^r} \right\}^{3/2} \exp\left\{ -\frac{3r^2}{2C|i-j|^r} \right\} d\tau. \quad (2.43)$$

Through substitution in Eq. (2.42), this leads to

$$P(\theta) = \frac{1}{N^2} \sum_i \sum_j \int \left\{ \frac{3}{2\pi C|i-j|^r} \right\}^{3/2} \exp\left\{ -\frac{3r^2}{2C|i-j|^r} \right\} \exp\left(\frac{2\pi i s \cdot r}{\lambda}\right) d\tau. \quad (2.44)$$

We replace the summation by integration and put $Z=i-j$, obtaining

$$P(\theta) = \frac{2}{N^2} \int_0^N (N-Z) \left(\frac{3}{2\pi CZ^r} \right)^{3/2} \exp\left(-\frac{3r^2}{2CZ^r}\right) \exp\left(\frac{2\pi i \mathbf{s} \cdot \mathbf{r}}{\lambda}\right) \times \\ \times dZ r^2 dr d\beta d(\cos \varphi), \quad (2.45)$$

where r, β and φ are polar coordinates and $d\tau = r^2 dr d\beta d(\cos \varphi)$, which after integration with respect to spatial coordinates, yields

$$P(\theta) = \frac{2}{N^2} \int_0^N (N-Z) e^{-u CZ^r} dZ, \quad (2.46)$$

with

$$u = \frac{2\pi^2 |\mathbf{s}|^2}{3\lambda^2} = \frac{8\pi^2}{3\lambda^2} \sin^2 \frac{\theta}{2}, \quad (2.47)$$

where θ is the angle between incident and scattered directions. Substitute this in Eq. (2.40) and take the limit for infinite dilution, then there results

$$\lim_{C \rightarrow 0} \frac{I(\theta)}{c} = \frac{2KM}{N^2} \int_0^N (N-Z) e^{-u CZ^r} dZ, \quad (2.48)$$

which is the equation to be used for obtaining the parameters r and C from the measurement of $I(\theta)$, and hence the extension of the chain by aid of Eq. (2.17).

In practice r and C are determined according to the following procedure. Expanding $\exp(-u CZ^r)$ in power series:

$$\exp(-u CZ^r) = 1 - u CZ^r + \frac{u^2 C^2 Z^{2r}}{2!} - \frac{u^3 C^3 Z^{3r}}{3!} + \dots, \quad (2.49)$$

we rewrite Eq. (2.46) as

$$P(\theta) = \frac{2}{N^2} \int (N-Z) \left\{ 1 - u CZ^r + \frac{u^2 C^2 Z^{2r}}{2!} - \frac{u^3 C^3 Z^{3r}}{3!} + \dots \right\} dZ \\ = 1 - \frac{2u CN^r}{1!(r+1)(r+2)} + \frac{2u^2 C^2 N^{2r}}{2!(2r+1)(2r+2)} \\ - \frac{2u^3 C^3 N^{3r}}{3!(3r+1)(3r+2)} + \dots \quad (2.49)$$

Thus, in limiting case $u \rightarrow 0$, we have

$$\lim_{u \rightarrow 0} \frac{dP(\theta)}{du} = - \frac{2CN^r}{(r+1)(r+2)} \equiv -G, \quad (2.50)$$

which expresses the gradient of the initial slope of the curve representing $P(\theta)$ as a function of u .

So long as u , and consequently θ , remains small, $P(\theta)$ can be represented with sufficient accuracy by the first three terms of Eq. (2.49), so that, if the ratio of the two values of $1-P(\theta)$ corresponding to θ_1 and θ_2 be denoted by D , it follows

$$\begin{aligned} D = \frac{1-P(\theta_1)}{1-P(\theta_2)} &= \frac{\frac{2u_1CN^r}{(\gamma+1)(\gamma+2)} - \frac{2u_1^2C^2N^{2r}}{2!(2\gamma+1)(2\gamma+2)}}{\frac{2u_2CN^r}{(\gamma+1)(\gamma+2)} - \frac{2u_2^2C^2N^{2r}}{2!(2\gamma+1)(2\gamma+2)}} \\ &= \frac{8(2\gamma+1)u_1 - (\gamma+1)(\gamma+2)^2u_1^2G}{8(2\gamma+1)u_2 - (\gamma+1)(\gamma+2)^2u_2^2G} \end{aligned} \quad (2.51)$$

This reduces to

$$fr^3 + 5fr^2 + (8f - 2g)r + 4f - g = 0, \quad (2.52)$$

where f and g represent, as functions of u ,

$$\left. \begin{aligned} f &= DGu_2^2 - Gu_1^2 \\ g &= 8Du_2 - 8u_1 \end{aligned} \right\} \quad (2.53)$$

Thus, in virtue of Eqs. (2.50) and (2.51) we can determine G and D by making use of $P(\theta)$ to be obtained from the measurement of $I(\theta)$, and consequently r from Eqs. (2.52) and (2.53) and C as well as the extension of high polymers from Eq. (2.50).

§ 7. Remarks

We have described two methods of determining the extension, one from the measurement of $[\eta]$ and the other from the measurement of $I(\theta)$. In the former case it was necessary to assume DEBYE-BUECHE's formula as the relation connecting $[\eta]$ with the extension and furthermore to attribute a special property to ϕ and α , namely that α satisfies Eq. (2.27) and $K_0\phi$ is a slowly varying function of M . In the latter case, on the other hand, only very few such arbitrary assumptions were involved, which means that from a purely theoretical standpoint the latter method is more preferable to the former.

In both of these methods we took Gaussian type distribution of chain elements for the basis of our argument. Originally, it is

true, this was derived for mathematical elements in vacuum, but not for the elements having volume in solution. But inasmuch as the experimental evidence has shown that the distribution of real chain elements is nearly Gaussian i.e. γ is not far different from unity, it is not unreasonable to promise a distribution function represented by Eq. (2.20).

§ 8. Experimental Results

1. Determination of Extension from $[\eta]$

We prepared benzene solutions of fractionated polystyrenes with six different molecular weights, the concentration of each polystyrene being varied as 0.1%, 0.2%, 0.3% and 0.4%. These solutions were subjected to heat-treatment at 65°C for about fifty hours. We measured their viscosities at various temperatures 20°, 30°, 40° and 50°C by the use of a capillary viscometer kept in a thermostat, of which the capillary had a length of 17 cm and inside diameter of 0.02 cm. Through extrapolation of the values of viscosities thus obtained to zero concentration, we obtained $[\eta]$. The molecular weights of fractionated polystyrenes were determined by making use of PEPPER's formula⁵⁾:

$$[\eta] = 2.7 \times 10^{-2} M^{0.66}, \quad (2.54)$$

in which the unit of $[\eta]$ is $g^{-1}cm^3$. The results are given in Table 4.

