

The Influence of Molecular Flexibility on the Intrinsic Viscosity, Sedimentation, and Diffusion of High Polymers

Robert Simha

Citation: *The Journal of Chemical Physics* **13**, 188 (1945); doi: 10.1063/1.1724020

View online: <http://dx.doi.org/10.1063/1.1724020>

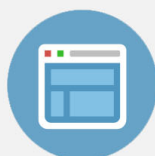
View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/13/5?ver=pdfcov>

Published by the [AIP Publishing](#)



Re-register for Table of Content Alerts

Create a profile.



Sign up today!



The Influence of Molecular Flexibility on the Intrinsic Viscosity, Sedimentation, and Diffusion of High Polymers*

ROBERT SIMHA

Department of Chemistry, Howard University, Washington, D. C.

(Received January 15, 1945)

Expressions for the mean square separation of chain ends and modifications of the formula for an ideal coil are discussed. On the basis of these and of the hydrodynamic theory of intrinsic viscosity, an interpretation of the modified Staudinger rule is offered. It relates the exponent a of the molecular weight to a flexibility parameter p of the chain in a given solvent, varying between zero and one (Eq. (4), (5)). Recent data on polystyrene and on cellulose nitrate are analyzed in greater detail. By means of the frictional ratio f/f_0 , the sedimentation constant s and the diffusion constant D , respectively, are connected with the degree of polymerization in terms of p (Eq. (9)). The limiting dependence of sedimentation and diffusion rate upon molecular weight for a straight chain and an ideal coil is also found in this manner. A comparison shows satisfactory agreement between values for p found from intrinsic viscosity and those determined from sedimentation or diffusion rates, for certain cellulose esters and starch derivatives. Effects of solvent and of inhomogeneity in respect to molecular weight are discussed briefly.

INTRODUCTION

THE physical methods employed to determine molecular weights of high polymers in solution are based either on the measurement of a colligative property like osmotic pressure or sedimentation equilibrium, or a rate phenomenon, such as the viscosity increment due to the solute or the rates of sedimentation and diffusion of the solute. The second type of procedure is more easily applicable from the experimental point of view, while its interpretation is more involved than that of measurements of the former type. The determination of polymerization degrees from viscosity data is based on Staudinger's empirical rule or a modification thereof obtained by calibration of the procedure by means of an absolute method. In this way an empirical relation is obtained between the intrinsic viscosity and the molecular weight. In the case of sedimentation-diffusion, an expression for the molecular weight is derived in a straightforward way. For polydisperse systems however, it is not immediately evident what type of molecular weight average results.

Present theories on the other hand, establish relations between the intrinsic viscosity and the shape of the solute molecule.¹ Similarly, the result

of a sedimentation-diffusion measurement can be related to the shape of the sedimenting particle by means of the so-called frictional ratio.² A connecting link between some of the empirical results in terms of molecular weight and present theories can be established, if the shape of long chain molecules in solution can be related to their degree of polymerization. In this manner it becomes possible also to relate the intrinsic viscosity and the molecular weight to the individual sedimentation or diffusion constants instead of their ratios only. It is the purpose of this article to examine certain aspects of these questions.

I. SHAPE OF LONG CHAIN MOLECULES IN SOLUTION

It has been shown by various authors³ following Rayleigh's⁴ treatment of the problem of random flight, that the mean square separation of ends in a chain consisting of N freely rotating links is given by

$$\lim_{N \rightarrow \infty} \langle R^2 \rangle_N = AN, \quad (1)$$

where A is the squared length of a link and R the

² *The Ultracentrifuge*, Ed. The Svedberg and Kai O. Pedersen (Oxford University Press, New York, 1940).

³ W. Kuhn, *Kolloid Zeits.* **68**, 2 (1934); E. Guth and H. Mark, *Monats.* **65**, 93 (1934).

⁴ Compare the excellent discussion by S. Chandrasekhar, *Rev. Mod. Phys.* **15**, 2 (1943).

* Publication assisted by The Graduate School of Howard University.

