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## The Rotatory Diffusion Constants of Flexible Molecules

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Using the model and methods of a previous paper, the average components of the rotatory diffusion tensor of a flexible molecule are calculated. The results obtained are found to be related to both the intrinsic viscosity and to the translational diffusion constant. In particular the rotatory diffusion constant of the molecule as a whole is shown to be a simple function of the intrinsic viscosity. The theory developed, in conjunction with the theory of intrinsic viscosity and translational diffusion coordinates the result of the various hydrodynamical physical methods used in high polymer research.

### I. INTRODUCTION

IF a system of molecules is aligned by an external force so that a particular direction in each molecule is made to coincide with an arbitrary reference axis, the removal of this force results in a gradual rotatory Brownian motion towards a uniform distribution of directions. The rate with which such diffusion occurs, when the constraining field is removed, is related to the molecular structure of the molecule through the rotatory diffusion constant. In the same way, a molecule having many internal degrees of rotatory freedom, can by internal rotatory Brownian motion take up a large number of configurations corresponding to different sets of possible coordinates of the diffusing segments. This latter consideration applies especially to the so-called flexible macromolecules, represented, for example, by the linear high polymers. Recognition of these facts has led to the statistical description of many of the properties of high polymers both in bulk and in the solution phase.

The concepts of both macro and micro Brownian motion has been of great importance in connection with a variety of different types of physical problems. Mention might be made of the phenomena of dielectric loss, mechanical properties, flow birefringence, and non-Newtonian flow.<sup>1</sup> In all of these problems a parameter, the rotatory diffusion constant, appears, related to the structure of the molecule under consideration. For rigid molecules, expressions for the rotatory diffusion constant have been obtained, utilizing the Einstein relationship between that quantity and the resistance constant. Thus, for spherical particles, the rotary diffusion constant is given by the expression

$$D = (kT/8\pi\eta a^3).$$

For ellipsoidal particles, Burgers<sup>2</sup> gives values for the rotational resistance, from which the rotational diffusion constant can be obtained.

<sup>1</sup> Kirkwood and Fuoss, J. Chem. Phys. 7, 911 (1939).

<sup>2</sup> J. M. Burgers, Chapter III; *Second Report on Viscosity and Plasticity of the Amsterdam Academy of Sciences* (Nordemann, New York, 1938).

In the case of flexible macromolecules Kirkwood<sup>1</sup> derives expressions for the components of the diffusion tensor, treating the macromolecule as made up of hydrodynamically independent elements. Actually, as has been discussed in an earlier paper, hydrodynamic interaction of the elements of the chain exist so that the over-all influence of the macromolecule on the fluid flow cannot be taken as merely a linear superposition of independent segment effects. To describe the fluid flow through the chain and calculate the components of the rotatory diffusion tensor, we shall use the model and methods described in our previous paper, to which the reader is referred.<sup>3</sup>

### II. THE INTERNAL ROTATORY DIFFUSION CONSTANT

We consider a polymer molecule, immersed in a fluid, the segments of which are considered to move with average velocity  $U_i$  relative to the solvent. This segmental velocity is derived from the angular motion of the individual elements about the various bonds joining the elements, in addition to the angular motion of the molecule as a whole.

$$U_i = \sum_{k=-n}^{i-1} (\Omega_k \times R_{ik}) + (\Omega_0 \times R_{0i}),$$

$$\Omega_k = \dot{\phi}_k b_k,$$

$$\Omega_0 = -i(\sin\phi)\dot{\theta} + j(\cos\phi)\dot{\theta} + k\dot{\phi}.$$
(1)

$\Omega_k$  is the angular velocity associated with the rotation about bond  $b_k$  and  $\Omega_0$  the angular velocity associated with the rotation of the molecule as a whole.  $\theta$  and  $\phi$  describe the orientations of a fixed direction, which we can take to be the bond joining elements 0 and 1, with a fixed rectangular coordinate system. The component of the torque  $T_j$  about the bond  $b_j$  can then be expressed by

$$T_j = \sum_{k=-n}^n \dot{\phi}_k \rho_{jk}$$
(2)

which defines the components of the rotational re-

<sup>3</sup> J. G. Kirkwood and J. Riseman, J. Chem. Phys. 16, 565 (1948).

sistance tensor around bond  $b_j$ . The rotational diffusion tensor can be obtained by means of the Einstein relation

$$D = kT\rho^{-1}, \quad (3)$$

$$\rho_{sk}^{-1} = (\Delta_{sk}/|\rho_{sk}|),$$

where  $|\rho_{sk}|$  is the determinant of the resistance tensor and  $\Delta_{sk}$  the co-factor of the corresponding element in the determinant. In particular, if the rotational resistance tensor contains only diagonal elements then

$$D_{ss} = (kT/\rho_{ss}). \quad (4)$$

Therefore to calculate the rotatory diffusion constants it is necessary to compute the torques about the various bonds. We shall here calculate the average torques and consequently the average diffusion constants, since physically it is these average quantities over all configurations of the molecule that one encounters experimentally.

