

## Rayleigh Scattering by Real Chain Molecules

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**Abstract:** The contribution to the intensity of Rayleigh scattering from a pair of units  $j, k$  of a chain molecule is shown to be proportional to  $\exp(-\mu^2 \langle r_{jk}^2 \rangle / 6)$ , the Gaussian approximation to the Fourier transform of the distribution function for the vector  $\mathbf{r}_{jk}$  connecting these scattering units (e.g.,  $\text{CH}_2$ ); here  $\mu = (4\pi/\lambda) \sin(\theta/2)$ ,  $\theta$  being the scattering angle. Higher order, non-Gaussian terms are unimportant in the Fourier transform of the distribution function throughout the range of  $\mu$  within which the groups may legitimately be treated as point scatterers. Realistic values of  $\langle r_{jk}^2 \rangle$  must be used, however. In particular, the customary assumption of proportionality of  $\langle r_{jk}^2 \rangle$  to  $|j - k|$  must be abandoned for shorter sequences, i.e., for  $|j - k| < ca. 200$  bonds in the case of polymethylene chains. Scattering functions  $P(\mu)$  for  $n$ -alkanes have been computed by summing the exponentials given above over all pairs  $j, k$ , the  $\langle r_{jk}^2 \rangle$  having been evaluated by rigorous statistical-mechanical methods. Average radii of gyration  $\langle s^2 \rangle = (n + 1)^{-2} \sum_{j,k} \langle r_{jk}^2 \rangle$  and the analogous sum of fourth moments  $(n + 1)^{-2} \sum_{j,k} \langle r_{jk}^4 \rangle$  have been computed as functions of chain length  $n$  using matrix methods recently developed which are applicable without approximation to the rotational isomeric state model. These sums provide the coefficients in the series expansions of  $P(\mu)$  and of  $P^{-1}(\mu)$  for terms in  $\mu^2$  and  $\mu^4$ . These and other approximations for the scattering function are compared with the more exact sum of exponentials cited above. The approximate Debye equation  $P(\mu) = (2/v^2) [v - 1 + \exp(-v)]$  for molecular scattering is rendered remarkably accurate, even for short chains in the case of polymethylenes, by redefining  $v$  as  $\mu^2 \langle s^2 \rangle$ , where  $s^2$  is the radius of gyration of the finite chain of length  $n$ .

In 1915 Debye<sup>1</sup> published his well-known relationship expressing the angular dependence of the intensity of Rayleigh radiation scattering by a system of identical, rigid molecules, mutually independent and randomly oriented in space, as a sum over all pairs of atoms of the molecule (see eq 1). Each term of the sum is determined by the distance  $r_{jk}$  of separation of atom pair  $j, k$ , the atoms being treated as point scatterers. Chain molecules in general and macromolecules in particular do not conform to the condition of rigidity. A system of such molecules presents, at a given instant, an array of configurations in which the distances  $r_{jk}$  vary over wide ranges from one molecule to another. The formulation of appropriate averages becomes necessary. Either of two procedures may be pursued: averages for the individual terms in the Debye sum may be sought and these averages summed, or the argument of the Debye equation may first be expanded in series and the sums over  $j, k$  of successive terms of the series subsequently averaged over the distribution of configurations (cf. below). Which procedure is the more appropriate will depend on the size (i.e., chain length) of the molecule in relation to the wavelength  $\lambda$  of the radiation and the scattering angle  $\theta$ .

Regardless of the choice of procedure, distribution functions for the distances  $r_{jk}$  are required. Thus, Rayleigh scattering by the system of chain molecules is intimately related to their configurational statistics, as was emphasized by Debye<sup>2</sup> in 1947. Over the ensuing 20 years, the use of light-scattering measurements as a means for characterizing the spatial configurational characteristics of macromolecules has gained widespread acceptance. Possibilities for extending the information to be gained from light scattering through use of X-rays have been indicated, notably by Kratky.<sup>3</sup> The ultimate utility for this purpose of X-ray scattering by dilute solutions of macromolecules remains to be

fully realized, however. A limitation has been imposed by inadequacies of approximations used in the past for treating the configurational statistics of pairs  $j, k$  of scattering elements separated by numbers of bonds which are small compared with the total chain length. Various models for chain molecules have been employed for this purpose, e.g., freely jointed chains, worm-like chains, and freely rotating chains. None is universally applicable to real chains of finite length, nor to pairs of scattering elements  $j, k$  of finite range within chains whose over-all length may be very great.

The inherent physical artificiality of these models poses an objection to their use which is more serious than the limitations of the mathematical functions they prescribe for various properties of the configuration distribution. (For example, the moments  $\langle r_{jk}^2 \rangle$  and  $\langle r_{jk}^4 \rangle$  are not generally represented satisfactorily for all values of  $|j - k|$  by any of these models.) Structural geometry, hindrances to rotation, etc., in the real chain cannot be transcribed, uniquely, to parameters of the model chains. The necessary correspondences do not exist. Hence, in adopting an artificial model, one severs connection with the very characteristics of the real chain which it is the purpose of theory to relate to the property (e.g., Rayleigh scattering) observed. Or, conversely, the legitimate object of the experiment may be to ascertain the relative energies of different conformations, for example, of the real chain. Expression of the results in terms of parameters of an artificial model thwarts achievement of this objective.

Newer methods<sup>4,5</sup> obviate resort to artificial models for treating real chains of finite length. The average (equilibrium) properties of real chains are now susceptible to quantitative treatment, without approximation other than the adoption of the rotational isomeric state scheme, which closely simulates the conformational character of the real chain and has broad precedent in the interpretation of small molecules. Molecular quan-

(1) P. Debye, *Ann. Physik*, **46**, 809 (1915).(2) P. Debye, *J. Phys. Chem.*, **51**, 18 (1947).(3) O. Kratky, *Pure Appl. Chem.*, **12**, 483 (1966).(4) P. J. Flory, *Proc. Natl. Acad. Sci. U. S.*, **51**, 1060 (1964).(5) P. J. Flory and R. L. Jernigan, *J. Chem. Phys.*, **42**, 3509 (1965).

tities of principal interest can be averaged over the configurations of the rotational isomeric chain by mathematical methods which are exact for chains of any length.