¹ See for instance R. Simha, *J. App. Phys.* **13**, 147 (1942).

distance between chain ends. The constancy of the valence angle merely introduces a numerical factor. Relation (1) will remain valid also if an energy barrier to rotation exists, provided that rotational symmetry is preserved (ethane-type of barrier). The factor A is modified and becomes a function of the height of the energy hump and of the temperature.⁵ Equation (1) can be generalized. If a distribution of "step" lengths,

$$\tau(x, y, z) dx dy dz,$$

exists in proceeding from the i th joint to the $(i+1)$ th, and τ is independent of the ordinal number i , where x, y, z denotes a set of coordinates through the joint, one obtains⁴

$$\lim_{N \rightarrow \infty} \langle R^2 \rangle_N = AN + BN^2. \quad (1a)$$

A indicates the mean square of the length of a "step" or effective length of a link, averaged over the distribution τ . B denotes the sum of the squares of the mean displacements in 3 directions

$$B = \langle \xi \rangle^2 + \langle \eta \rangle^2 + \langle \zeta \rangle^2.$$

The system ξ, η, ζ results from the original one by means of a certain orthogonal transformation which need not be specified here. If the function τ possesses the previously mentioned symmetry properties, $B=0$. Thus again a random distribution of chain end distances is obtained, however superimposed upon that resulting from a straight extension of the chain. B is a measure of the geometrical anisotropy existing in the structure.

Considering now an actual chain molecule, the fact that "tracing back of steps" or back coiling of the chain is restricted because of the space filling effect of the substituents, requires a modification of the considerations leading to relation (1). It is extremely difficult to evaluate this effect in detail, since the direction of each successive link now becomes dependent upon that of the preceding one. However, it may be seen that, on the average, a straightening out of the chain coil will occur, larger values of the separation of chain ends, than in the ideal case, being more probable. The actual chain may therefore be replaced in a first approximation by one in which there exists a distribution τ of displacements around each joint, and independent of its

position within the molecule, giving rise to a mean value $\langle R^2 \rangle_N$ as in (1a). For the large degrees of polymerization involved, even slight deviations from symmetry can lead to appreciable values for the second term in (1a). Unless the range of N -values is large, this equation can be approximately replaced by a single term with an intermediate exponent, thus

$$\langle R^2 \rangle_N = CN^{1+x}; \quad 0 < x < 1, \quad (1b)$$

C is a constant. $x=0$ corresponds to the ideal coil, as defined in (1), $x=1$ to a straight chain. Thus we arrive at a result similar to the one suggested previously by Kuhn.³ It may be noted that in the transition from (1a) to (1b), x increases with B while C decreases. For $N \approx 10^3$, a value of x of 0.4–0.5 can increase the value of $(\langle R^2 \rangle_N)^{1/2}$ for a paraffin chain by a factor of several units. Finally the influence of the solvent must be taken into account. Stuart's⁶ experiments on models propose to reproduce the difference between an inert and a good solvent. In the latter system the chains are straightened out. The solvent in this instance prevents the polymer molecule from curling up. This may be due in part to actual solvation and in part may be considered analogous to the conditions which prevent the formation of a drop and lead to spreading of a film. As is well known,⁷ this occurs when the energy of adhesion between upper and lower liquid exceeds the cohesion within the former one. Of course, in our case, the entropy factor is the primary source for the tendency in the single polymer molecule to form a "drop." Furthermore these considerations can apply to dilute solutions only.

II. INTRINSIC VISCOSITY, MOLECULAR WEIGHT, AND DIMENSIONS

Since Staudinger first proposed his relation, it has become necessary to modify it. For relatively small molecular weights, not exceeding 30,000 as a weight average, addition of a constant term⁸ has been found satisfactory. For larger molecular

⁶ H. A. Stuart, *Naturwiss.* **31**, 123 (1943).

⁷ Compare for instance N. K. Adam, *The Chemistry and Physics of Surfaces* (Oxford University Press, New York, 1941).

⁸ R. Fordyce and H. Hibbert, *J. Am. Chem. Soc.* **61**, 1912 (1939); P. J. Flory and P. B. Stickney, *J. Am. Chem. Soc.* **62**, 3032 (1940); W. O. Baker, C. S. Fuller and J. H. Heiss, Jr., *J. Am. Chem. Soc.* **63**, 3316 (1941).

⁵ S. E. Bresler and J. I. Frenkel, *Acta Physicochimica, U.S.S.R.* **11**, 485 (1939).

weights, in accordance with Houwink,⁹ the following equation has been applied

$$\eta_i = KM^a = K'Z^a, \quad (2)$$

where η_i is the intrinsic viscosity, found by extrapolation from a plot of η_{sp}/c vs. c . M is the molecular weight of the fraction as determined by an absolute method, Z the degree of polymerization. Since the partial specific volume of the polymer is almost always practically independent of molecular weight, the result remains unaltered if c is expressed as a volume ratio rather than a ratio of weight to volume. A few examples are presented in Table I. The molecular weights were determined partly from osmotic pressure and partly from ultracentrifuge data. In several cases only three points were available for computing a . The homogeneity of the samples varied, those investigated by Mosimann and Gralén being quite inhomogeneous. The meaning of the last column is discussed later on. This table is by no means complete. However, it seems to indicate that the exponent a lies roughly between 0.5 and 1.5. It may be noted that relatively slight inaccuracies in the viscosities or molecular weights can produce noticeable variations in a .