The notation used in this paper is similar to that in our previous paper.<sup>3</sup> For convenience, however, we review the definitions of the terms being used.

$k$  = Boltzmann's constant,

$T$  = the absolute temperature,

$R_{lj}$  = the position of an element  $j$  of the chain, relative to an element 1,

$b_j$  = the unit vector directed from chain element  $j-1$  to  $j$ ,

$\zeta$  = the friction constant associated with the elements of the chain,

$v_{0l}$  = the unperturbed fluid flow at the location of element  $l$ , if that element were absent,

$u_l$  = the velocity of element  $l$ ,

$\eta_0$  = the coefficient of viscosity of the solvent,

$Z$  = the degree of polymerization equal to  $M/M_0$  where  $M$  and  $M_0$  are, respectively, the molecular weights of the polymer and monomer units, CHX.

The net torque about an arbitrary element  $j$ , caused by the forces acting on elements  $l$  is

$$T_j = - \sum_{l=j+1}^n (R_{lj} \times F_l) + \sum_{l=-n}^{j-1} (R_{lj} \times F_l), \quad (5)$$

where  $-F_l$  is the force acting on element  $l$ .<sup>3</sup> The component of this net torque about bond  $b_j$ , is associated with the rotatory motion about  $b_j$  as an axis.

$$T_j = T_j \cdot b_j = - \sum_{l=j+1}^n b_j \cdot (R_{lj} \times F_l) + \sum_{l=-n}^{j-1} b_j \cdot (R_{lj} \times F_l). \quad (6)$$

The average of  $T_j$  over-all configurations of the

molecule is

$$\langle T_j \rangle_{Av} = - \sum_{l=j+1}^n \langle b_j \cdot (R_{lj} \times F_l) \rangle_{Av} + \sum_{l=-n}^{j-1} \langle b_j \cdot (R_{lj} \times F_l) \rangle_{Av}, \quad (7)$$

$$\langle T_j \rangle_{Av} = \sum_{k=-n}^n \phi_k \langle \rho_{jk} \rangle_{Av}.$$

The quantities  $\langle b_j \cdot (R_{lj} \times F_l) \rangle_{Av}$  are now evaluated using the Oseen equation

$$F_l = -\zeta(v_{0l} - u_l) - \zeta \sum_{\substack{s=-n \\ s \neq l}}^n T_{ls} \cdot F_s. \quad (8)$$

Setting  $(v_{0l} - u_l)$  in (8) equal to  $U_l$ ,<sup>1</sup> multiplying vectorially by the quantity  $(b_j \cdot R_{lj} \times)$  and averaging, we obtain

$$\langle b_j \cdot R_{lj} \times F_l \rangle_{Av} = -\zeta \langle b_j \cdot R_{lj} \times U_l \rangle_{Av} - \zeta \sum_{\substack{s=-n \\ s \neq l}}^n \langle b_j \cdot R_{lj} \times T_{ls} \cdot F_s \rangle_{Av},$$

$$\langle b_j \cdot R_{lj} \times U_l \rangle_{Av} = \frac{2}{3} b^2 (l-j) \phi_j \delta_{jk} \quad l > j$$

$$= 0, \quad l < j$$

$$\langle b_j \cdot R_{lj} \times T_{ls} \cdot F_s \rangle_{Av} = \langle b_j \cdot R_{lj} \times \langle T_{ls} \rangle_{Av} \cdot F_s \rangle_{Av} + \langle b_j \cdot R_{lj} \times (T_{ls} - \langle T_{ls} \rangle_{Av}) \cdot F_s \rangle_{Av},$$