Here we present relationships for calculating the statistical mechanical averages of quantities required by the Debye equation for its application to Rayleigh scattering by real chain molecules of any length, and over the entire range of wavelength and scattering angle. Illustrative calculations are reported for polymethylene chains  $\text{H}-(\text{CH}_2)_{n+1}-\text{H}$ . Numerical results are compared with approximate formulas.

### Theory

**The Scattering Factor.** The Debye scattering factor  $P(\theta) = I(\theta)/I(0)$  expresses the intensity  $I(\theta)$  scattered at an angle  $\theta$  from the incident beam to the intensity  $I(0)$  scattered in the direction ( $\theta = 0$ ) of the incident beam. For a system of rigid molecules disoriented at random, it is given by<sup>1</sup>

$$P(\theta) \equiv I(\theta)/I(0) = (n+1)^{-2} \sum_{j,k} (\mu r_{jk})^{-1} \sin(\mu r_{jk}) \quad (1)$$

where  $r_{jk}$  is the distance between scattering elements  $j$  and  $k$  and  $\mu$  is the difference between the scattered and incident wave vectors  $\mathbf{k}$  and  $\mathbf{k}_0$ , *i.e.*

$$\mu = |\mathbf{k} - \mathbf{k}_0| = (4\pi/\lambda) \sin(\theta/2) \quad (2)$$

where  $\lambda$  is the wavelength of the radiation in the scattering medium. The double sum in eq 1 includes all scattering elements (*e.g.*,  $\text{CH}_2$  groups);  $n+1$  is the number of such scatterers,  $n$  being the number of skeletal bonds joining them in the chain molecule. Chain elements are assumed to act as point scatterers. The solution in which the molecules are dispersed is taken to be sufficiently dilute so that the distribution of the molecular centers over space is uncorrelated and therefore random. Contributions of individual molecules to the total scattered intensity are thus assured to be independent and additive. The series obtained<sup>2</sup> by expanding the sine functions in eq 1 is

$$P(\theta) = P(\mu) = (n+1)^{-2} \sum_{j,k} (1 - \mu^2 r_{jk}^2/3! + \mu^4 r_{jk}^4/5! - \dots) \quad (3)$$

The result obtained by averaging eq 1 over all configurations of the chain molecule is

$$P(\mu) \equiv \langle I(\theta)/I(0) \rangle = (n+1)^{-2} \sum_{j,k} \langle (\mu r_{jk})^{-1} \sin(\mu r_{jk}) \rangle \quad (4)$$

where angle brackets denote the statistical mechanical average of the quantity enclosed therein. Letting  $W(\mathbf{r}_{jk})$  represent the distribution of vectors  $\mathbf{r}_{jk}$ , we have

$$\langle (\mu r_{jk})^{-1} \sin(\mu r_{jk}) \rangle = \int_0^\infty (\mu r_{jk})^{-1} \sin(\mu r_{jk}) \times 4\pi r_{jk}^2 W(\mathbf{r}_{jk}) dr_{jk} \quad (5)$$

$$= \int \exp(i\mu \cdot \mathbf{r}_{jk}) W(\mathbf{r}_{jk}) d\mathbf{r}_{jk} \quad (6)$$

Equations 5 and 6 are alternative expressions for the Fourier transform of  $W(\mathbf{r}_{jk})$ . Hence, we may utilize a series developed by Nagai<sup>6</sup> for the Fourier transform

(6) K. Nagai, *J. Chem. Phys.*, **38**, 924 (1963).

of the distribution function of the end-to-end vector. After replacement of the end-to-end vector by  $\mathbf{r}_{jk}$ , we obtain

$$\langle (\mu r_{jk})^{-1} \sin(\mu r_{jk}) \rangle = \exp(-\mu^2 \langle r_{jk}^2 \rangle / 6) [1 - (1/8)(1 - 3\langle r_{jk}^4 \rangle / 5\langle r_{jk}^2 \rangle^2)(\mu^2 \langle r_{jk}^2 \rangle / 3)^2 + \dots] \quad (7)$$

This expression is a series in the even moments of the pair distances  $r_{jk}$  multiplied by the Fourier transform of the Gaussian distribution. In the limit  $|k-j| \rightarrow \infty$ , only the leading term remains in eq 7.

For values of  $\mu^2 \langle r_{jk}^2 \rangle / 3$  much in excess of 2, the magnitude of  $\langle (\mu r_{jk})^{-1} \sin(\mu r_{jk}) \rangle$  is rendered small by the exponential factor in eq 7. At this point the second term of the series in brackets in eq 7 is

$$-(1/2)(1 - 3\langle r_{jk}^4 \rangle / 5\langle r_{jk}^2 \rangle^2)$$

Its contribution is significant compared to unity only if the quantity in parentheses is of the order of 0.1 or greater. For polymethylene  $|j-k|$  must be less than about 25 bonds in order for  $3\langle r^4 \rangle / 5\langle r^2 \rangle^2$  to depart from unity by such an amount.<sup>7</sup> For chain sequences of this length  $\langle r^2 \rangle^{1/2}$  is only *ca.* 20 Å or less. Scattering experiments affording information on distances in this range must of course be carried out with X-rays; *i.e.*, the required values of  $\mu$  can in practice be covered only through use of radiation in the X-ray range. The foregoing root-mean-square inter-unit distance of 20 Å is to be compared with a mean diameter of the polymethylene chain of about 5 Å. Obviously, the approximation of the scattering elements ( $\text{CH}_2$ , for example) as point centers when  $r_{jk}$  is as small as 20 Å is no longer valid. We conclude that, for any combination of parameters validating the approximation of the scattering groups by point scatterers, omission of higher terms of the series in eq 7 will certainly be justified for a random-coil chain molecule having a tortuosity comparable with, or not much less than, that of polymethylene. Only for very stiff chains of intermediate length, *e.g.*, for poly-L-proline, may circumstances arise where higher terms than those specifically included in eq 7 will be needed.