As mentioned before, present hydrodynamic theories of intrinsic viscosity introduce as fundamental parameter the shape of the solute molecule.^{1,10} If it is approximated by an ellipsoid of revolution, the length-thickness ratio l/d appears in the final result.¹ For the case of overwhelming Brownian motion in the viscosimeter, η_i becomes a rather complicated function of l/d , which has been evaluated in the range between $l/d=1$ and 300.¹¹ Using these data, Kraemer¹² has given an interpolation formula in the form of a polynomial. However, a simpler equation can be given, which is more useful for our purposes, namely:

$$\left. \begin{aligned} \eta_i &\approx 0.233(l/d)^{1.698}; \quad 20 \leq l/d \leq 100; \\ &\quad \text{Average deviation 1.2 percent} \\ \eta_i &\approx 0.207(l/d)^{1.732}; \quad 20 \leq l/d \leq 300; \\ &\quad \text{Average deviation 2.3 percent} \end{aligned} \right\} \quad (3)$$

⁹ R. Houwink, J. prakt. Chem. **157**, 15 (1940).

¹⁰ W. Kuhn, Helv. Chim. Acta **26**, 1394 (1943), where previous references are given. In the present author's opinion, Kuhn's hydrodynamic treatment and others derived therefrom, contains an incorrect assumption for the limit of vanishing shear gradient, which makes the result for η_i too small. See R. Simha, J. Phys. Chem. **44**, 25 (1940).

¹¹ J. W. Mehl, J. L. Oncley and R. Simha, Science **82**, 132 (1940).

¹² E. O. Kraemer, J. Frank. Inst. **231**, 1 (1941).

TABLE I.

Solute	Solvent	a	p
Polyisobutylene	Diisobutylene	0.64 ^a	0.38
Polystyrene (polymerization temperature 60°C)	Toluene	0.70 ^b	0.42
Polystyrene, 120°C	Toluene	0.81 ^b	0.47
Polystyrene, 180°C	Toluene	1.14 ^b	0.68
Cellulose	Schweitzer's reagent	0.80 ^c	0.47
Amylose acetate	Methyl acetate	0.95 ^d	0.57
Cellulose acetate	Acetone	1.0 ^e	0.59
Cellulose nitrate	Acetone	1.0 ^f	0.60
Polyvinyl chloride	Cyclohexanone	1.0 ^g	0.59
Amylose	Ethylene diamine	1.5 ^h	0.88

^a P. J. Flory, J. Am. Chem. Soc. **65**, 372 (1943).

^b See reference 15.

^c See reference 19.

^d See reference 22.

^e M. Harris and A. Sookne, private communication. Molecular weights from osmotic pressure.

^f See reference 18.

^g D. J. Mead and R. M. Fuoss, J. Am. Chem. Soc. **64**, 277 (1942).

^h J. F. Foster and R. M. Hixon, J. Am. Chem. Soc. **66**, 557 (1944).

With increasing axis ratio, the exponents increase slowly but do not reach a value of two within the range of importance. For smaller values of l/d , the exponent in (3) assumes a value of 1.72, the factor equals 0.217, and a constant equal to 2.283 is to be added, similarly as in the correction to Staudinger's rule.⁸ η_i is expressed in terms of volume concentration. The axis ratios computed from measured viscosities represent the dimensions of the effective ellipsoid which makes the same contribution to η_i as the actual molecule. This is certainly not more than a rough approximation. For high degrees of polymerization, where the chains form preferentially compact coils,¹⁰ this should be more satisfactory than for intermediate ones. For short chains on the other hand, where curling up is insignificant, this approximation should again be more adequate. However in the following, we shall be concerned only with the former extreme. Furthermore, the possibility of solvation in good solvents contributing to the observed large intrinsic viscosities has been disregarded and the whole effect attributed to the asymmetry of the unsolvated structure. In the case of globular proteins, it has been possible to discriminate to some extent between these two possibilities by comparison of viscosity and diffusion-sedimentation data.¹¹ The difficulties encountered at present in the evaluation of such measurements for chain polymer systems, make this possibility appear doubtful in our cases. However, for high asymmetries, the solvation effect can produce only errors which