TABLE 4. Intrinsic Viscosity of Polystyrene-Benzene Solutions

M. W.	$[\eta] \text{ g}^{-1} \text{ cm}^3$			
	20°C	30°C	40°C	50°C
742,000	202.0	181.0	159.0	137.0
668,000	189.0	169.5	150.5	131.5
560,000	168.0	151.5	135.5	119.0
327,000	118.0	108.5	99.0	89.0
208,000	87.5	80.5	73.5	66.5
50,600	37.0	36.5	36.0	35.0

In Fig. 1 are illustrated the curves of $[\eta]^{3/5}/M^{4/5}$ versus $[\eta]/M$.

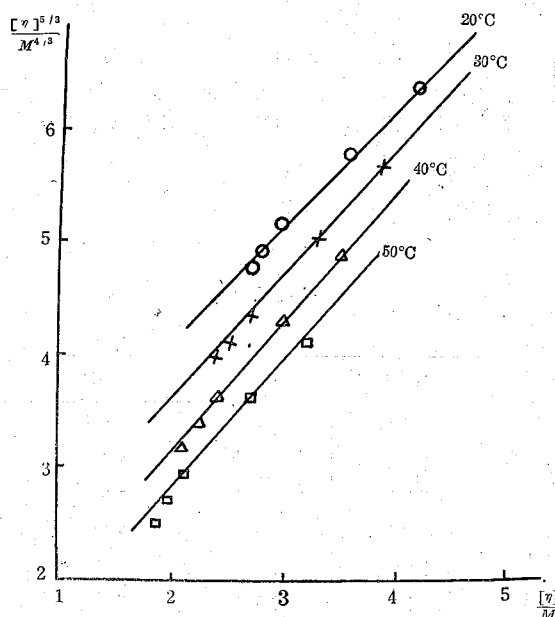


Fig. 1. Relation between $[\eta]^{5/3}/M^{4/3}$ and $[\eta]/M$.

As can be seen from this figure, there holds nearly perfect linearity between these quantities, which fact shows that $K_0\phi$ is independent of M and that the gradient of the lines directly gives $K_0\phi$.

Thus, if $K_0\phi$ is assumed to be independent of M , the calculation of a in Eq. (2.31) becomes very simple; namely we get, from Eqs. (2.25) and (2.31)

$$a = \frac{d \log \alpha}{d \log N} = \frac{1}{3} \frac{d \log [\eta]}{d \log N} - \frac{1}{6}. \quad (2.55)$$

r is then given by

$$r/2 = 1/2 + a, \quad (2.37)$$

and by aid of this value of r and Eqs. (2.37), (2.36), (2.8) and (2.37) ϕ can be calculated. Values of $K_0\phi$, r , ϕ and a at various temperatures are given in Tables 5 and 6.

TABLE 5.

Temp.	20°C	30°C	40°C	50°C
$K_0\phi$	1.472×10^9	1.146×10^9	1.225×10^9	1.196×10^9
$r/2$	0.548	0.541	0.527	0.518
ϕ	2.31	2.32	2.35	2.34

TABLE 6.

M. W.	α			
	20°C	30°C	40°C	50°C
742,000	1.298	1.216	1.138	1.074
668,000	1.290	1.210	1.138	1.078
560,000	1.278	1.175	1.135	1.072
327,000	1.242	1.175	1.115	1.067
208,000	1.212	1.145	1.088	1.048
50,600	1.152	1.116	1.086	1.067

Table 6 indicates that the values of α are greater than unity and moreover depend on temperature, so that r 's are likewise dependent on temperature in conformity with Eq. (2.19). The radii R of polystyrene molecules, as calculated from Eq. (2.7), come out as given in Table 7.

TABLE 7. Radius of Polystyrene Molecules in Solution

M. W.	R (Å)			
	20°C	30°C	40°C	50°C
742,000	296	286	272	259
668,000	280	270	258	247
560,000	254	245	235	225
327,000	188	183	177	171
208,000	147	143	138	133
50,600	68.7	68.4	67.6	67.1

In order to determine the end-to-end distance $\bar{r} = \alpha b N^{1/2}$, we have further to compute the values of K_0 from Table 5, and the values

of b by the help of Eq. (2.38). The obtained values of k_0 , b and $\bar{r}$ at various temperatures are presented in Table 8 and 9.

TABLE 8.

Temp.	20°C	30°C	40°C	50°C
K_0	0.638×10^{11}	0.493×10^{11}	0.521×10^{11}	0.511×10^{11}
b	7.98×10^8	7.34×10^8	7.48×10^8	7.43×10^8

TABLE 9. End-to-End Distance of Polystyrene Molecules in Solution

M. W.	$\bar{r} = abN^{1/2}$ (Å)			
	20°C	30°C	40°C	50°C
742,000	873	753	720	673
668,000	826	706	683	641
560,000	746	645	623	585
327,000	552	478	465	446
208,000	426	376	367	348
50,600	204	181	177	172

§ 9. As to the Extension in Vacuum

As described above, it has been proved experimentally that $r/2 > 1/2$. Being based upon this fact we can obtain a knowledge on the distribution of chain elements in vacuum as follow: From Eq. (2.17) the volume V of a high polymer becomes

$$V \propto (\bar{r})^3 = C^{3/2} N^{3r/2}, \quad (2.56)$$

whence

$$v = \frac{V}{N} \propto C^{3/2} N^{3r/2-1}, \quad (2.57)$$

which gives the volume per element. From the relation

$$r/2 > 1/2, \quad (2.58)$$

therefore, it follows that the value of v becomes the larger, the larger the value of N ; in other words, the distribution of chain

elements becomes sparser as N increase, that is, the elements are more thinly distributed at the boundary than at the center.

Now conceive that a chain molecule, whose elements are non-uniformly distributed in vacuum, be put in a solvent, then solvent molecules will penetrate into the free space within the chain molecule causing a swelling or spreading of elements to take place. This spreading will be the more remarkable, the larger the density of elements, so that the distribution will exhibit a tendency to become uniform; that is to say, the distribution will become more uniform in solution than in vacuum. Now that this tendency corresponds to the decrease of r , the fact that there exists the relation $r/2 > 1/2$ for a chain in solution leads to a logical conclusion that the relation $r/2 > 1/2$ must be still more valid for a chain in vacuum.