$$\langle T_{ls} \rangle_{Av} = \frac{1}{(6\pi^2)^{1/2} \eta_0 b |l-s|^{1/2}},$$

$$\delta_{jk} = 0 \quad j \neq k$$

$$= 1 \quad j = k. \quad (9)$$

Equation (8) therefore becomes

$$\phi_l = f_l - \frac{\lambda}{n^{1/2}} \sum_{\substack{s=-n \\ s \neq l}}^n \frac{\phi_s}{(|l-s|)^{1/2}} \quad j < l,$$

$$\phi_l = -\frac{\lambda}{n^{1/2}} \sum_{\substack{s=-n \\ s \neq l}}^n \frac{\phi_s}{(|l-s|)^{1/2}} \quad j > l,$$

$$\phi_s = \langle b_j \cdot R_{lj} \times F_s \rangle_{Av},$$

$$f_l = -\frac{2}{3} \zeta b^2 (l-j) \phi_j,$$

$$\lambda = \frac{\zeta}{(12\pi^2)^{1/2} \eta_0 b} \left( \frac{M}{M_0} \right)^{1/2}. \quad (10)$$

The Eqs. (10) are a set of linear equations in the variables  $\phi_k$ , which for large  $n$  can be asymptotically

approximated by the integral equations

$$\begin{aligned}\phi(x) &= f(x) - \lambda \int_{-1}^1 \frac{\phi(t)}{(|l-t|)^{\frac{1}{2}}} dt \quad j < nx, \\ \phi(x) &= -\lambda \int_{-1}^1 \frac{\phi(t)}{(|l-t|)^{\frac{1}{2}}} dt \quad j > nx, \\ f(x) &= -\frac{2}{3} \zeta b^2 \phi_j (nx - j), \\ x &= l/n, \quad t = s/n.\end{aligned}\quad (11)$$

For  $j < nx$ , the integral equation is of the form encountered in the viscosity theory, and using those results we can write

$$\begin{aligned}\phi(x) &= \phi_0 + \sum_{\substack{m=-\infty \\ m \neq 0}}^{\infty} \phi_m e^{im\pi x}, \\ \phi_0 &= \frac{f_0}{1 + \frac{8}{3}\sqrt{2}\lambda}, \\ \phi_m &= \frac{f_m - u_m f_0}{1 + \lambda(2/|m|)^{\frac{1}{2}}}, \\ u_m &= \frac{\lambda(-1)^{m+1}}{(m\pi)^{\frac{1}{2}}} I_m \int_0^{2\pi m} \frac{e^{iu}}{u^{\frac{1}{2}}} du, * \\ f_0 &= \frac{2}{3} b^2 \zeta \phi_j j, \\ f_m &= \frac{\frac{2}{3} b^2 \zeta n \phi_j i (-1)^{m+1}}{m\pi}, \quad i = \sqrt{-1}.\end{aligned}\quad (12)$$

For  $j > nx$  we have a linear, homogenous, integral equation. Solutions other than the trivial one  $\phi(x) = 0$  are obtained only for particular values of  $\lambda$ .<sup>4</sup> Such values of  $\lambda$  are the eigenvalues of the kernel  $1/(|x-s|)^{\frac{1}{2}}$ . Insofar as  $\lambda$ , in this case, is an experimental constant, the probability of such values of  $\lambda$  arising would be very small. If necessary, should a  $\lambda$  occur which is an eigenvalue, then we could always change the numerical value of  $\lambda$  by one in the last decimal place, destroy its eigenvalue character and in no way change the physical results.

In terms of the variables  $\phi(x)$ , Eq. (7) for the average component of the torque about bond  $b_j$  becomes

$$\langle T_j \rangle_{Av} = \sum_{l=j+1}^n \phi(l/n). \quad (13)$$

It is obvious from symmetry considerations, that the methods that have been applied above to evaluate the component of the torque about the

bond  $j$  could have been applied to obtain the torque about bond  $-j$ . That is, the elements of either half of the chain could have been designated by positive integers. Then for the lower half of the chain, remembering that a change of direction occurs

$$\begin{aligned}\Omega_k &= -\phi_k' b_k, \\ T_k &= -T_k \cdot b_k.\end{aligned}\quad (14)$$

It is therefore unnecessary to repeat the above calculations.