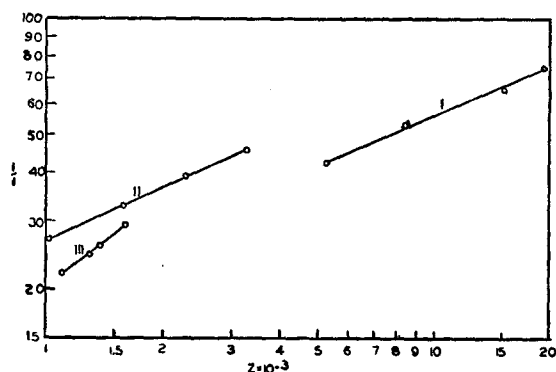


FIG. 1. Double logarithmic plot of asymmetries l/d vs. degree of polymerization Z for polystyrene:

- I Polymerization temperature 60°C.
- II Polymerization temperature 120°C.
- III Polymerization temperature 180°C.

are minor compared with those arising from other difficulties. In our applications two further points must be kept in mind. First the fact, that for a given degree of polymerization, the length and diagonal dimensions are only statistically defined. Therefore Eq. (3) must be modified to contain $\langle(l/d)^q\rangle_{av}$, where q is the exponent in (3) and the average is formed over the distribution of dimensions in the coil in solution. The exact form of this distribution is not known except for idealized cases, in which expressions of an essentially Gaussian type are obtained.⁴ However, the above average will differ from $\langle(l/d)^2\rangle^{1/2}_{av}$ only by a numerical factor of the order of unity. Secondly, the polydispersity of the solute must be taken into account. The mean axis ratio determined from the intrinsic viscosity of a mixture is:

$$\langle l/d \rangle_{av} = \left\{ \sum_i (l/d)_i W_i \right\}^{1/q},$$

where W_i is the weight fraction of species i with axis ratio $(l/d)_i$ in the mixture. The higher the molecular asymmetry, the greater the effect of inhomogeneity.¹²

To provide, with these reservations, a bridge between Eqs. (2) and (3), the dimensions of the polymer molecule must be expressed as a function of the degree of polymerization. It is not difficult to obtain the result in two limiting cases, namely those of a perfectly straight chain and an ideal flexible coil respectively. In the first instance, the longest dimension increases proportionally to the molecular weight, the cross section remains constant in a homologous series, and the axis

ratio is therefore proportional to Z . In the other extreme, the mean separation of chain ends is given by relation (1). Kuhn⁸ has shown that in such a structure on the average all dimensions increase at the same rate with the molecular weight. Thus the axis ratio becomes independent of the degree of polymerization. Our previous considerations in Part I lead for a chain in solution to an equation of type (1b), corresponding to a certain anisotropy of the structure. We may therefore expect an expression,¹

$$l/d = CZ^p; \quad 0 < p < 1, \quad (4)$$

to hold approximately. The lower limit of the exponent characterizes the ideal coil, the upper one a straight rigid chain. Combination of Eqs. (4) and (3) leads directly to the empirical formula (2) with

$$a \doteq 1.7p. \quad (5)$$

In this manner most of the values in the last column of Table I were computed, with the exception of the values for polystyrene and nitrocellulose which were found directly from suitable plots and are slightly different. However (5) is sufficiently accurate for a rapid calculation of p from a or *vice versa*. It follows from (4) and (5), that the maximum possible value of the viscosity exponent a should lie around 1.7. In those cases in which Staudinger's equation holds, a value for p of 0.59 results, approximately halfway between zero and one. According to this theory no particular physical significance is to be attached to the case $a=1$. Furthermore it is understandable for instance, that for polyisobutylene the value lies below that for the cellulose esters. Also it may be expected that for a given polymer, in a poorer solvent or solvent mixture, the p -values will be smaller than in a thermodynamically better one. The behavior of cellulose acetate in acetone-methanol mixtures seems to be in agreement with this conclusion, since p decreases with the addition of methanol.¹³ Measurements of the depolarization factor of the light scattered by the particle¹⁴ should also reveal an increased degree of coiling upon addition of precipitant. Furthermore, preferential forward scattering should appear at higher molecular weights in the poorer solvent system.

¹³ H. Mark, private communication.

¹⁴ See for instance P. Debye, J. App. Phys. **15**, 338 (1944).