It is of great importance that we could get a deeper insight into the characteristics of high polymer in vacuum from the measurement performed for its solution. It has been confirmed that among a number of theoretical treatments of the extension of chain molecule those which do not give $r > 1$ in the equation $\langle r^2 \rangle = CN^r$ is to be rejected because of their contradiction to experiment.

Chapter III. Theoretical Treatment of Extension of High Polymer Molecules in Solution

§ 1. Introduction

With a view to investigate the relations between the extension of high polymer molecules in solution and the properties of solvents, we first develop a theory of high polymer solution based on the lattice model.

Consider the extreme case of an infinite dilution, where there is no interaction between solute molecules so that their behavior can be regarded as independent of one another. It may then be sufficient for the investigation of their behavior to consider a system of solution which contains only one high polymer molecule.

In order to take into consideration the temperature dependency of mutual interaction between the chain elements of the high polymer molecule and the solvent molecules, it is convenient to

assume that the solvent contains holes besides the solvent molecules, that is, to regard the solution as consisting of chain elements, solvent molecules and holes.

Take a system of solution with volume V containing a single high polymer molecule, of which the entropy, the internal energy, and hence the Gibbs free energy are to be calculated. We assume a lattice model for the solution, and denote the volume of high polymer molecule by V_r , the number of lattice points in unit volume by ν , the number of chain elements (p) which constitute a high polymer molecule by N , the total number of solvent molecules (s) by N_s , the numbers of s within and outside the volume V_r by N_s^i and N_s^o respectively, the total number of holes (h) by N_h , and the numbers of h within and outside the volume V_r by N_h^i and N_h^o respectively.

If the number of pairs of constituent elements, their energies, and the number of their possible configurations be determined, we can obtain the total energy, the entropy and hence the Gibbs free energy G of the system. In terms of G thus obtained, the value of mean square end-to-end distance $\langle r^2 \rangle$ of a chain comes out to be

$$\langle r^2 \rangle = \int r^2 e^{-G/kT} dr / \int e^{-G/kT} dr. \quad (3.1)$$

The reason that the Gibbs free energy has been used instead of Helmholtz free energy is based on the fact that N_h and hence V is the function of end-to-end distance r and temperature T . N_h must generally be selected so as to make G minimum. If, however, we assume that the holes outside the volume V_r interact only with solvent molecules, the value of N_h can be determined from the equilibrium condition of the system consisting of solvent molecules and holes. When, for the sake of simplicity, we further assume that the temperature dependency of the volume of solvent is determined by the change in number of the holes, N_h^o can be

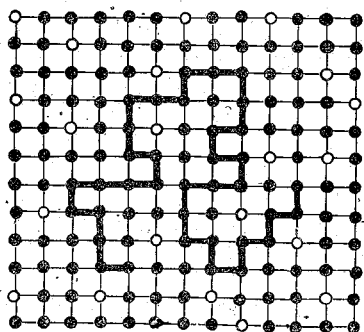


Fig. 2.

Lattice model for polymer solution.

- : chain element,
- : solvent molecule
- : hole

represented by N_s^0 , T and expansion coefficient β . We have then only to determine N_h^i so that it may make a minimum of G of the whole system.

§ 2. Gibbs Free Energy G

Internal energy E , entropy S , volume V and pressure P of the system are related to the Gibbs free energy by

$$G = E - TS + PV, \quad (3.2)$$

so that, in order to obtain the expression for G and hence the mean square end-to-end distance $\langle r^2 \rangle$ by Eq. (3.1), it is necessary to express E , S , and V as functions of r . This can be performed as follows.

1. Entropy S .

The entropy S of a system composed of the elements p , s and h can be obtained by using a lattice model and calculating the configurational number ω of these elements, in terms of which S is given by

$$S(r) = k \log \omega(r). \quad (3.3)$$

We first calculate the coordination number D_p of chain elements, the end-to-end distance of the chain being kept constant. Next we seek for the coordination number D_{sh} of solvent molecules and holes at the lattice points which are not occupied by the chain elements. Since this number is independent of the arrangement of chain elements, the product $D_p \cdot D_{sh}$ is equal to the coordination number ω of the whole system consisting of chain elements, solvent molecules and holes.

Evidently we have, for N_s^i and N_s^0 , the relations

$$N_s^i = \nu V_r - N - N_h^i \quad (3.4)$$

and

$$N_s^0 = N_s - N_s^i = N_s - \nu V_r + N + N_h^i. \quad (3.5)$$

As for N_h^0 , we assume that the change in number of the holes is responsible for the temperature variation of the volume of the liquid outside V_r , N_h^0 can thus be expressed by

$$N_h^0 = \beta N_s^0 = \beta (N_s - \nu V_r + N + N_h^i), \quad (3.6)$$

β being the expansion coefficient, whence we obtain

$$N_h = N_h^i + N_h^0 = \beta N_s + N_h^i - \beta (\nu V_r - N - N_h^i). \quad (3.7)$$

Let the probability that the end-to-end distance of a high polymer molecule takes a value between r and $r+dr$ be written as

$$W_N(r) dr = \left(\frac{3}{2\pi CN^r} \right)^{3/2} \exp\left(-\frac{3r^2}{2CN^r}\right) 4\pi r^2 dr, \quad (3.8)$$

where C and r are the appropriate parameters such that the mean square end-to-end distance of a high polymer molecule in vacuum can be represented by CN^r . Since the coordination number of each chain element can be put nearly equal to νV and, moreover, the coordination number of the chain whose end-to-end distance is r is proportional to $W_N(r)$, the coordination number of the chain elements for a given end-to-end distance r becomes

$$D_p = K(\nu V)^N W_N(r) = K(\nu V)^N \left(\frac{3}{2\pi CN^r} \right)^{3/2} \exp\left(-\frac{3r^2}{2CN^r}\right) 4\pi r^2, \quad (3.9)$$

K being a proportionality constant.

