

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS, AND DARTMOUTH COLLEGE, HANOVER, NEW HAMPSHIRE 03755]

Low-Frequency Electrical Response of Flexible Chain Molecules¹

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RECEIVED MAY 17, 1964

Dielectric dispersion, relaxation of the Kerr effect, and relaxation of the Benoit-Wippler effect are discussed for flexible chain molecules in terms of the model used by Zimm to treat viscoelastic behavior of dilute polymer solutions. Low-frequency dispersion is related to the long-wave Fourier components of the electrical charge distribution along the chain backbone.

Introduction

Dielectric dispersion in dilute solutions of flexible polar macromolecules has been discussed theoretically by many authors. Some writers have concerned themselves principally with the shape or breadth of the dispersion, which inevitably spreads over a frequency range rather greater than that for a simple Debye⁴ mechanism in which all dipoles relax at the same specific rate. It has been clear since the analysis of Kirkwood and Fuoss⁵ that a set of dipoles coupled¹ to each other by more or less rigid attachment to a flexible polymer chain will naturally display a spectrum of relaxation times; but deviations from the Debye equation are also common in nonpolymeric polar liquids⁶ and at present remain less than completely understood. We shall not be principally concerned with this problem.⁷

More uniquely polymeric questions concern the influence of chain structure and chain length on the number of distinct dispersion regions which occur and on the frequency of maximum dielectric loss in each such region. In general, these questions can be answered only by treating quite realistic models of the chain, and such treatments are extremely difficult. Thus, for example, the very general diffusion theory of Kirkwood⁸ has been applied to the dielectric relaxation problem⁹ only with the introduction of considerable mathematical simplification, and the final results are certainly doubtful.¹⁰ There are, however, special cases in which correct and useful predictions can be made by means of the simple but tractable ball-and-spring model associated with the names of Kuhn, Slonimsky, Bueche, Rouse, and many others. The most complete treatment of this type of model is probably that of Zimm,¹¹ in which the hydrodynamic interactions between parts of the chain are most explicitly considered. In the present paper, we amplify Zimm's discussion of dielectric dispersion and also work out the results for two closely related observable properties, the Kerr effect and the Benoit-Wippler effect (influence of an electric field on the angular distribution of scattered light). The relaxation phenomena associated with the two latter

effects have not previously been discussed for flexible chains.

As is well known, the Rouse-Zimm model is characterized by subdivision of long flexible gaussian chains into an arbitrary number of gaussian submolecules, each of which is described configurationally only by its end-to-end vector. The fine details of chain structure are thus obscured from the start. It may be asserted that such a model contains its own internal standard of application: if the final equations derived for any observable property are sensitive to the number of submolecules into which the chain is thought to be divided, they are surely untrustworthy; but if, on the other hand, they are invariant to the details of the subdivision, then the results are valid. A good analog is furnished by the Debye theory of the heat capacity of crystals, which correctly describes the low-frequency vibrations and gives the characteristic temperature in terms of macroscopic properties (the elastic constants) but which is not reliable for description of the high-frequency part of the vibrational spectrum, where greater knowledge of the crystal structure is needed.

The Model and the Distribution Function

The reader is assumed to be familiar with the work of Zimm,¹¹ so that the discussion of the formulation is here minimized. Let there be $N + 1$ beads connected to each other by N gaussian subchains ("springs"), each with a mean square extension equal to b^2 . The mean square extension of the whole molecule is therefore Nb^2 , which is invariant to the number of subchains.

Let the spatially uniform but temporally variable electric field E act on the solution along the x axis. For simplicity, let the solvent be of low polarity with a dielectric constant ϵ_0 , so that the local field $F = E(\epsilon_0 + 2)/3$ acts on each portion of the chain. The polar character of the chain is described by assigning electrical charges e_i to the beads i . To treat the quadratic field effects, it is also necessary to consider induced polarization. Here we follow Kuhn and Grün,¹² considering that each of the gaussian submolecules of the model consists of an indefinite number of axially symmetric "statistical chain elements." Each of these elements has a low-frequency polarizability in excess of displaced solvent equal to α_1 along its axis and α_2 in the perpendicular directions. The electrical anisotropy of a submolecule is found to be $3(\alpha_1 - \alpha_2)h^2/5b^2$, where h is the end-to-end length of the submolecule. The relation of the model quantity $(\alpha_1 - \alpha_2)/b^2$ to the actual molecular structure is a formidable problem in polymer

(1) Aided by the U. S. Army Research Office (Durham) and the National Science Foundation.

(2) To whom inquiries should be addressed at Dartmouth College.

(3) National Science Foundation Predoctoral Fellow, 1957-1958.

(4) P. Debye, "Polar Molecules," The Chemical Catalog Co., Inc., New York, N. Y., 1929, Chapter V.

(5) J. G. Kirkwood and R. M. Fuoss, *J. Chem. Phys.*, **9**, 239 (1941).