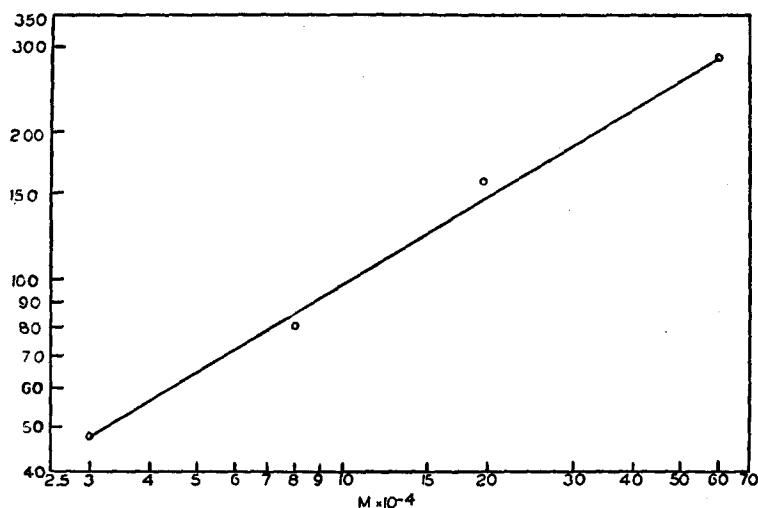


FIG. 2. Double logarithmic plot of asymmetries l/d vs. molecular weight M for cellulose nitrate.

Figure 1 gives logarithmic plots of l/d , as determined from viscosity,^{10,11} vs. Z for the three series of polystyrenes. Equation (4) is satisfied. Tables II–IV contain the experimental data together with the dimensions l and d computed therefrom. No data on the partial specific volumes of the fractions were reported. Therefore a value of 0.93 was assumed for all three series. The third column was computed from Eq. (4). Using a value of 2.5A-units for the monomer, a maximum length l_{\max} can be found. l_{\max}/l varies in the three series respectively from 15.5 to 9.1, 6.3 to 4.2, and 5.4 to 4.9, indicating degrees of coiling increasing with Z , as is to be expected. An increase of the viscosity exponent α and the flexibility parameter p is accompanied by an increase of the slope of the reduced osmotic pressure curves.¹⁵ According to present theories,¹⁶ this indicates a better solvent, in which a relative straightening out of the chains becomes understandable. On the basis of the fact, that his “constants” K decreased with increasing temperature of polymerization, Staudinger suggested that branching is favored under such conditions. This question can of course not be decided on the basis of viscosity alone. True, the proportionality factors in the equations for l/d decrease between

60° and 180°. However, this may not be more than a consequence of the increase in p , as discussed in connection with Eqs. (1a) and (1b). This increase in p indicates increased stiffening of the chains. Now a branched structure offers more resistance to convolutions of the chain than a linear one. Furthermore the chains become more symmetrical (smaller l/d), for the same degree of polymerization, as may be seen by comparison of the first and last rows in Table IV with the last two in the preceding one. Clearly more measurements on overlapping fractions prepared at different temperatures are needed.¹⁷

Mosimann's¹⁸ measurements on nitrocellulose were also analyzed. Figure 2 shows plots of $\log l/d$ vs. $\log M$. Equation (4) is applicable to the four highest molecular weights, ranging from 613,000 to 30,000. The degrees of nitration are slightly different. The two smallest degrees of polymerization were found by means of equilibrium measurements in the ultracentrifuge, the

TABLE II. Polystyrene 60°.

η_i	$Z(\text{obs}) \times 10^{-3}$	$Z(\text{calc}) \times 10^{-3}$	l/d	$l \times 10^{-3}$ (Å)	d (Å)
355	19.7	19.6	75	3.18	42
295	15.2	15.0	67	2.77	41
200	8.6	8.8	53.5	1.95	36
140	5.3	5.2	43	1.45	34

$$\eta_i = 3.37 \times 10^{-1} Z^{.70}; l/d = 1.17 Z^{.42}; l = 7.50 Z^{.61}; d = 6.41 Z^{.19}$$

¹⁵ T. Alfrey, A. Bartovics, and H. Mark, J. Am. Chem. Soc. **65**, 2319 (1943). I am indebted to Dr. H. Mark for making available the data in more detail than in the publication.

¹⁶ P. J. Flory, J. Chem. Phys. **10**, 51 (1942); M. L. Huggins, Ann. N. Y. Acad. Sci. **43**, 1 (1942).

¹⁷ See also M. L. Huggins, J. Am. Chem. Soc. **66**, 1991 (1944).