For the simplicity's sake, we take it for granted that the probability of finding an element (chain element, solvent molecule or hole) at any lattice point is independent of what kind of element occupies its immediate neighborhood, so that the coordination number of solvent molecules and holes at the lattice points not occupied by the chain elements may be given, in virtue of Eq. (3.7), by

$$D_{sh} = \frac{(N_s + N_h)!}{N_s! N_h!} = \frac{\{(1+\beta)N_s + N_h^i - \beta(\nu V_r - N - N_h^i)\}!}{N_s! \{\beta N_s + N_h^i - \beta(\nu V_r - N - N_h^i)\}!}. \quad (3.10)$$

Thus the coordination number of the whole system, inclusive of chain elements, solvent molecules, and holes, will be, for a given V_r ,

$$\begin{aligned} \omega = D_p \cdot D_{sh} &= K(\nu V)^N \left(\frac{3}{2\pi CN^r} \right)^{3/2} \exp\left(-\frac{3r^2}{2CN^r}\right) 4\pi r^2 \\ &\times \frac{\{(1+\beta)N_s + (1+\beta)N_h^i - \beta(\nu V_r - N)\}!}{N_s! \{\beta N_s + (1+\beta)N_h^i - \beta(\nu V_r - N)\}!}. \end{aligned} \quad (3.11)$$

Hence, the entropy of the system comes out to be

$$\begin{aligned}
S &= k \log \omega \\
&= k \left[\log K \nu^N \left(\frac{3}{2\pi C N^r} \right)^{3/2} + N \log V - \frac{3r^2}{2C N^r} + \log 4\pi r^2 \right. \\
&\quad + \log \left\{ (1+\beta)N_s + N_h^i - \beta(\nu V_r - N - N_h^i) \right\} ! \\
&\quad \left. - \log N_s! - \log \left\{ \beta N_s + N_h^i - \beta(\nu V_r - N - N_h^i) \right\} ! \right]. \quad (3.12)
\end{aligned}$$

Since the volume occupied by one lattice point is $1/\nu$, total volume V is given by

$$V = \frac{1}{\nu} (N + N_s + N_h) = \frac{1}{\nu} \left\{ (1+\beta)N_s + N + N_h^i - \beta(\nu V_r - N - N_h^i) \right\}. \quad (3.13)$$

Using Eq. (3.13) and STIRLING's formula

$$\log z = z \log z - z, \quad (3.14)$$

we rewrite Eq. (3.12) as

$$\begin{aligned}
S &= k \left[\log K \nu^N \left(\frac{3}{2\pi C N^r} \right)^{3/2} + N \log \frac{1}{\nu} \left\{ (1+\beta)N_s + N + N_h^i \right. \right. \\
&\quad \left. \left. - \beta(\nu V_r - N - N_h^i) \right\} - \frac{3r^2}{2C N^r} + \log 4\pi r^2 \right. \\
&\quad + (1+\beta)N_s + N_h^i - \beta(\nu V_r - N - N_h^i) \\
&\quad \times \log \left\{ (1+\beta)N_s + N_h^i - \beta(\nu V_r - N - N_h^i) \right\} - N_s \log N_s \\
&\quad \left. - \left\{ \beta N_s + N_h^i - \beta(\nu V_r - N - N_h^i) \right\} \log \left\{ \beta N_s + N_h^i - \beta(\nu V_r - N - N_h^i) \right\} \right]. \quad (3.15)
\end{aligned}$$

If, furthermore, we take account of the approximate relation

$$N_h^i - \beta(\nu V_r - N - N_h^i) \simeq N_h^i - \beta N_s^i \simeq 0 \quad (3.16)$$

and the well-known expansion formula,

$$\log(1+z) = z - \frac{z^2}{2} + \frac{z^3}{3} - \dots, \quad (3.17)$$

we obtain

$$\begin{aligned}
\log \frac{1}{\nu} \left\{ (1+\beta)N_s + N + N_h^i - \beta(\nu V_r - N - N_h^i) \right\} &\simeq \log \frac{1}{\nu} \left\{ (1+\beta)N_s + N \right\} \\
&+ \frac{N_h^i - \beta(\nu V_r - N - N_h^i)}{(1+\beta)N_s + N}, \quad (3.18)
\end{aligned}$$

$$\log \{(1+\beta)N_s + N_h^i - \beta(\nu V_r - N - N_h^i)\} \simeq \log(1+\beta)N_s + \frac{N_h^i - \beta(\nu V_r - N - N_h^i)}{(1+\beta)N_s} \quad (3.19)$$

and

$$\log \{\beta N_s + N_h^i - \beta(\nu V_r - N - N_h^i)\} \simeq \log \beta N_s + \frac{N_h^i - \beta(\nu V_r - N - N_h^i)}{\beta N_s} \quad (3.20)$$

Substitution of Eqs. (3.18), (3.19) and (3.20) in (3.15) yields

$$\begin{aligned} S = & k \left[\log K \nu^N \left(\frac{3}{2\pi C N r^3} \right)^{3/2} + N \log \frac{1}{\nu} \{(1+\beta)N_s + N\} \right. \\ & + \frac{N \{N_h^i - \beta(\nu V_r - N - N_h^i)\}}{(1+\beta)N_s + N} - \frac{3r^2}{2CNr^3} + \log 4\pi r^2 \\ & + \{\beta N_s + N_h^i - \beta(\nu V_r - N - N_h^i)\} \log \frac{1+\beta}{\beta} \\ & \left. + N_s \log(1+\beta) - \frac{\{N_h^i - \beta(\nu V_r - N - N_h^i)\}^2}{\beta(1+\beta)N_s} \right] \quad (3.21) \end{aligned}$$

This equation holds good whatever values N_s and N_h^i may take.

2. Energy E

On the assumption that the interactions come into play between p and p , and p and s as well as s and s only when they are the immediate neighbors, we calculate the numbers of such pairs for obtaining the energy E of the whole system.

Since each chain element is connected with its neighboring chain element by a bond, the chain can occupy only a limited range of volume. Within this volume, however, the configuration of p as well as of s may well be considered to be rather arbitrary, inasmuch as any two chain elements can behave independently of each other, only if they are separated from each other by a few intervening elements. Thus the number of pairs, p - p , p - s , and s - s , may approximately be computed, all the elements within V_r being regarded as independent of one another.

Neglecting the interaction of s lying outside V_r with p , we first calculate the numbers of p - p and p - s pairs. Denote the number of the nearest neighbors around a lattice point by σ . Since

the probability of finding an element p at a lattice point in V_r is given by $N/\nu V_r$ and similarly for an element s by $(\nu V_r - N - N_h^i)/\nu V_r$, the numbers of p and s out of σ around one p are

$$\left. \begin{aligned} \sigma_{pp} &= \sigma \frac{N}{\nu V_r} \\ \text{and} \\ \sigma_{ps}^i &= \sigma \frac{\nu V_r - N - N_h^i}{\nu V_r} \end{aligned} \right\} \quad (3.22)$$

respectively. Accordingly the number of p - p pairs, N_{pp} , and that of p - s pairs, N_{ps} , are given by

$$N_{pp} = \frac{\sigma N^2}{2\nu V_r} \quad (3.23)$$

and

$$N_{ps} = \frac{\sigma N (\nu V_r - N - N_h^i)}{\nu V_r}. \quad (3.24)$$

Next we consider the number of s - s pairs, which exist both within and outside the volume V_r . Considering that the average number of s in the nearest neighborhood of an element s inside the volume V_r is

$$\sigma_{ss}^i = \frac{\sigma (\nu V_r - N - N_h^i)}{\nu V_r}, \quad (3.25)$$

and that the average number of s among the nearest neighbors of an element s outside V_r is

$$\sigma_{ss}^0 = \frac{\sigma (N_s - \nu V_r + N + N_h^i)}{\nu (V - V_r)}, \quad (3.26)$$

we get for the number N_{ss} of s - s pairs in the whole system :

$$\begin{aligned} N_{ss} &= N_{ss}^i + N_{ss}^0 \\ &= \frac{\sigma (\nu V_r - N - N_h^i)^2}{2\nu V_r} + \frac{\sigma (N_s - \nu V_r + N + N_h^i)^2}{2\nu (V - V_r)}. \end{aligned} \quad (3.27)$$