In fact, for most flexible chains it will be justified, within the limitations of the point-scattering approximation, to replace the series in brackets in eq 7 by unity under all conditions (*i.e.*, for any feasible  $\mu$ ), giving

$$\langle (\mu r_{jk})^{-1} \sin(\mu r_{jk}) \rangle = \exp(-\mu^2 \langle r_{jk}^2 \rangle / 6) \quad (8)$$

and

$$P(\mu) = (n+1)^{-2} \sum_{j,k} \exp(-\mu^2 \langle r_{jk}^2 \rangle / 6) \quad (9)$$

This result was obtained by Debye<sup>2</sup> and it has been used by Kratky, Porod, and coworkers<sup>8</sup> in their treatment of X-ray scattering of chain molecules. These expressions are tantamount to representation of  $W(\mathbf{r}_{jk})$  in the Gaussian approximation. It is known from previous analysis<sup>7</sup> of the series for the Fourier transform of  $W(\mathbf{r})$ , where  $\mathbf{r} \equiv \mathbf{r}_{on}$  is the end-to-end vector for the entire chain, that conditions for compliance with the Gaussian form, eq 8 and 9, for the Fourier transform are less stringent than for  $W(\mathbf{r})$  itself to be Gaussian.

(7) R. L. Jernigan and P. J. Flory, submitted for publication; R. L. Jernigan, Thesis, Stanford University, 1967.

(8) S. Heine, O. Kratky, G. Porod, and P. J. Schmitz, *Makromol. Chem.*, **46**, 690 (1961).

For small values of  $\mu$  accessible in light-scattering experiments, the exponent in eq 9 is appreciably large only for long chains, thereby leading to a dependence on  $\theta$  which is contributed primarily by segment pairs at long average separations. With X-ray scattering, *i.e.*, large  $\mu$ , terms in the sum in eq 9 are significant only if  $j$  and  $k$  are at small separations.

For sufficiently large values of  $|j - k|$  (greater than about 200 bonds for polymethylene), it is legitimate to assume proportionality between  $\langle r_{jk}^2 \rangle$  and  $|j - k|$ , provided that the chain is unperturbed by volume exclusion or other long-range interactions. Under these conditions we have

$$\langle r_{jk}^2 \rangle \cong ml^2 \langle (r_m^2) / ml^2 \rangle_{m \rightarrow \infty} = ml^2 \langle (r^2) / nl^2 \rangle_{n \rightarrow \infty} \quad (10)$$

where  $m = |j - k|$ . Substitution in eq 9 and simplification of the series gives

$$P(\mu) = (n + 1)^{-1} + 2/(n + 1)^2 \sum_{m=1}^n (n - m + 1) \times \exp \left[ \frac{-\mu^2 ml^2 \langle (r^2) \rangle}{6 \left( \frac{\langle r^2 \rangle}{nl^2} \right)_{n \rightarrow \infty}} \right] \quad (11)$$

Replacement of the summation in eq 11 by integration yields

$$P(\mu) = (n + 1)^{-1} + \frac{2n}{v^2(n + 1)^2} \times \{ (n - v) \exp(-v) + n(v - 1) \exp(-v/n) \} \quad (12)$$

where  $v$  is defined by

$$v = \frac{\mu^2 nl^2 \langle (r^2) \rangle}{6 \left( \frac{\langle r^2 \rangle}{nl^2} \right)_{n \rightarrow \infty}} \quad (13)$$

Some of the error introduced by assuming  $\langle r_{jk}^2 \rangle$  to be proportional to  $|j - k|$  may be compensated by redefining  $v$  as

$$v = \mu^2 \langle s^2 \rangle \quad (14)$$

where  $\langle s^2 \rangle$  is the mean-square radius of gyration for a chain of length  $n$ . Alternatively, in the limit of infinite chains eq 14 could be replaced by

$$v = \mu^2 \langle r^2 \rangle / 6 \quad (15)$$

In eq 14 and 15,  $\langle s^2 \rangle$  and  $\langle r^2 \rangle$  are to be assigned their values for the finite chains of length  $n$ ; asymptotic values for the ratios  $\langle s^2 \rangle / nl^2$  and  $\langle r^2 \rangle / nl^2$  are not implied. Equation 14 would be expected to compensate the error introduced by the integration better than does eq 15. Confirmation of this expectation will be demonstrated later.

Debye<sup>2</sup> has derived a limiting form of eq 12 by deleting terms which are small when  $n \gg 1$  and  $n \gg v$ . Consequently, his equation should be valid for long chains and small values of  $\mu$ . His result is

$$P(\mu) = (2/v^2)[v - 1 + \exp(-v)] \quad (16)$$

In the domain of small  $\mu$  and large  $n$ , this equation is expected to perform more satisfactorily than eq 12 because most of the terms neglected are negative. Hence, their omission partially compensates the error introduced by the integration.

Equations 12-16 are strictly valid only for chains at the  $\theta$  point, *i.e.*, when they are free of long-range perturbations associated with the excluded volume

effect. However, these equations should remain approximately valid for perturbed chains, provided that perturbed values of  $\langle s^2 \rangle$  or  $\langle r^2 \rangle$  are used.

The series expansion of eq 16 is

$$P(\mu) = 1 - (2/3!)v + (2/4!)v^2 - (2/5!)v^3 + (2/6!)v^4 - \dots \quad (17)$$

and its reciprocal is

$$P^{-1}(\mu) = 1 + v/3 + v^2/36 - v^3/540 - v^4/6480 + \dots \quad (18)$$

It should be noted that the approximation of proportionality, eq 10, between  $\langle r_m^2 \rangle$  and  $m = |j - k|$ , which is required to integrate over the separation of scattering elements, is much less realistic than the assumption that  $W(\mathbf{r}_{jk})$  is Gaussian in form. The two approximations are essentially unrelated. Therefore, eq 9 should be more widely applicable than eq 11, 12, or 16.