If the sums, defining  $\langle T_j \rangle_{Av}$  both for positive and negative  $j$ , are approximated by integrals, we finally obtain

$$\begin{aligned}\langle T_j \rangle_{Av} &= \langle \rho_{jj} \rangle_{Av} \phi_j, \\ \langle \rho_{jj} \rangle_{Av} &= -\frac{2}{3} \zeta b^2 \left\{ |j| \left( |j| - \frac{Z}{2} \right) \right. \\ &\quad \left. + F(\lambda) + G(j, \lambda) - H(j, \lambda) \right\}, \\ F(\lambda) &= \frac{Z^2}{2\pi^2} \sum_{m=1}^{\infty} \frac{1}{m^2 [1 + \lambda(2/m)^{\frac{1}{2}}]}, \\ G(j, \lambda) &= \frac{Z^2}{2\pi^2} \sum_{m=1}^{\infty} \frac{(-1)^{m+1} \cos 2m\pi \left( \frac{|j|+1}{Z} \right)}{[m^2 (1 + \lambda(2/m)^{\frac{1}{2}})]}, \\ H(j, \lambda) &= \frac{|j|Z}{1 + \frac{8}{3}\sqrt{2}\lambda} \sum_{m=1}^{\infty} \frac{u_m \sin 2m\pi \left( \frac{|j|+1}{Z} \right)}{m\pi [1 + \lambda(2/m)^{\frac{1}{2}}]}, \\ Z &= \frac{M}{M_0}, \\ \langle D_{jj} \rangle_{Av} &= \frac{kT}{\langle \rho_{jj} \rangle_{Av}}.\end{aligned}\quad (15)$$

In the limit of small  $\lambda$ , corresponding to negligible hydrodynamic interaction we obtain from (15)

$$\langle \rho_{jj} \rangle_{Av} = \frac{1}{3} \zeta b^2 (n - |j|)^2$$

which is the result obtained for this case by Kirkwood.<sup>1</sup>

### III. THE ROTATIONAL DIFFUSION CONSTANT

This calculation proceeds in a manner analogous to the calculation of the internal rotatory diffusion constants. The total torque about the center of mass is

$$\begin{aligned}T &= \sum_{l=-n}^n T_l, \\ T_l &= -R_{0l} \times F_l.\end{aligned}\quad (16)$$

\* See E. Jahnke and F. Emde, *Funktionstafeln* (Dover Publications, New York, 1943).

<sup>4</sup> R. Courant and D. Hilbert, *Methoden Der Mathematischen Physik* (Verlag. Julius Springer, Berlin 1931).

Defining quantities

$$\begin{aligned}\langle R_{0l'} \times F_l \rangle_{Av} &= -(4/9)\zeta b^2 n \phi_{l,l'}, \\ \langle T \rangle_{Av} &= (4/9)\zeta b^2 n^2 \int_{-1}^1 \phi(x, x) dx, \\ x &= l/n, \quad y = l'/n, \quad (17)\end{aligned}$$

we obtain from the Oseen Eq. (8) after multiplying by  $(R_{0l'} \times)$  and averaging over-all internal configurations of the chain,

$$\begin{aligned}\phi_{l,l'} &= f_{l,l'} + \frac{9}{4b^2 n} \sum_{\substack{s=-n \\ s \neq l}}^n \langle R_{0l'} \times T_{ls} \cdot F_s \rangle_{Av} \\ &\quad - n \leq l \leq +n \\ &\quad - n \leq l' \leq +n \\ f_{l,l'} &= \frac{1}{8n^2} [3(l^2 + l'^2) - 6n|l - l'| + 2n^2] \Omega_0. \quad (18)\end{aligned}$$

Here as in the other cases we assume the fluctuation

$$\langle R_{0l'} \times (T_{ls} - \langle T_{ls} \rangle_{Av}) \cdot F_s \rangle_{Av}$$

can be neglected and therefore introduce the approximation

$$\langle R_{0l'} \times T_{ls} \cdot F_s \rangle_{Av} = \langle R_{0l'} \times \langle T_{ls} \rangle_{Av} \cdot F_s \rangle_{Av}. \quad (19)$$

Equation (18) therefore reduces to the following set of linear equations in the variables  $\phi_{l,l'}$

$$\phi_{l,l'} = f_{l,l'} - \frac{\lambda}{n^{\frac{1}{2}}} \sum_{\substack{s=-n \\ s \neq l}}^n \frac{\phi_{l',s}}{(|l-s|)^{\frac{1}{2}}}. \quad (20)$$

We again replace (20) by the asymptotic integral equation

$$\phi(x, y) = f(x, y) - \lambda \int_{-1}^1 \frac{\phi(t, y)}{(|x-t|)^{\frac{1}{2}}} dt. \quad (21)$$