If we assume that

$$N_h^i \ll N_s \quad (3.28)$$

we have the relations

$$\nu(V - V_r) = (1 + \beta) N_s \left(1 - \frac{\nu V_r - N - N_h^i}{N_s} \right) \quad (3.29)$$

and

$$(N_s - \nu V_r + N + N_h^i)^2 = N_s^2 \left(1 - 2 \frac{\nu V_r - N - N_h^i}{N_s} \right). \quad (3.30)$$

Thus substitution of Eqs. (3.29) and (3.30) in (3.27) gives

$$N_{ss} = \frac{\sigma(\nu V_r - N - N_h^i)^2}{2\nu V_r} + \frac{\sigma N_s}{2(1 + \beta)} \left(1 - \frac{\nu V_r - N - N_h^i}{N_s} \right). \quad (3.31)$$

Let the intermolecular potential energy for the pairs $p-p$, $p-s$ and $s-s$ be $-U_{pp}$, $-U_{ps}$, and $-U_{ss}$, respectively. Then the potential energy of the whole system comes out, by the use of Eqs. (3.23), (3.24) and (3.31), to be

$$E = -N_{pp}U_{pp} - N_{ps}U_{ps} - N_{ss}U_{ss} = -\frac{\sigma N^2}{2\nu V_r}U_{pp} - \frac{\sigma N(\nu V_r - N - N_h^i)}{\nu V_r}U_{ps} \\ - \frac{\sigma(\nu V_r - N - N_h^i)^2}{2\nu V_r}U_{ss} - \frac{\sigma N_s}{2(1 + \beta)} \left(1 - \frac{\nu V_r - N - N_h^i}{N_s} \right) U_{ss}. \quad (3.32)$$

Using Eqs. (3.2), (3.13), (3.21) and (3.32), we obtain the expression for the Gibbs free energy of the whole system as a function of the volume V_r of the high polymer molecule:

$$G = -\frac{\sigma N^2}{2\nu V_r}U_{pp} - \frac{\sigma N(\nu V_r - N - N_h^i)}{\nu V_r}U_{ps} - \frac{\sigma(\nu V_r - N - N_h^i)^2}{2\nu V_r}U_{ss} \\ - \frac{\sigma N_s}{2(1 + \beta)} \left(1 - \frac{\nu V_r - N - N_h^i}{N_s} \right) U_{ss} - kT \left[\log K \nu^N \left(\frac{3}{2\pi C N^r} \right)^{3/2} \right. \\ + N \log \frac{1}{\nu} \{ (1 + \beta) N_s + N \} + \frac{N \{ N_h^i - \beta(\nu V_r - N - N_h^i) \}}{(1 + \beta) N_s + N} - \frac{3r^2}{2C N^r} \\ + \log 4\pi r^2 + \{ \beta N_s + N_h^i - \beta(\nu V_r - N - N_h^i) \} \log \frac{1 + \beta}{\beta} \\ + N_s \log (1 + \beta) - \left. \frac{\{ N_h^i - \beta(\nu V_r - N - N_h^i) \}^2}{\beta(1 + \beta) N_s} \right] \\ + \frac{P}{\nu} \{ (1 + \beta) N_s + N + N_h^i - \beta(\nu V_r - N - N_h^i) \}. \quad (3.33)$$

It is obvious from the nature of holes that the number of holes must have a particular value for which the Gibbs free energy

G becomes minimum. Since we assumed that N_h^0 is given by Eq. (3.6), N_h^0 has a definite value independent of G , so that only N_h^i is determined from the condition that makes G minimum. Namely, the equation for determining N_h^i is

$$\frac{\partial G}{\partial N_h^i} = 0. \quad (3.34)$$

Thus from Eqs. (3.33) and (3.34),

$$N_h^i = \frac{\left(-\frac{\sigma N}{\nu V_r} U_{ps} - \frac{\sigma(\nu V_r - N)}{\nu V_r} U_{ss} + \frac{\sigma U_{ss}}{2(1+\beta)} + \frac{kTN(1+\beta)}{(1+\beta)N_s + N} \right.}{\frac{2kT(1+\beta)}{\beta} + kT(1+\beta) \log \frac{1+\beta}{\beta} + \frac{2kT(\nu V_r - N)}{N_s} - P \frac{1+\beta}{\nu}} \cdot \frac{\frac{2kT(1+\beta)}{\beta N_s} - \frac{\sigma U_{ss}}{\nu V_r}}{.} \quad (3.35)$$

In order to simplify Eq. (3.35), we estimate the order of magnitude of each term appearing in this equation for 0.1% solution of polystyrene whose molecular weight is 200,000. According to the theory of DEBYE and BUECHE¹⁾, the mean value of V_r of polystyrene molecule in a benzene solution is 4.17×10^{-17} cc, so that $\nu = 1.62 \times 10^{21}$ and $N_s = 5.36 \times 10^5$. We get, therefore, since $\beta \simeq 10^{-3}$ and $\sigma \simeq 6$

$$2/\beta N_s \gg \sigma/\nu V_r. \quad (3.36)$$

Moreover, if we assume that the interaction energies U_{pp} and U_{ps} as well as U_{ss} are of the same order of magnitude as kT , Eq. (3.35) may be rewritten as

$$N_h^i = a_0 \{1 + a + b\nu V_r + c(\nu V_r)^{-1}\}, \quad (3.37)$$

$$f = kT(1+\beta) \log \frac{1+\beta}{\beta} - \frac{P(1+\beta)}{\nu} - \frac{1+2\beta}{2(1+\beta)} \sigma U_{ss}, \quad (3.38)$$

with

$$\left. \begin{aligned} a_0 &= \frac{f\beta N_s}{2kT(1+\beta)}, & a &= -\frac{kTN}{fN_s} \frac{(1+\beta)N_s + 2N}{(1+\beta)N_s + N}, \\ b &= \frac{2kT}{fN_s}, & c &= \frac{\sigma\beta N_s U_{ss}}{2(1+\beta)kT} - \frac{\sigma N(U_{ps} - U_{ss})}{f}. \end{aligned} \right\} \quad (3.39)$$