¹⁸ H. Mosimann, Helv. Chim. Acta **26**, 61 (1943).

remainder from rate data. No inhomogeneity coefficients are given for these samples except for $M=30,000$ which had a ratio of 1.65 between weight- and number-average molecular weight. In view of the magnitude of the average axis ratios, ranging from 285 to 47.5, this represents quite high a value. In the original article, values for the molecular asymmetries are presented. They were computed on the basis of theories criticized elsewhere¹⁰ by the present author. A comparison of these l/d -values with the maximum values for a straight chain also shows that they are too large. Using our values for l/d , ratios of l_{\max}/l between 2.7 and 1.2 were computed. No detailed analysis of other data presented in Table I was undertaken but merely approximate values of p were computed from Eq. (5).

Equation (4) is based on (1b). For wider ranges of molecular weights in a series, it may be necessary to use a formula modified in accordance with (1a). The Staudinger-type relation (2a) would then be replaced by a corresponding two-term equation.

III. SEDIMENTATION, DIFFUSION, AND MOLECULAR WEIGHT

The basis for the determination of molecular weights from rate measurements in the ultracentrifuge is given by the familiar equation²:

$$M = (RT/1 - V\rho) \cdot s/D. \quad (6)$$

$(1 - V\rho)$ represents the Archimedes-factor, V indicating the partial specific volume of the solute, ρ the density of the solvent. s is the sedimentation constant, D the diffusion constant of the particle. The importance of extrapolating both parameters to zero concentration has been repeatedly emphasized.^{18,19} These constants can be

TABLE III. Polystyrene 120°.

η_i	$Z(\text{obs}) \times 10^{-3}$	$Z(\text{calc}) \times 10^{-3}$	l/d	$l \times 10^{-3} \text{ (Å)}$	$d \text{ (Å)}$
155	3.3	3.3	46.3	1.29	28
118	2.3	2.3	39.5	1.03	26
86	1.6	1.6	33.0	.82	25
62	1.0	1.1	27.0	.62	23

$\eta_i = 2.26 \times 10^{-1} Z^{.81}$; $l/d = 1.02 Z^{.47}$; $l = 6.83 Z^{.65}$; $d = 6.72 Z^{.18}$

¹⁹ N. Gralén, Thesis, Upsala, 1944. The exponent is calculated from the author's sedimentation-diffusion data in the manner described below.

related to the shape of the sedimenting particle by means of the frictional ratio f/f_0 .² It indicates the ratio between the frictional resistance of the actual molecule and a sphere occupying the same volume. If the partial specific volume V of the polymer is independent of the molecular weight, the following equation is obtained:

$$f/f_0 = \text{const.}/DM^{1/2}. \quad (7)$$

For an ellipsoidal particle, f/f_0 can be expressed

TABLE IV. Polystyrene 180°.

η_i	$Z(\text{obs}) \times 10^{-3}$	$Z(\text{calc}) \times 10^{-3}$	l/d	$l \times 10^{-3} \text{ (Å)}$	$d \text{ (Å)}$
73	1.6	1.6	29.5	.75	26
59	1.4	1.4	26.0	.67	26
53	1.3	1.3	24.5	.62	25
45	1.1	1.1	22.0	.54	25

$\eta_i = 1.58 \times 10^{-2} Z^{1.14}$; $l/d = 1.91 \times 10^{-1} Z^{.68}$;
 $l = 2.25 Z^{.79}$; $d = 11.74 Z^{.11}$

as function of l/d .²⁰ It has been tabulated up to a value of hundred for the axis ratio,² and recently for higher values up to three hundred.¹⁹ Although the original equation is not as cumbersome to evaluate as the viscosity formula, it is again useful for our purposes, to write it as an exponential expression. The interpolation formula:

$$f/f_0 \div 0.506(l/d)^{0.454}; \quad 20 \leq l/d \leq 300; \quad (8)$$

Av. dev. 1.3 percent,

represents the values well.

Axis ratios calculated from the frictional ratios and those obtained from viscosity measurements have been found to agree^{11,21} in the case of proteins. The discrepancies become greater for chain polymers, as indicated, for instance, by measurements of Signer and collaborators,^{2,1} Gralén,¹⁹ Dombrow and Beckmann²² and of Mosimann.¹⁸ A comparison of Eqs. (8) and (3) shows that for polydisperse systems, different types of averages for l/d are obtained. Furthermore the molecular weights in (7), if determined from (6), are usually calculated as a ratio of some average sedimentation constant to a weight average diffusion constant, rather than as an average ratio of the two constants. Finally the

²⁰ F. Perrin, J. de phys. et rad. **7**, 1 (1936).