We recognize (21) to be identical with the integral equation encountered in the viscosity theory so that<sup>3</sup>

$$\begin{aligned}\phi(x, y) &= \sum_{\substack{m=-\infty \\ m \neq 0}}^{\infty} \frac{f_m(y) e^{im\pi x}}{1 + \lambda(2/m)^{\frac{1}{2}}}, \\ f_m(y) &= \left( \frac{3}{4\pi^2 m^2} e^{-im\pi y} + \frac{(-1)^{m+1} 3iy}{4\pi |m|} \right) \Omega, \quad (22)\end{aligned}$$

and from (17)

$$\begin{aligned}\langle T \rangle_{Av} &= (4/9)\zeta b^2 n^2 F(\lambda) I \cdot \Omega_0, \\ F(\lambda) &= \frac{6}{\pi^2} \sum_{m=1}^{\infty} \frac{1}{[m^2(1 + \lambda(2/m)^{\frac{1}{2}})]}, \\ \langle T \rangle_{Av} &= \langle \rho_{00} \rangle_{Av} \cdot \Omega_0. \quad (23)\end{aligned}$$

We have, therefore, obtained the average of the over-all rotational resistance tensor

$$\begin{aligned}\langle \rho_{00} \rangle_{Av} &= (4/9)b^2 n^2 \zeta F(\lambda) I, \\ \langle \rho_{\theta\theta} \rangle_{Av} &= \langle \rho_{\phi\phi} \rangle_{Av} = \frac{1}{2} \langle \rho_{00} \rangle_{Av}, \\ \langle D_{\theta\theta} \rangle_{Av} &= \langle D_{\phi\phi} \rangle_{Av} = 2 \langle D_{00} \rangle_{Av} = \frac{9kT}{2b^2 n^2 \zeta F(\lambda)}. \quad (24)\end{aligned}$$

For small  $\lambda$ ,  $\langle \rho_{00} \rangle_{Av}$  reduces to Kirkwood's expression

$$(4/9)b^2 n^2 \zeta I.$$

#### IV. DISCUSSION

It is interesting to point out here that in terms of the parameters  $\xi$  and  $b$  which have been discussed in the previous paper,<sup>3</sup> we have been able to correlate the hydrodynamic behavior of long chain molecules with regard to the various tools used in high polymer research. Thus evaluating  $\xi$  and  $b$  from viscosity data, for example, allows one to predict the behavior of the long chain molecule in a centrifugal field or in a diffusion cell or in a streaming birefringence experiment. In the latter case notice must be taken of the fact that the averages over all internal configurations are performed with the understanding that they pertain to an equilibrium distribution, not affected by the fluid flow. This means that the values as given pertain to small rates of shearing strain. At high rates of shearing strain, some stretching of the molecule will occur so that, in such a field, a different distribution of internal configurations will result. Therefore, the rotatory diffusion constants obtained experimentally from streaming birefringence measurements should be extrapolated to small shear rates in order to compare with our theory.

On the other hand, values of  $b$  can be obtained by comparing this theory with the experimental determination, by means of streaming birefringence, of rotatory diffusion constants. In this case one might expect  $b$  the effective hydrodynamic distance between chain elements to increase with increase in velocity gradient and therefore rate of shearing strain. One could, therefore, follow this change of molecular length with velocity gradient.

For purposes of calculation the quantities  $F(\lambda)$ ,  $G(j, \lambda)$  and  $H(j, \lambda)$  are readily evaluated.  $F(\lambda)$  is tabulated in our viscosity paper,<sup>3</sup> and the latter two quantities converge sufficiently rapidly so that one may take the first 10 terms to obtain a result good to 10 percent. The value of  $\lambda$  necessary for the evaluation of the sums are easily obtained from intrinsic viscosity data.

It was mentioned above that Eq. (21) was similar in form to the integral equation of the intrinsic viscosity theory. If we write for the intrinsic

TABLE I.