For the above-mentioned solution

$$|a| \leq 1, \quad (3.40)$$

and, if V_r means the mean value of the volume of high polymer molecule, we have

$$b\nu V_r \leq 1 \quad (3.41)$$

and

$$c(\nu V_r)^{-1} \leq 1. \quad (3.42)$$

Hence we get

$$(N_h^*)^2 = a^2 \{1 + 2a + 2b\nu V_r + 2c(\nu V_r)^{-1}\}. \quad (3.43)$$

Substituting Eqs. (3.37) and (3.43) in (3.33), there results

$$G = -kT \left\{ \log K\nu^N \left(\frac{3}{2\pi CN^r} \right)^{3/2} - \frac{3r^2}{2CN^r} + \log 4\pi r^2 \right\} \\ + G_0 + G_1\nu V_r + G_2(\nu V_r)^2 + G_{-1}(\nu V_r)^{-1} + G_{-2}(\nu V_r)^{-2}, \quad (3.44)$$

with

$$G_0 = \frac{f^2\beta N_s}{4kT(1+\beta)} \left\{ 1 - \frac{2kTN}{fN_s} \frac{(1+\beta)N_s + 2N}{(1+\beta)N_s + N} \right\} + \left\{ \frac{\sigma(1+2\beta)U_{ss}}{2(1+\beta)} \right. \\ - kT \frac{N(1+\beta)}{(1+\beta)N_s + N} - kT(1+\beta) \log \frac{1+\beta}{\beta} - \frac{2N}{N_s} \\ + \frac{P}{\nu}(1+\beta) \left\{ \frac{f\beta N_s}{2kT(1+\beta)} \left\{ 1 - \frac{kTN}{fN_s} \frac{(1+\beta)N_s + 2N}{(1+\beta)N_s + N} \right\} \right. \\ - \frac{f\beta}{1+\beta} \left\{ \frac{\sigma\beta N_s U_{ss}}{(1+\beta)kT} - \frac{\sigma N(U_{ps} - U_{ss})}{f} \right\} + \sigma N(U_{ps} - U_{ss}) \frac{\beta}{1+\beta} \\ - kT \left\{ N \log \frac{(1+\beta)N_s + N}{\nu} + \frac{\beta N^2}{(1+\beta)N_s + N} + N_s \log(1+\beta) \right. \\ \left. + \beta(N_s + N) \log \frac{1+\beta}{\beta} - \frac{\beta N^2}{(1+\beta)N_s} \right\} \\ \left. - \sigma \left\{ NU_{ps} - NU_{ss} + \frac{N_s + N}{2(1+\beta)} U_{ss} \right\} + \frac{P}{\nu}(1+\beta)(N_s + N) \right\}, \quad (3.45)$$

$$G_1 = \frac{\sigma\beta^2}{2(1+\beta)^2} U_{ss} + \frac{\beta kTN}{(1+\beta)N_s} \frac{(1+\beta)N_s + 2N}{(1+\beta)N_s + N},$$

$$G_2 = -\frac{kT\beta}{(1+\beta)N_s},$$

$$G_{-1} = -\frac{\sigma f^2 \beta^2 N_s^2 U_{ss}}{8k^2 T^2 (1+\beta)^3} + \frac{\sigma f \beta^2 N_s N \{(1+\beta)N_s + 2N\} U_{ss}}{2kT(1+\beta)^2 \{(1+\beta)N_s + N\}}$$

$$\left. \begin{aligned} & - \frac{\sigma\beta N^2 \{(1+\beta)N_s + 2N\}}{(1+\beta)\{(1+\beta)N_s + N\}} (U_{ps} - U_{ss}) + \frac{\sigma f\beta N_s N (U_{ps} - U_{ss})}{2kT(1+\beta)} \\ & + \sigma N^2 \Delta U \end{aligned} \right\} \quad (3.46)$$

and

$$\left. \begin{aligned} G_{-2} = & -\sigma U_{ss} \left\{ \frac{\sigma\beta^3 f^2 N_s^3 U_{ss}}{8k^3 T^3 (1+\beta)^3} - \frac{\sigma\beta^2 f N_s^2 N (U_{ps} - U_{ss})}{4k^2 T^2 (1+\beta)^2} \right\} \\ & + \sigma N (U_{ps} - U_{ss}) \left\{ \frac{\sigma f\beta^2 N_s^2 U_{ss}}{4k^2 T^2 (1+\beta)^2} - \frac{\sigma\beta N_s N (U_{ps} - U_{ss})}{2kT(1+\beta)} \right\}, \end{aligned} \right\}$$

where

$$\Delta U \equiv U_{ps} - \frac{1}{2} (U_{pp} + U_{ss}). \quad (3.47)$$

§ 3. Mean Square End-to-End Distance of a Chain $\langle r^2 \rangle$

Using Eqs. (3.44) and (3.1) one obtains

$$\langle r^2 \rangle = \frac{\int r^4 \exp(A_1 + A_2 + A_3 + A_4 + A_5) dr}{\int r^2 \exp(A_1 + A_2 + A_3 + A_4 + A_5) dr}, \quad (3.48)$$

where

$$\left. \begin{aligned} A_1 = & -\frac{3r^2}{2CN^r}, & A_2 = & -\frac{G_1}{kT} \nu V_r, \\ A_3 = & -\frac{G_2}{kT} (\nu V_r)^2, & A_4 = & -\frac{G_{-1}}{kT} (\nu V_r)^{-1} \\ & & & \\ & & & \\ A_5 = & -\frac{G_{-2}}{kT} (\nu V_r)^{-2}. \end{aligned} \right\} \quad (3.49)$$

This is the expression for the mean square end-to-end distance of high polymer molecule, from which many important properties of solution can be derived.