²¹ M. A. Lauffer, J. Am. Chem. Soc. **66**, 1188 (1944).

²² B. A. Dombrow and C. O. Beckmann, private communication. Molecular weights from sedimentation-diffusion.

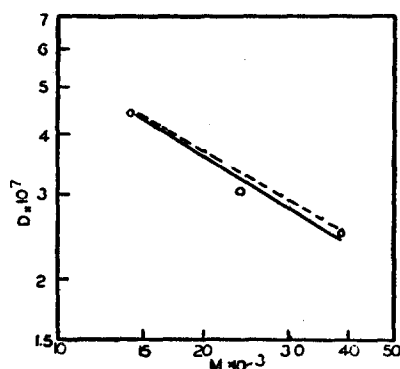


FIG. 3. Double logarithmic plot of diffusion constant D vs. molecular weight M for methyl cellulose. Circles indicate experimental values, dashed line the experimental slope, solid line the computed one.

accuracy in determining f/f_0 is limited to a greater extent than that in viscosity measurements, errors up to 20 percent not being out of the ordinary. This makes the above-mentioned discrepancies understandable.

It is assumed now that the particle in the ultracentrifuge has the same l/d -ratio as in the viscosimeter for a given solvent. This should be true for small shear gradients, since the deformation of a flexible coil is a second-order effect.¹⁰ Then it is possible to derive an expression for the separate dependence of the sedimentation or diffusion constant upon the molecular weight from viscosity data by elimination of the axis ratio l/d . Introduction of formula (4) into (8) and combination with (7) yields the result:

$$\left. \begin{aligned} D &= \text{const } M^{-(1+0.454p)}; \quad s = \text{const } M^{\frac{1}{2}-0.454p} \\ \text{Consequently for } p=1: \\ D &= \text{const } M^{-0.79}, \quad s = \text{const } M^{0.21}; \\ \text{for } p=0: \quad D &= \text{const } M^{-1}, \quad s = \text{const } M^{\frac{1}{2}}. \end{aligned} \right\} \quad (9)$$

The constants are independent of the molecular weight in a given series, having a given p -value.

In the limit of a straight chain, the sedimentation constant becomes almost independent of molecular weight. This is to be expected, since s depends for long chains mainly upon the ratio M/l . If Staudinger's rule holds, $p=0.59$ and

$$D = \text{const } M^{-0.60}, \quad s = \text{const } M^{0.40}. \quad (9a)$$

Equation (9) is not strictly applicable to the extreme of an ideal coil ($p=0$), since it is based on relation (7), valid if the molecular volume of the polymer increases with the first power of M .

For the average Kuhn-coil, however, it is proportional to $M^{\frac{1}{2}}$, thus causing the diffusion constant to vary with the reciprocal square root of M . The experimental data presented below give exponents in the neighborhood of $\frac{1}{2}$. Their interpretation on such a basis, however, is incompatible with the observed viscosity behavior. Kuhn's recent considerations¹⁰ are not in agreement with (9) and (9a). This arises from the corresponding divergence in the interpretation of Staudinger's rule, pointed out in Part II. A formula of type (9) has been proposed by Gralén,¹⁹ without any relation to viscosity or the degree of internal flexibility of the chain. From his empirical exponents for cellulose, cellulose nitrate in acetone and sodium cellulose xanthate, approximate values of p equal to 0.47, 0.78, 0.41 and of a equal to 0.80, 1.32 and 0.70 are calculated.

For an inhomogeneous system, Eq. (9) indicates that no number- or weight-average molecular weight is obtained by forming the ratio

$$\langle s \rangle_{\text{av}} / \langle D \rangle_{\text{av}}.$$

The same holds for measurements of free diffusion or of ultracentrifuge rates. Equation (9) indicates what type of average is to be expected, if the viscosity-molecular weight relation (2) is known for the series. It may be noted that the variations in the dependence of s and D upon M with the nature of the polymer and solvent system are much slighter than in respect to viscosity behavior.

In Table V are presented p -values computed from the observed dependence of s or D upon M (Eq. 9), and are compared with those obtained from viscosity by means of relation (5) or directly from the axis ratios. In Figs. 3 and 4,

TABLE V. Values of flexibility parameter p .