By returning to eq 4 and performing a series expansion of the sine function, one obtains

$$P(\mu) = 1 - (2/3!)S_2\mu^2 + (2/5!)S_4\mu^4 - (2/7!)S_6\mu^6 + \dots \quad (19)$$

where

$$S_{2p} = (n + 1)^{-2} \sum_{0 \leq j < k \leq n} \langle r_{jk}^{2p} \rangle \quad (20)$$

The first of these sums is just the average square radius of gyration, *i.e.*,  $S_2 = \langle s^2 \rangle$ . Equation 19 may be written alternatively as follows

$$P(\mu) = 1 - v/3 + (3S_4/20S_2^2)(v/3)^2 - (3S_6/280S_2^3)(v/3)^3 + \dots \quad (19')$$

where we choose to define  $v$  according to eq 14; *i.e.*,  $v = \mu^2 S_2$ . In the limit of infinite chains, eq 19 converges to eq 17, provided that long-range perturbations which would vitiate eq 17 are not operative. Direct correspondence of terms in eq 17 and 19 leads to the limiting values of  $S_{2p}$  as follows

$$\lim_{n \rightarrow \infty} S_{2p} = \frac{(2p + 1)!}{(p + 2)!} S_2^p \quad (\text{for } 1 \leq p) \quad (21)$$

For small  $\mu$ , *e.g.*, optical scattering, usually the quantity considered is the inverse scattering factor. Inversion of eq 19 yields

$$P^{-1}(\mu) = 1 + (S_2/3)\mu^2 + (S_2^2/9 - S_4/60)\mu^4 + (S_2^3/27 - S_2S_4/90 + S_6/2520)\mu^6 + \dots \quad (22)$$

or

$$P^{-1}(\mu) = 1 + (v/3) + (1 - 3S_4/20S_2^2)(v/3)^2 + (1 - 3S_4/10S_2^2 + 3S_6/280S_2^3)(v/3)^3 + \dots \quad (22')$$

In analogy to the expression of the Fourier transform of the distribution function  $W(\mathbf{r}_{jk})$  as its limiting Gaussian exponential multiplied by a series in the even moments of  $r_{jk}$ , we may factor out the limiting form of  $P(\mu)$  given in eq 16, thereby obtaining

$$P(\mu) = (2/v^2)[v - 1 + \exp(-v)] \times \left[ 1 + \left( \frac{2}{4!} \right) \left( \frac{S_4}{5S_2^2} - 1 \right) v^2 - \left( \frac{2}{5!} \right) \times \left( \frac{S_6}{42S_2^3} - \frac{S_4}{3S_2^2} + \frac{2}{3} \right) v^3 + \dots \right] \quad (23)$$

**Derivation of the Required Sums Over Moments of the Distribution.** Equations 19, 22, and 23 express the angular dependence of the scattered intensity as power series in  $\sin^2(\theta/2)$ . The practicality of these equivalent renditions of  $P(\mu)$  depends of course on the convergence of the series, which in turn is dependent in first approximation on the magnitude of the quantity  $S_2\mu^2 = [4\pi \sin(\theta/2)]^2 \langle s^2 \rangle / \lambda^2$ . In general, the root-mean-square radius of gyration  $\langle s^2 \rangle^{1/2}$  must be less than about  $\lambda/10$  in order for the series to converge satisfactorily for values of  $\theta$  up to  $150^\circ$ , the usual range for light-scattering measurements on polymer solutions. Determination of the extent to which the third terms (*i.e.*, the terms which are quadratic in  $\mu^2$ , or in  $\sin^2\theta/2$ ) of eq 19 and 22 contribute relative to the second terms requires evaluation of  $S_4$  in addition to  $S_2 \equiv \langle s^2 \rangle$ . The method for the calculation of these quantities is outlined below.

The rotational isomeric state model<sup>9</sup> replaces the continuous range of rotational angle about a given bond by several discrete angles, judiciously chosen. The bond is treated as if restricted to adoption of one or another of these rotational states to the exclusion of all other angles. The states are generally so chosen as to coincide with minima in the rotational hindrance potentials. The validity of such an approximation for alkane chains has been amply demonstrated for treatment of a variety of properties.<sup>10-14</sup> The number of states is taken to be three, in conformity with the threefold potential for a  $-\text{CH}_2-\text{CH}_2-$  bond. The states may be located at  $0^\circ$  (*trans*),  $120^\circ$  (*gauche*<sup>+</sup>), and  $240^\circ$  (*gauche*<sup>-</sup>). Small departures of the potential minima from these positions are easily compensated by minor adjustments of statistical weight parameters<sup>14</sup> (*cf.* below). Bond rotations exhibit an interdependence which is conveniently taken into account by assignment of statistical weights to pairs of rotational states. The set of statistical weights for a given bond pair is appropriately presented in the form of a matrix, with rows indexing the rotational state of bond  $i - 1$  and the columns indexing the state of bond  $i$ . The configurational partition function  $Z$  is readily generated by taking the serial product of such matrices, *i.e.*

$$Z = \mathbf{J}^* \mathbf{U}_1^{(n)} \mathbf{J}$$

where  $\mathbf{J}^*$  is a  $1 \times \nu$  row composed of unity followed by  $\nu - 1$  zeros,  $\nu$  being the number of rotational states and therefore the order of  $\mathbf{U}_j$ .  $\mathbf{J}$  is the  $\nu \times 1$  column of ones; the notation  $(\ )_1^{(n)}$  signifies the serial product of  $n$  terms, the first possessing serial index 1. By condensation of previous results<sup>5,15</sup> for  $\langle r^2 \rangle$ , we have for the mean-square distance between chain elements  $j$  and  $k$

$$\langle r_{jk}^2 \rangle = 2Z^{-1} \mathbf{J}^* \mathbf{U}_1^{(j)} \mathcal{G}_{j+1}^{(k-j)} \mathcal{B} \mathbf{U}_{k+1}^{(n-k)} \mathbf{J} \quad (24)$$

where supermatrices  $\mathcal{A}$ ,  $\mathcal{B}$ , and  $\mathcal{G}$  are defined by

(9) M. V. Volkenstein, "Configurational Statistics of Polymeric Chains" (English translation), Interscience Publishers, Inc., New York, N. Y., 1963.

(10) C. A. J. Hoeve, *J. Chem. Phys.*, **35**, 1266 (1961).

(11) K. Nagai and T. Ishikawa, *ibid.*, **37**, 496 (1962).

(12) W. J. Leonard, Jr., R. L. Jernigan, and P. J. Flory, *ibid.*, **43**, 2256 (1965).

(13) A. Abe, R. L. Jernigan, and P. J. Flory, *J. Am. Chem. Soc.*, **88**, 631 (1966).

(14) R. L. Jernigan and P. J. Flory, *J. Chem. Phys.*, **47**, 1999 (1967).