Molecular weight	Benzene		Methyl ethyl ketone	
	$[\eta]$	$\langle D_{\phi\phi} \rangle_{Av} \times 10^{-3}$	$[\eta]$	$\langle D_{\phi\phi} \rangle_{Av} \times 10^{-3}$
1,540,000	4.00	2.08	1.54	12.22
1,070,000	3.06	3.93	1.24	21.88
650,000	2.11	9.39	0.976	45.80
400,000	1.49	21.50	0.734	98.60
265,000	1.10	44.06	0.535	204.2
162,000	0.765	103.7	0.409	437.2
116,000	0.593	186.8	0.342	728.6
75,000	0.432	396.4	0.246	1573
45,000	0.294	991.8	0.188	3412
23,000	0.179	3110	0.127	9922

viscosity

$$[\eta] = \frac{N\zeta b^2}{3600\eta_0 M_0} ZF(\lambda)$$

and compare with (24), we see that

$$\langle \rho_{\phi\phi} \rangle_{Av} = 200 \frac{M}{N} \eta_0 [\eta],$$

$$\langle D_{\phi\phi} \rangle_{Av} = \frac{NkT}{200M\eta_0 [\eta]}.$$

This yields an interesting relationship between the intrinsic viscosity and the component of the rotatory diffusion constant of the molecule as a whole. This result is not unexpected as can be seen by comparing the rotational diffusion constant for a spherical particle with the Einstein intrinsic viscosity formula.<sup>5</sup> In Table I, we present values of  $\langle D_{\phi\phi} \rangle_{Av}$  of polystyrene calculated from the intrinsic viscosity data of our previous paper.<sup>3</sup> In the poorer solvent, in which the root mean square end to end length of the molecule is smaller than in the good solvent benzene, the values of the rotatory diffusion constant are larger, as is to be expected. The ratio in the poor and good solvents decreases from a value of 6 at the high molecular weight range to about 3 at 23,000, where the effect resulting from the differences in hydrodynamic shielding because of the more compact configuration in the poor solvent would be decreased. One might expect that the influence of a high velocity gradient upon such a compact configuration would be more marked than in the case of the more extended one in a good solvent, leading to a more noticeable increase of

<sup>5</sup> Simha in a personal communication mentions the fact that the form of the relationship between the diffusion constant and the intrinsic viscosity is general, with the specific nature of the model affecting only the numerical factor. Consequently, for a flexible molecule one would expect a variation of this factor with molecular weight.

TABLE II. Experimental and calculated values of the translational diffusion constant of polystyrene in butanone.

M. W. (ultra-centrifuge)	$(D \times 10^7)$ exp.	$(D \times 10^7)$ calc.
96,900	9.22	9.60
244,000	4.95	5.89
584,000	3.16	3.91
933,000	2.44	2.95
982,000	2.43	2.87

measured rotatory diffusion constant with increase in velocity gradient.

Some preliminary streaming birefringence experiments on polystyrene in toluene, carried out at the Brooklyn Polytechnic Institute, gave for a fraction having intrinsic viscosity about 10 and molecular weight about  $4 \times 10^6$  a diffusion constant of about 800. This experimental value compares favorably as to order of magnitude with our theoretical calculations. The present difficulty in the theoretical interpretation of streaming birefringence data does not allow us to do more than compare orders of magnitude.

We are very grateful to Mr. Melvin Schoenberg of the Brooklyn Polytechnic Institute for making available to us his preliminary flow birefringence data on polystyrene.

## APPENDIX

### Comparison of Experimental and Theoretical Diffusion Constants of Polystyrene in Butanone

In a recent publication,<sup>3</sup> the first of this series, the following result for the translational diffusion constant of a flexible molecule was obtained.

$$D = [1 + (8\lambda_0/3)Z^{\frac{1}{2}}] \frac{kT}{Z\zeta}.$$

Because of the absence of reliable data no comparison of this theoretically derived result with experimental data was possible. Recently,<sup>\*\*</sup> diffusion constant measurements of fractionated polystyrene in butanone were made. In making a comparison of this data with our theoretical results, shown in Table II, we have used for the values of the hydrodynamic parameters  $b$  and  $\zeta$  the results mentioned in our previous paper.<sup>3</sup> It would have been preferable in making such comparison to have calculated these parameters from viscosity measurements on polystyrene fractions identical with those on which the diffusion constant measurements were made. The absence of such concurrent experimental data therefore compels us to use the results from the viscosity measurements on polystyrene fractions in one laboratory to calculate diffusion constants for comparison with those obtained in another laboratory.

The agreement between experiment and theory is about as good as one could expect for high polymeric systems.

<sup>\*\*</sup> The diffusion data presented here is from the doctoral thesis of A. Schick, Polytechnic Institute of Brooklyn, 1948.