Now let us inquire into the limits of integration in Eq. (3.48). Since $(V_r)_{\min}$ corresponds to the case where the chain elements are closely packed, it is given by

$$(V_r)_{\min} = Nb^3 = 2.37 \times 10^{-18} \quad (3.50)$$

in which b means the bond length of the chain. If we assume a random flight model for the chain, the relation between the

mean square distance $\langle R^2 \rangle$ of chain elements from the center of gravity of the chain and the mean square end-to-end distance $\langle r^2 \rangle$ of the chain proves to be

$$\langle R^2 \rangle = \frac{1}{6} \langle r^2 \rangle, \quad (3.51)$$

so that we have

$$r \simeq 3.5 V_r \quad (3.52)$$

or for the minimum value of r

$$r_{\min} = 2.02 \times 10^{-6} \text{ cm} . \quad (3.53)$$

On the other hand, $(V_r)_{\max}$ is V , so that it follows that

$$\left. \begin{aligned} (V_r)_{\max} &= 3.3 \times 10^{-16} \text{ cc} , \\ r_{\max} &= 10.5 \times 10^{-6} \text{ cm} . \end{aligned} \right\} \quad (3.54)$$

The integral may therefore be taken between the limits $r_{\min} = 2.02 \times 10^{-6} \text{ cm}$ and $r_{\max} = 10.5 \times 10^{-6} \text{ cm}$. Since, however, the present theory involves many assumptions, it is to be examined whether or not the Gibbs free energy G comes out correct within this range.

- a) We have assumed that $N_h^i \ll N_s$ (Eq. (3.28)). Since, when we consider a mean value of V_r for a 0.1% benzene solution of polystyrene whose molecular weight is 200,000, $V_r/V = 0.126$, the relation (3.28) is nearly correct. This relation holds good so long as V_r is less than its mean value, whereas it gradually becomes invalid as V_r increases.
- b) For the calculation of N_h^i (Eq. (3.37)), we made use of the relation (3.36) which is valid for V_r above its mean value. This relation, however, becomes less valid as V_r decreases.
- c) For the calculation of $(N_h^i)^2$ we used the relations (3.41) and (3.42). One of these relations, $b\nu V_r \ll 1$, remains valid for the mean value of V_r and below, while it gradually fails to be true as V_r increases. The other relation $C(\nu V_r)^{-1} \ll 1$ holds for the mean value of V_r and upward, but diminishes in validity as V_r decreases.

We can conclude from (a), (b) and (c) that the expression for G , (3.44), is correct only for the values of V_r not far from

its mean value. Since, however, the general expression valid for the whole range of V_r is very difficult to obtain, we will use the expression (3.44), applying it to the limited range, where it remains correct, and draw some conclusion as to the natures of $\langle r^2 \rangle$ of the chain in solution.

The range over which the expression for G is to be regarded as correct will be determined as follows: The upper limit of this range can be determined from the relation $(V_r/V)^2 \ll 1$ which corresponds to Eqs. (3.28) and (3.41). If we assume that the upper limit r_2 of r corresponds to the relation $(V_r/V)^2 = 0.1$, it comes out to be

$$r_2 = 7.15 \times 10^{-6} \text{ cm} . \quad (3.54)$$

The lower limit r_1 of r can be determined from the relation $(\sigma\beta N_s/2\nu V_r)^2 \ll 1$ which corresponds to Eqs. (3.36) and (3.42). If r_1 be assumed as corresponding to the relation $(\sigma\beta N_s/2\nu V_r)^2 = 0.1$, we obtain

$$r_1 = 2.32 \times 10^{-6} \text{ cm} . \quad (3.55)$$

Thus it is to be asserted that we had better use these limits as the limits of integration in Eq. (3.48) instead of $r_{\min}$ and $r_{\max}$ above estimated. The variation with r of $\sum A_i \equiv A_1 + A_2 + A_3 + A_4 + A_5$, which appears in Eq. (3.47), $(U_{ps} - U_{ss})/kT$ and $\Delta U/kT$ being taken as parameters, is shown in Figs. 3 and 4. From this we obtain the relation between the mean square end-to-end distance $\langle r^2 \rangle$ and the mixing heat ΔU , as given in Figs. 5 and 6.

§ 4. Discussion

As can clearly be seen from Figs. 5 and 6, $\langle r^2 \rangle$ decreases as ΔU decreases and at a certain critical value of ΔU it diminishes very rapidly, then tending to a very small value. That $\langle r^2 \rangle$ takes a small value means that chain elements are closely packed, which results from the circumstance that when ΔU is small the close packing of chain elements brings about a lowering of G .

If one is allowed to assume that the same holds good of a solution which contains a number of high polymer molecules, they will coagulate, sticking to one another, so as to make G of the solution minimum. Thus it may be inferred that the critical point of ΔU corresponds to the precipitation of the high polymer

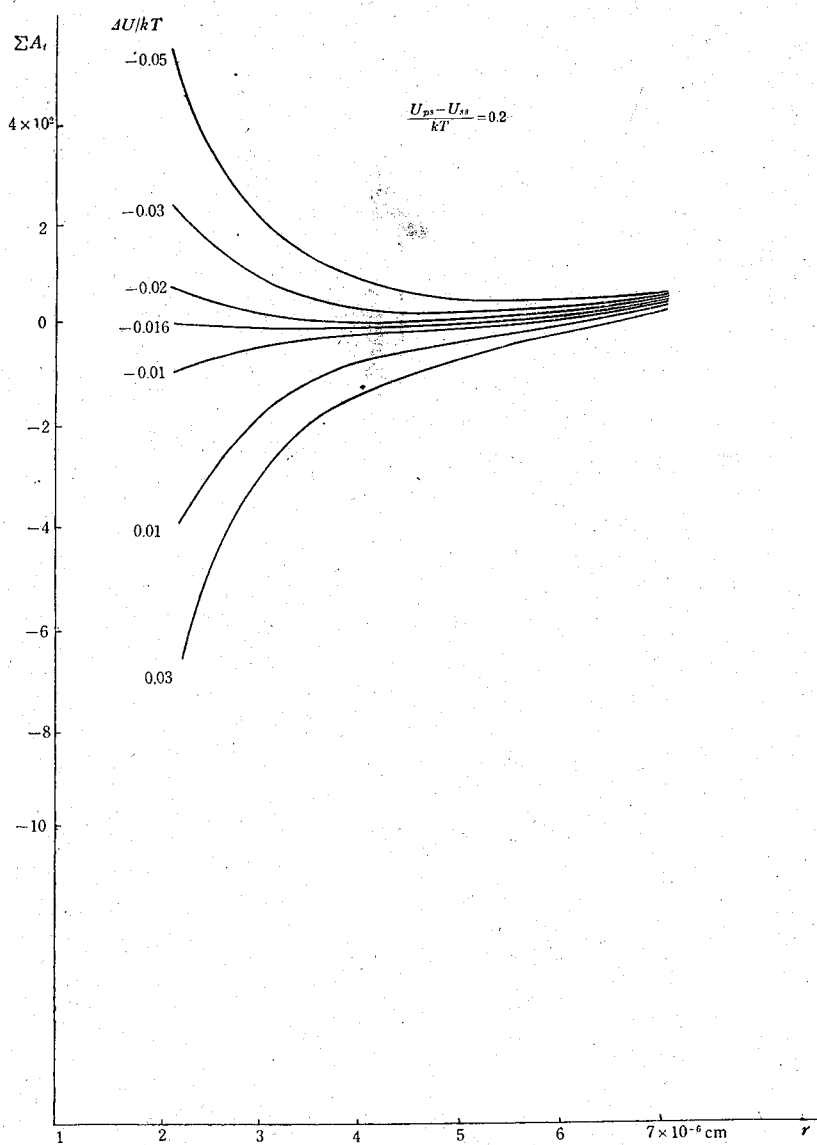


Fig. 3. Variation of ΣA_i with end-to-end distance.