(15) K. Nagai, *ibid.*, **47**, 2052 (1967).

$$\alpha = [\mathbf{E}_\nu, \mathbf{0} \cdots \mathbf{0}]$$

$$\mathcal{B} = \begin{bmatrix} \mathbf{0} \\ \vdots \\ \mathbf{0} \\ \mathbf{E}_\nu \end{bmatrix}$$

and

$$\mathcal{G}_j = \begin{bmatrix} \mathbf{U} (\mathbf{U} \otimes \mathbf{1}^T) \|\mathbf{T}\| & (l^2/2)\mathbf{U} \\ \mathbf{0} (\mathbf{U} \otimes \mathbf{E}_3) \|\mathbf{T}\| & \mathbf{U} \otimes \mathbf{1} \\ \mathbf{0} \mathbf{0} & \mathbf{U} \end{bmatrix}_j \quad (25)$$

$\mathbf{E}$  is the unit matrix of order denoted by its subscript;  $\otimes$  denotes the direct product;  $\mathbf{T}_j$  is the matrix that transforms quantities expressed in the coordinate system based upon bond  $j + 1$  into their representations in the coordinate system related to bond  $j$ ;  $\|\ \|\$  is an operator which forms a diagonal supermatrix from a matrix which is a function of the rotational angle. For example

$$\|\mathbf{F}\| = \begin{bmatrix} \mathbf{F}(1) \\ \vdots \\ \mathbf{F}(\nu) \end{bmatrix}$$

The bond vector is represented as

$$\mathbf{l}_j = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \mathbf{l}_j$$

The subscript appended to matrices as in eq 25 and elsewhere designates the index of all serially dependent quantities within the matrix. As required by eq 20,  $S_2$  is the sum of terms given by eq 24 over all values of  $j$  and  $k$ . An extension of the matrix method used to generate  $\langle r^2 \rangle$  yields an exact result for  $S_2$ .

$$S_2 = 2(n+1)^{-2} Z^{-1} \mathbf{J}^* \mathcal{A} s_1^{(n)} \mathcal{B} \mathbf{J} \quad (26)$$

where

$$s_j = \begin{bmatrix} \mathbf{U} \mathcal{A} \mathcal{G} (l^2/2)\mathbf{U} \\ \mathbf{0} \mathcal{G} \mathcal{B} \\ \mathbf{0} \mathbf{0} \mathbf{U} \end{bmatrix}_j \quad (27)$$

In eq 26 the factor  $\mathcal{A}$  extracts the first  $\nu$  rows (*i.e.*, the first super-row) of the product of  $s$  factors, and the factor  $\mathcal{B}$  rejects all but the final  $\nu$  columns of these rows. Thus, only the right-most of the three terms in the first super-row of the serial product  $s_1^{(n)}$  is retained. It is easily verified that the second super-element of  $\mathcal{A} s_1^{(j-1)}$  always contains terms which are collected, after multiplication by one more  $s$  matrix, into the position from which the answer is extracted.

In a completely analogous manner<sup>5,16</sup>

$$\langle r_{jk}^4 \rangle = 4Z^{-1} \mathbf{J}^* \mathbf{U}_1^{(j)} \mathcal{K} \mathcal{K}_{j+1}^{(k-j)} \mathcal{B} \mathbf{U}_{k+1}^{(n-k)} \mathbf{J} \quad (28)$$

with  $\mathcal{K}_j$  defined by the matrix shown in eq 29. From eq 28 it follows by analogy with eq 24, 26, and 27 that

(16) The condensation of the previous formulation<sup>5</sup> of the fourth moment to eq 28 and 29 will be published elsewhere.

$$\mathcal{K}_j = \begin{bmatrix} \mathbf{U} & P\mathbf{U} & 2(\mathbf{U} \otimes I^T) \parallel \mathbf{T} \parallel & P^2(\mathbf{U} \otimes I^T) \parallel \mathbf{T} \parallel & \mathbf{0} & (\mathbf{U} \otimes I^T \otimes I^T) \parallel \mathbf{T} \otimes \mathbf{T} \parallel & \mathbf{0} & \mathbf{0} & (P^4/4)\mathbf{U} \\ \mathbf{0} & \mathbf{U} & \mathbf{0} & (\mathbf{U} \otimes I^T) \parallel \mathbf{T} \parallel & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & (P^2/2)\mathbf{U} \\ \mathbf{0} & \mathbf{0} & (\mathbf{U} \otimes E_3) \parallel \mathbf{T} \parallel & (P^2/2)(\mathbf{U} \otimes E_3) \parallel \mathbf{T} \parallel & \mathbf{U} \otimes \mathbf{1} & (\mathbf{U} \otimes E_3 \otimes I^T) \parallel \mathbf{T} \otimes \mathbf{T} \parallel & [\mathbf{U} \otimes (\Pi^T)] \parallel \mathbf{T} \parallel & \mathbf{0} & (P^2/2)(\mathbf{U} \otimes \mathbf{1}) \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & (\mathbf{U} \otimes E_3) \parallel \mathbf{T} \parallel & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{U} \otimes \mathbf{1} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{U} & \mathbf{0} & (\mathbf{U} \otimes I^T) \parallel \mathbf{T} \parallel & \mathbf{0} & (P^2/2)\mathbf{U} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & (\mathbf{U} \otimes E_3 \otimes \mathbf{1}) \parallel \mathbf{T} \parallel & (\mathbf{U} \otimes \mathbf{1} \otimes E_3) \parallel \mathbf{T} \parallel & \mathbf{U} \otimes \mathbf{1} \otimes \mathbf{1} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & (\mathbf{U} \otimes E_3) \parallel \mathbf{T} \parallel & \mathbf{0} & \mathbf{U} \otimes \mathbf{1} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & (\mathbf{U} \otimes E_3) \parallel \mathbf{T} \parallel & \mathbf{U} \otimes \mathbf{1} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{U} \otimes \mathbf{1} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{U} \otimes \mathbf{1} \end{bmatrix}_j \quad (29)$$

the sums required by eq 20 for  $S_4$  are generated by the following matrix multiplications

$$S_4 = 4(n+1)^{-2} \mathbf{Z}^{-1} \mathbf{J}^* \mathcal{R}_1^{(n)} \mathcal{B} \mathbf{J} \quad (30)$$

where

$$\mathcal{R}_j = \begin{bmatrix} \mathbf{U} & \mathcal{K} & (P^4/4)\mathbf{U} \\ \mathbf{0} & \mathcal{K} & \mathcal{K}\mathcal{B} \\ \mathbf{0} & \mathbf{0} & \mathbf{U} \end{bmatrix}_j \quad (31)$$