Compound	From diffusion	From sedimentation	From viscosity	Max. dev. %
Methyl cellulose ^a	0.57 ^b	—	0.59 ^c	5
Cellulose nitrate ^d	—	0.48	0.60	11
Amylose acetate ^e	0.48	0.49	0.53–0.57 ^f	11 (sed.)

^a See reference 2.

^b See reference 24.

^c The values for l/d originally given in Table III of reference 1 are erroneous and should be replaced respectively by 38.5, 55.5, 69.5, resulting in the above exponent.

^d See reference 7 of Table I.

^e See reference 22.

^f The lower value results from a comparison of the axis ratios determined by means of f/f_0 with the molecular weights. The upper one is derived from the viscosity values of l/d and has been used in Fig. 4.

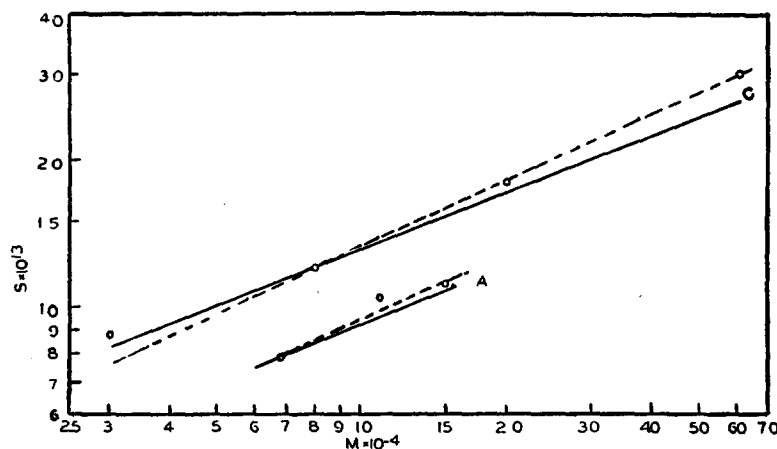


FIG. 4. Double logarithmic plot of sedimentation constants s vs. molecular weight M for amylose acetate (A) and cellulose nitrate (C). Circles indicate experimental values, dashed lines experimental slopes, solid lines computed ones.

D or s are plotted vs. M for these three polymer systems. For cellulose nitrate, the slope of the line through the second and the last point was calculated; in the other cases the two end points were used. The computed D or s were fitted through the second point in the former case and through the first one otherwise, using the p -values from viscosity in Eq. (9). The extent of the agreement between viscosity data and ultracentrifuge results, as interpreted by the present theory, is shown by a comparison of the slope of the solid lines (the p from viscosity data), and that of the dashed lines (the p from rate data). The last column in the table above contains the maximum deviations between experimental sedimentation or diffusion data and those calculated. In view of the accuracy obtainable and of factors discussed above, it does not appear necessary to determine the slopes in a more accurate manner. The molecular weights used in Figs. 3 and 4 represent ultracentrifuge values. It would be very desirable to have osmotic determinations in addition. The agreement obtained seems satisfactory, in spite of the fact that in two cases only two points were available for determining the slope, as may be judged from the graphs. Attempts to apply this theory to Signer's and Gross'²³ sedimentation data on some polystyrene samples and to Polson's²⁴ data on cellulose

acetate meet with failure, the exponents p turning out to be too small or too large. It would be very desirable to have sedimentation and diffusion data on the polystyrene and cellulose acetate fractions referred to in Table I.

Summarizing, it may be stated that by means of a combination of the present theory^{1,10} of intrinsic viscosity of long molecules with certain semi-empirical results on the shape of flexible chains in solution, it is possible to interpret the empirical relation between intrinsic viscosity and average degree of polymerization arising from a modification of Staudinger's rule, and to account for variations in the exponent with the nature of the polymer and of the solvent or solvent mixture.²⁵ Application of the hydrodynamic theory of sedimentation and diffusion combined with the above results gives the sedimentation or diffusion constant as a function of the molecular weight and the variation of this function with the internal flexibility of the chain and with the medium.

The author wishes to express his appreciation to Dr. John J. Grebe for the interest shown in this work.

Aid in carrying out the numerical calculations was received from Misses M. E. Chaplin and D. R. Simmons.

²³ R. Signer and H. Gross, *Helv. Chim. Acta* **17**, 348 (1934).

²⁴ Computed from data by A. Polson, *Kolloid Zeits.* **83**, 172 (1938).

²⁵ The influence of such factors on higher terms in the viscosity-concentration relation has since been discussed by E. M. Frith, *Trans. Faraday Soc.* **41**, 17, 90 (1945).