(6) R. H. Cole, *Ann. Rev. Phys. Chem.*, **11**, 149 (1960).

(7) For a review of the older literature, see L. de Broekere and M. Mandel in "Advances in Chemical Physics," Vol. 1, I. Prigogine, Ed., Interscience Publishers, New York, N. Y., 1958, p. 77.

(8) J. H. Kirkwood, *J. Polymer Sci.*, **12**, 1 (1953).

(9) W. G. Hammerle and J. G. Kirkwood, *J. Chem. Phys.*, **23**, 1743 (1955).

(10) F. Bueche, *J. Polymer Sci.*, **54**, 597 (1961).

(11) B. H. Zimm, *J. Chem. Phys.*, **24**, 269 (1956).

(12) W. Kuhn and F. Grün, *Kolloid-Z.*, **101**, 248 (1942).

chain statistics,¹³ but for present purposes it need not be pursued further.

The electrical force on bead i is now given by

$$e_i F + 3F^2(\alpha_1 - \alpha_2)(2x_i - x_{i+1} - x_{i-1})/5b^2$$

and the resulting diffusion equation is¹⁴

$$\partial\psi/\partial t = (\partial/\partial\mathbf{x})^T [D\mathbf{H}(\partial\psi/\partial\mathbf{x}) - D\beta F\psi\mathbf{H}\mathbf{e} + \sigma(1 - \beta^2 F^2 q^2)\mathbf{H}\mathbf{A}\mathbf{x}\psi] \quad (1)$$

where most of the symbols are those of Zimm: ψ is the distribution function, t is the time, D is the diffusion coefficient of a bead, and $\sigma = 3D/b^2$. The column vectors \mathbf{x} and \mathbf{e} describing the x coordinates and the charges of the beads are familiar, as are the square matrices \mathbf{A} (spring forces) and \mathbf{H} (hydrodynamic interactions). We have also introduced the symbols $\beta = 1/kT$ and $q^2 = (\alpha_1 - \alpha_2)/5\beta$.

Explicitly aping Zimm, we now introduce the linear transformations

$$\mathbf{x} = \mathbf{Q}\xi \quad (2a)$$

$$\boldsymbol{\varepsilon} = \tilde{\mathbf{Q}}\mathbf{e} \quad (2b)^{15}$$

and obtain complete separation of variables. Writing ψ as a product of functions $\psi_k(\xi_k, t)$, one for each normal coordinate ξ_k , we find

$$2\tau_k' \partial\psi_k/\partial t = \partial^2\psi_k/\partial u_k^2 - \beta F a_k \partial\psi_k/\partial u_k + 2(1 - \beta^2 F^2 q^2) \partial(u_k \psi_k)/\partial u_k \quad (3)$$

with

$$u_k = (\sigma\lambda_k/2D\nu_k)^{1/2}\xi_k$$

$$\tau_k' = 1/\sigma\lambda_k$$

$$a_k = \epsilon_k(2D\nu_k/\sigma\lambda_k)^{1/2}$$

In these relations, the symbols λ_k and ν_k refer to the elements of the diagonal matrices¹¹

$$\Lambda = \mathbf{Q}^{-1}\mathbf{H}\mathbf{A}\mathbf{Q} \quad (4a)$$

$$\mathbf{N} = \mathbf{Q}^{-1}\mathbf{H}\tilde{\mathbf{Q}}^{-1} \quad (4b)$$

The relaxation times τ_k' are just the ones encountered by Zimm in his treatment of the dielectric problem.

Solving eq. 3 to the second-order perturbations in the field is entirely standard business, in the course of which Hermite polynomials naturally appear.¹¹ Writing F for the amplitude of the local field, we have

$$\psi_k = \exp(-u_k^2) [1 + \beta F a_k u_k \varphi_k(t) + \beta^2 F^2 (2u_k^2 - 1) c_k(t) + \dots] \quad (5)$$

where the time functions depend on the experimental conditions. The first-order term is altogether familiar; for example, in an alternating field

$$\varphi_k = (1 + i\omega\tau_k')^{-1} \exp(i\omega t) \quad (6a)$$

or for transient decay after a steady field is shut off

$$\varphi_k = \exp(-t/\tau_k') \quad (6b)$$

(13) M. V. Volkenstein, "Configurational Statistics of Polymer Chains," translated by S. N. Timasheff and M. J. Timasheff, Interscience Publishers, Inc., John Wiley and Sons, Inc., New York, N. Y., 1963, Chapter 7.

(14) Except in this equation, where superscript T is used, the transpose of a matrix is denoted by a tilde; for example, $\tilde{\mathbf{Q}}$.

(15) Note the correction to the misprinted eq. 106 of Zimm, in which the transpose superscript to $\tilde{\mathbf{Q}}$ was omitted. Also, do not confuse the column matrix $\boldsymbol{\varepsilon}$ with the dielectric constant.