### Numerical Calculations for Polymethylene Chains

The statistical weight matrix for alkane chains<sup>14</sup> is

$$\mathbf{U}_j = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix} \text{ for } 1 < j < n \quad (32)$$

With *gauche* rotational states chosen at  $\pm 120^\circ$ , the appropriate statistical weights<sup>14</sup> are  $\sigma = \exp(-500 \text{ cal mole}^{-1}/RT)$  and  $\omega = \exp(-2000 \text{ cal mole}^{-1}/RT)$ . Matrices  $\mathbf{U}$  for terminal bonds are to be represented by the identity, i.e., by  $\mathbf{U}_1 = \mathbf{U}_n = \mathbf{E}_\nu$ . Throughout the calculations presented below, all skeletal bond angles  $\angle \text{CCC}$  were taken to be  $112^\circ$ , and a temperature of  $140^\circ$  was adopted. Figure 1 depicts the dependence of  $S_2$  and  $S_4$  on chain length. For comparison, results

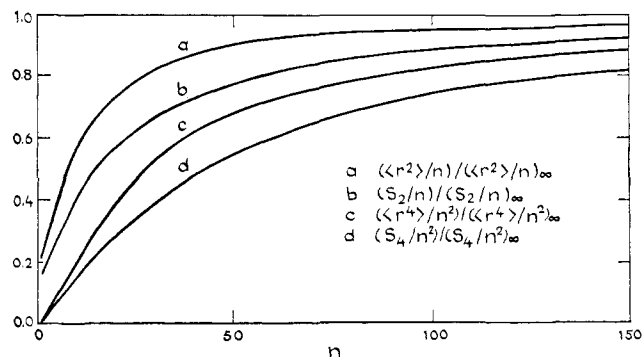


Figure 1. Reduced moments  $\langle r^2 \rangle/n$ ,  $S_2/n$ , etc. calculated for  $n$ -alkane chains, plotted against the number  $n$  of skeletal bonds. The reduced moments are divided by their values in the limit  $n \rightarrow \infty$  in each instance.

of calculations of  $\langle r^2 \rangle$  and  $\langle r^4 \rangle$  on the same basis are also presented. All quantities are plotted as dimensionless ratios:  $(\langle r^2 \rangle/n) / (\langle r^2 \rangle/n)_{n \rightarrow \infty}$ ,  $(S_2/n) / (S_2/n)_{n \rightarrow \infty}$ ,  $(\langle r^4 \rangle/n^2) / (\langle r^4 \rangle/n^2)_{n \rightarrow \infty}$ , and  $(S_4/n^2) / (S_4/n^2)_{n \rightarrow \infty}$ , each of which converges to unity for  $n = \infty$ .

The order of decreasing rates of convergence is  $\langle r^2 \rangle/n$ ,  $S_2/n$ ,  $\langle r^4 \rangle/n^2$ ,  $S_4/n^2$ . The relationship between  $\langle r^2 \rangle/n$  and  $S_2/n$  parallels that between  $\langle r^4 \rangle/n^2$  and  $S_4/n^2$ , as should be expected from the fact that  $S_2$  and  $S_4$  are equivalent sums of the second and fourth moments of  $r$ . Because of the presence in these sums for a given chain length of a large number of moments for shorter sequences whose ratios have not reached

their limits, the convergence of  $S_2$  and  $S_4$  is more protracted than the convergence of the corresponding moments of  $r$ . The slower convergence of higher moments with chain length as compared with lower moments was observed previously for other types of molecules as well as for artificial chain models.<sup>7</sup>

Numerical evaluation of  $S_2$  and  $S_4$  for finite chains furnishes the coefficients of  $v$  and  $v^2$  in eq 19', 22', and 23. The sufficiency of these terms with neglect of higher ones in the several series bears examination. The convergence of each series depends on the ratios  $S_4/S_2^2$ ,  $S_6/S_2^3$ , etc., whose limiting values for  $n \rightarrow \infty$  (see eq 21) are 5, 42, etc., respectively. The ratio  $S_4/5S_2^2$  plotted against  $n$  in Figure 2 converges slowly

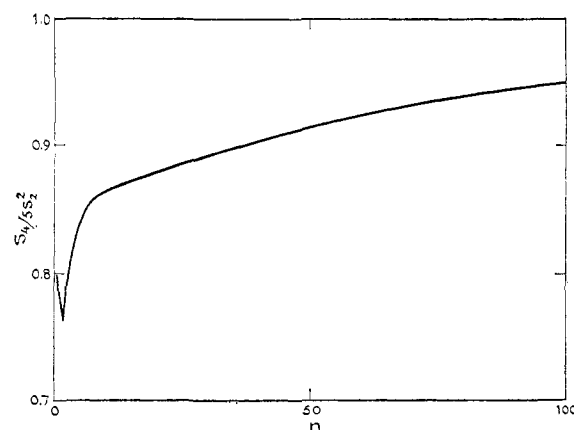


Figure 2. The ratio  $S_4/5S_2^2$  calculated for short  $n$ -alkane chains.

to its limiting value of unity for  $n = \infty$ , but it exceeds 0.8 for all values of  $n$  beyond the sharp minimum at  $n = 2$ . Numerical values of higher sums  $S_{2p}$  for short chains ( $n < 10$ ), which were obtained by calculating  $S_{2p}$  for every allowed configuration and then summing with appropriate weights, show the ratios  $S_6/42S_2^3$ , etc., likewise to be near their limits even for small  $n$ .