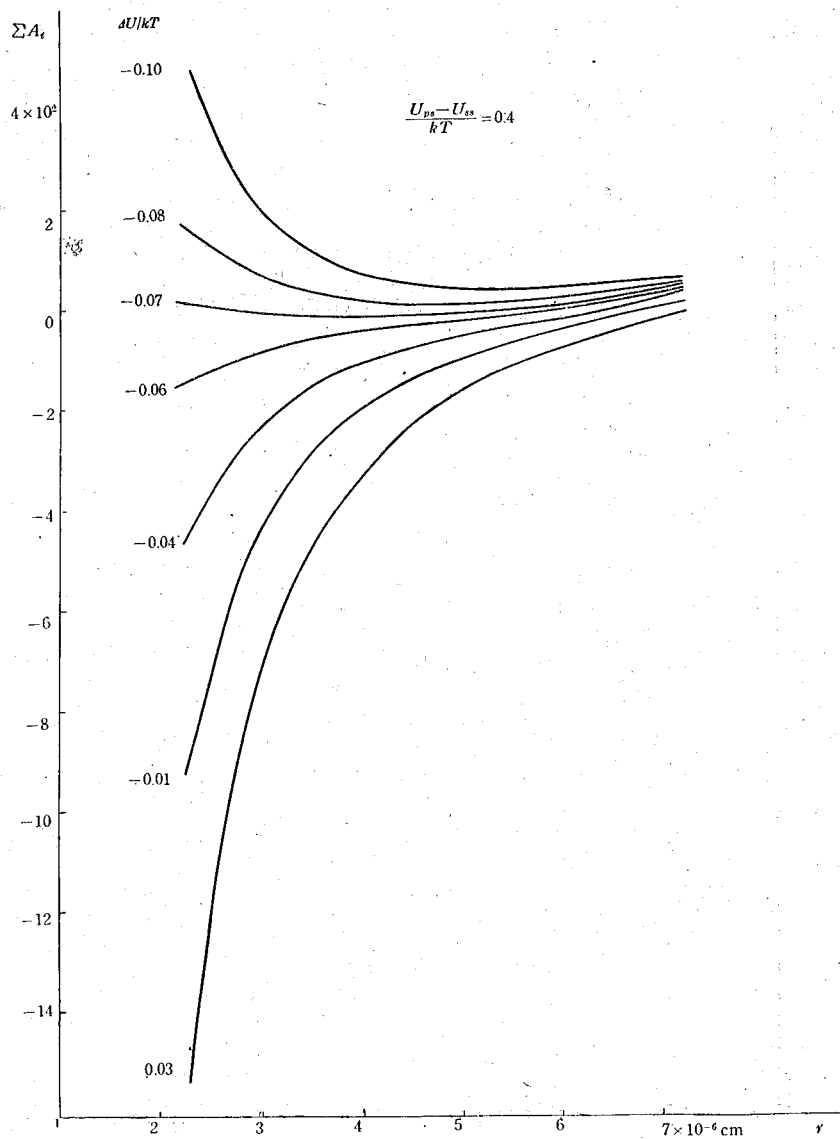


Fig. 4. Variation of ΣA_z with end-to-end distance.

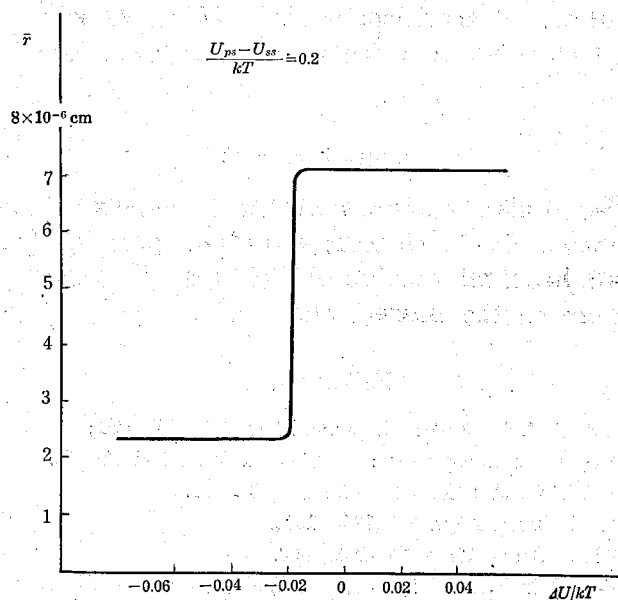


Fig. 5. Relation between root mean square end-to-end distance and mixing heat.

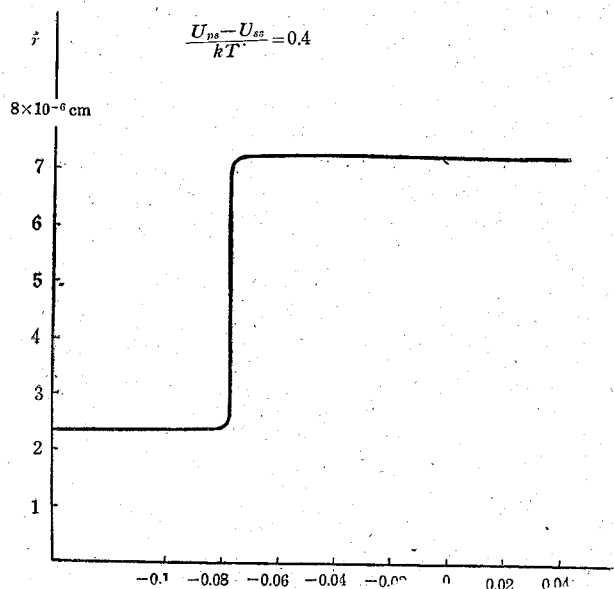


Fig. 6. Relation between root mean square end-to-end distance and mixing heat.

from the solution. This critical value of ΔU is inversely proportional to N , as will be seen from the term G_{-1} , (3.46), in which ΔU is included.

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