It follows from these observations that the series for  $P^{-1}(\mu)$  given by eq 22' (or by eq 22) converges more rapidly than the series for  $P(\mu)$  given by eq 19' (or by eq 19). The series in eq 23 converges much more rapidly than either as will readily be apparent from comparison of corresponding coefficients of the respective series. Moreover, the coefficients of powers of  $v$  in eq 19' and 22' approach constant values with increase in chain length  $n$ , but those of the series in eq 23 vanish with increase in  $n$ . The latter series therefore converges more rapidly the greater the chain length. In fact, for polymethylene chains of length  $n > 10$ , all terms beyond unity of the series in eq 23 may be neglected for values of  $v$  of the order of unity or less. This range of  $v$  includes light-scattering experiments and indeed any experimental situation suitable for determination

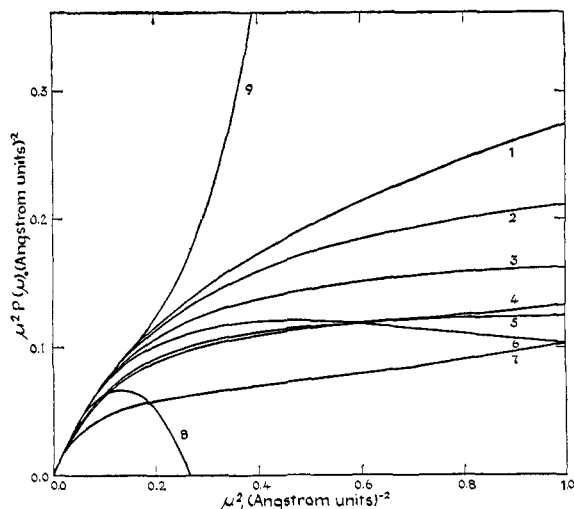


Figure 3. Plots of  $\mu^2 P(\mu)$ , variously calculated, against  $\mu^2$  for a polymethylene (*n*-alkane) chain with  $n = 10$ : curve 1, eq 9 with the  $\langle r_{jk}^2 \rangle$  calculated for sequences of  $|j - k|$  units; curve 2, eq 22 truncated at term in  $\mu^2$  (or  $v$ ); curve 3, eq 16 with  $v = \mu^2 \langle s^2 \rangle$  (eq 14); curve 4, eq 12 with  $v = \mu^2 \langle s^2 \rangle$ ; curve 5, eq 16 with  $v = \mu^2 \langle r^2 \rangle / 6$  (eq 15); curve 6, eq 22 truncated at term in  $\mu^4$  (or  $v^2$ ); curve 7, eq 11; curve 8, eq 19 truncated at  $\mu^2$  (or  $v$ ); curve 9, eq 19 truncated at  $\mu^4$  (or  $v^2$ ).

of the moments of the molecule as a whole. Higher terms in eq 23 may play a more important role for stiffer chains, *e.g.*, for poly-L-proline.<sup>17</sup>

In Figure 3 we show the results of calculations of the scattering factor, plotted as  $\mu^2 P(\mu)$  against  $\mu^2$ , for a polymethylene chain of only  $n = 10$  skeletal bonds (*n*-undecane). The chain length is too low to justify the point-scatterer approximation, but the choice serves to accentuate differences between the various approximations. Curve 1 has been calculated according to eq 9 by taking the sum of exponentials over all pairs  $j, k$ . Inasmuch as calculations<sup>7</sup> show  $\langle r_{jk}^2 \rangle$  for a sequence of specified length  $m = |j - k|$  to depend very little on the length of the chain of which the sequence is a part, or on its location in the chain, the  $\langle r_{jk}^2 \rangle$  were equated to the  $\langle r_m^2 \rangle$  for a finite sequence  $m$  in an infinite chain. In fact, the ratio  $\langle r_m^2 \rangle / ml^2$  for a sequence of  $m$  bonds within a polymethylene chain of great length closely approximates the corresponding ratio  $\langle r^2 \rangle / nl^2$  for an independent chain of the same number of bonds, *i.e.*, with  $n = m$ .<sup>7,18</sup> This representation of the scattering factor is the most accurate, for reasons given above. It is essential, however, to avoid the substitution  $\langle r_{jk}^2 \rangle = |j - k| (\langle r^2 \rangle / nl^2)_{n \rightarrow \infty}$ .

Curves 2 to 9 in Figure 3 represent other approximations for  $P(\mu)$  as specified in the legend to this figure. The Debye equation (16) with  $v$  defined by eq 14 is shown by curve 3. This identification of  $v$  with  $\mu^2 \langle s^2 \rangle$ , where  $\langle s^2 \rangle$  is the radius of gyration calculated for  $n = 10$ , is unprecedented in previous treatments of Rayleigh scattering. Equation 26 yields the requisite numerical values of  $\langle s^2 \rangle$  for chains of finite length. Curve 5, calculated from eq 16 with  $v$  given by eq 15, is a less satisfactory approximation to curve 1. Surprisingly, the unabridged eq 12 with  $v$  defined by eq 14 offers a poorer approximation (curve 4) than eq 16 ob-

(17) P. R. Schimmel and P. J. Flory, *Proc. Natl. Acad. Sci. U. S.*, **58**, 52 (1967).

(18) K. Nagai, *J. Chem. Phys.*, **45**, 838 (1966).

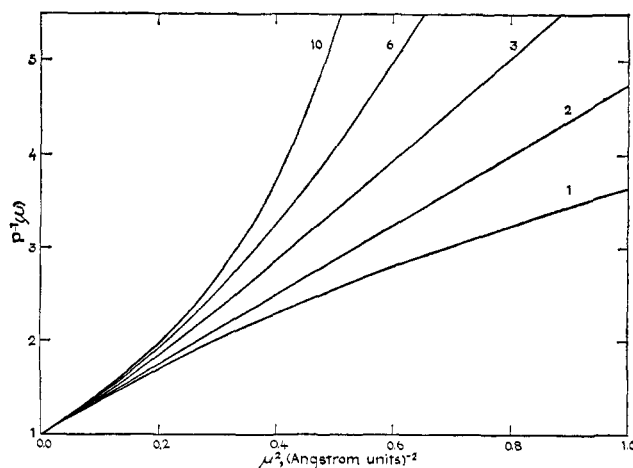


Figure 4. The reciprocal of the scattering function,  $P(\mu)^{-1}$ , plotted against  $\mu^2$  for chains of length  $n = 10$ . See legend for Figure 3 for identification of the curves numbered 1, 2, 3, and 6. Curve 10 represents eq 23 truncated after the term in  $v^2$ . The value of  $S_2$  used as required here and in Figure 3 is  $11.2 \text{ \AA}^2$ .

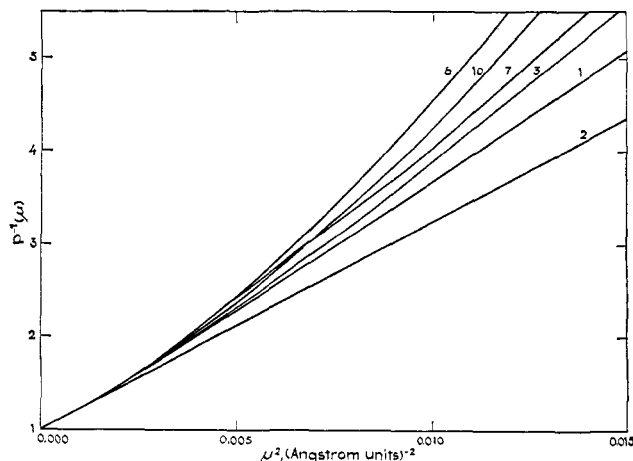


Figure 5. Reciprocal scattering function for an *n*-alkane chain with  $n = 263$ . Numerals identify curves calculated as specified in the legends to Figures 3 and 4.  $S_2$  is  $668 \text{ \AA}^2$ .

tained from eq 12 by omission of terms in  $1/n$  (curve 3). Terms of lower order in  $n$  are of course included in eq 11, shown by curve 7. Yet, this curve departs markedly from curve 1. The disparity arises in large part from the error in taking  $\langle r_{jk}^2 \rangle$  to be proportional to  $|j - k|$  in calculating curve 7. Truncation of eq 22, or 22', for  $P^{-1}(\mu)$  after the second term offers the best approximation (curve 2) to curve 1 for this very short chain. Inclusion of the term in  $\mu^4$ , or  $v^2$ , yields the less satisfactory curve 6. Truncation of eq 19, or 19', for  $P(\mu)$  at the second or third term results in curves 8 and 9, respectively, which depart markedly from curve 1 at large values of  $\mu^2$ .

In Figure 4, curves 1, 2, 3, and 6 from Figure 3 are plotted as  $P^{-1}(\mu)$  against  $\mu^2$ . Also included is curve 10 representing eq 23 truncated after the second term of the series. It shows the largest deviation from curve 1 for *n*-undecane.

Similar calculations for a polymethylene chain consisting of 263 bonds are shown in Figure 5. The scattering factor obtained by taking the sum of Gaussian terms in eq 9 should be subject to a negligible error in

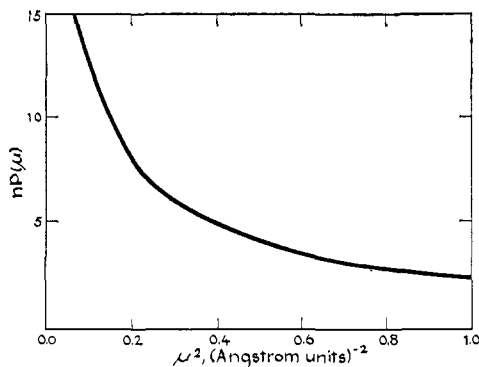


Figure 6. The relative intensity,  $nP(\mu)$ , per scattering element calculated by eq 33 for polymethylene in the limit  $n \rightarrow \infty$ , plotted against  $\mu^2$ .

this case. It is again shown as curve 1; numeration of other curves corresponds to their designations in Figures 3 and 4. The Debye equation (16) with  $v$  defined by eq 14 (curve 3) offers the best approximation to curve 1. The series for  $P^{-1}(\mu)$  is slightly less satisfactory for this longer chain; curves 2 and 6, representing this series truncated at its second and third terms, respectively, exhibit deviations setting in at small values of  $\mu^2$ . Curve 10, representing eq 23, offers a much better approximation than the corresponding curve for  $n = 10$  in Figure 4. It is to be observed that the range of  $v$  encompassed in these figures is large, going much be-

yond that normally covered in experiments on molecular scattering. Higher values of  $v$  were included in these calculations in order to accentuate differences between the various curves.

For very long chains measured at finite values of  $\mu^2$  such that  $\mu^2 \langle s^2 \rangle \gg 1$ , the pairs  $j, k$  which contribute appreciably to the scattering function are those for which  $|j - k| \ll n$ . The intensity  $I(\theta)$  per scattering element observed at an angle  $\theta > 0$  is proportional to  $nP(\mu)$ , and it is independent of the subdivision of the  $Nn$  scattering elements into separate molecules, subject to fulfillment of the conditions stated.

According to eq 9 with approximations appropriate in the limit  $n \rightarrow \infty$

$$nP(\mu) = n^{-1} \sum_{j,k} \exp(-\mu^2 \langle r_{jk}^2 \rangle / 6) = 2 \sum_{m=1}^{\infty} \exp(-\mu^2 \langle r_m^2 \rangle / 6) \quad (33)$$

This function, computed from the values of  $\langle r_m^2 \rangle$  for finite sequences as above, is plotted against  $\mu^2$  in Figure 6. Similar calculations for chain molecules other than polymethylene and comparisons with artificial models and with results of X-ray scattering by polymer solutions will be presented in a later paper.

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## Relaxation Effects in Associating Electrolytes<sup>1</sup>

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*Contribution from the Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut. Received December 4, 1967*

**Abstract:** The dissociation-recombination kinetics in associating electrolytes are shown to provide an additional mechanism for the relaxation of the asymmetric charge distributions produced in the ionic atmospheres by migration of the ions in an external field. The relaxation effects are reduced significantly (the Onsager relaxation field by as much as 23%) when two conditions are satisfied: (1) the rate of ionic recombination is within two orders of magnitude of the diffusion-controlled rate, and (2) the lifetime of the associated species is at least comparable to the relaxation time of the ionic atmosphere. The theory of Debye and Falkenhagen for conductance and dielectric dispersion in alternating weak fields is modified to include this effect for associating binary electrolytes. The important limiting case of stationary weak fields is discussed in detail.

A weak electrolyte has been generally regarded as a solution of free ions in a solvent of neutral molecules, whereby the recombined ion pairs would function as another neutral component of the solvent for the remaining free ions and play no special role in electrolytic conduction. The theory of electrostatic interaction of ions has been applied in this spirit, assuming that the relaxation effects of the ionic atmospheres, as

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(2) National Science Foundation Graduate Fellow, 1964-1967.

well as the electrophoretic effects and the modifications of chemical equilibrium, would be functions of the free ion concentrations only.

We have looked into the possibility that the recombination kinetics might provide an additional mechanism for the relaxation of the asymmetric charge distributions produced in the ionic atmospheres by migration of the ions. We find that the relaxation effects are significantly reduced when two conditions are fulfilled. First, the rate of recombination must be at least comparable to the fastest permitted by diffusion. Second, the lifetime of the associated species must be at least comparable to the relaxation time of the ionic