The second-order term is simplest for transient decay where we get

$$c_k = \varphi_k^2(a_k^2 + 2q^2)/4 \quad (7)$$

For an alternating field, the second-order term is a little more unwieldy and may be found in the Appendix.

Average quantities are easily obtained from the distribution function. The ones needed later (written here for transient decay) are

$$\langle \xi_k \rangle = (\beta F b^2 \epsilon_k / 3\mu_k) \varphi_k \quad (8)$$

$$\langle \xi_k^2 \rangle = (b^2/3\mu_k) [1 + \beta^2 F^2 \varphi_k^2 (q^2 + b^2 \epsilon_k^2 / 3\mu_k)] \quad (9)$$

with $\mu_k = \lambda_k/\nu_k$. Note that $\langle \xi_k \xi_n \rangle = \langle \xi_k \rangle \langle \xi_n \rangle$ for $k \neq n$ because of the separability.

Dielectric Dispersion

The average dipole moment of the chain in the presence of the external field is given by

$$\langle p \rangle = \langle \tilde{\mathbf{e}}\mathbf{x} \rangle = \langle \boldsymbol{\varepsilon}\xi \rangle = \sum_k \epsilon_k \langle \xi_k \rangle = (\beta F b^2 / 3) \sum_k (\epsilon_k^2 / \mu_k) \varphi_k \quad (10)$$

Since the equilibrium mean square dipole moment in the absence of a field is

$$\langle p^2 \rangle_0 = 3 \sum_k \sum_n \epsilon_k \epsilon_n \langle \xi_k \xi_n \rangle_0 = b^2 \sum_k \epsilon_k^2 / \mu_k \quad (11)$$

we see that the correct result is obtained in static fields, where $\varphi_k = 1$, and also that the dynamic eq. 10 can be written in the form

$$\langle p \rangle = (\beta F / 3) \sum_k \langle p^2 \rangle_k \varphi_k \quad (12)$$

with $\langle p^2 \rangle_k = b^2 \epsilon_k^2 / \mu_k$. In this form it is seen to be just a special case of Kirkwood's general formula.⁸ However, for the most general chain diffusion operator, the eigenfunctions and eigenvalues are not easily evaluated as they are for the model we have studied.

For dilute solutions we then have the following expression for the increment in the dielectric constant due to permanent dipoles in the macromolecule

$$M(\epsilon - \epsilon_0)/c = (4\pi N_A \beta / 27)(\epsilon_0 + 2)^2 \sum_k \langle p^2 \rangle_k \varphi_k \quad (13)$$

where c is polymer concentration in mass per unit volume and N_A is Avogadro's number. The essential quantities that specify the dielectric spectrum of the polymer are thus seen to be the matrix elements ϵ_k ; more explicitly

$$\epsilon_k = \sum_{i=0}^N Q_{ki} e_k \quad (14a)$$

or, if we again follow Zimm and go over for long chains to the continuous variable $r = (2i - N)/N$, this becomes

$$\epsilon_k = (2/N)^{1/2} \int_{-1}^{+1} \alpha_k(r) e(r) dr \quad (14b)$$

where the $\alpha_k(r)$ denote the eigenfunctions for the continuous case and $e(r)$ is an appropriate charge density along the chain contour. In the case of hydrodynamic free draining the $\alpha_k(r)$ are exactly trigonometric functions,¹¹ and they remain approximately so for arbi-

trarily strong hydrodynamic interactions.¹⁶⁻¹⁸ Adopting this approximation as adequate for all practical purposes, we may then truly regard the ϵ_k as the Fourier components of the electrical charge distribution along the contour of the chain. In the same approximation, $\mu_k = \pi^2 k^2 / N^2$ for $k \ll N$.

To help in visualizing this result, we describe several specific examples.

(i) In the case specifically worked out by Zimm,¹¹ only the two end beads of the chain model carry charges; we have $e_0 = -e$, $e_N = +e$, all other $e_i = 0$. The dielectric spectrum consists of a single peak, not too much broader than a Debye dispersion, with a relaxation time that is essentially equal to the longest relaxation time τ_1' of the molecule, which corresponds in large measure to a molecular rotation, and which can be estimated from viscosity data (see later).

(ii) The model studied by Van Beek and Hermans¹⁹ in the free-draining approximation consists of an even number of beads with charges alternating in sign; thus, N is odd and $e_i = (-1)^i e$. In this case there are two dispersion regions, each contributing half of the static polarization: one near τ_1' and the other near the highest molecular relaxation time τ_N' permitted by the model. It is a striking fact, easily verified, that the low-frequency relaxation can be reduced to negligible proportions by halving the charges on the two end beads, thus eliminating the elements ϵ_k of low k value, which correspond to the long-wave slow relaxation processes. As to the high-frequency dispersion, it can only be said that the model parameters which enter can be given no molecular significance, for the value of τ_N' depends on the value of N , which is a number to be chosen arbitrarily.

(iii) Let the charge distribution along the chain backbone be represented by a sawtooth function, such that the charge density $e(r)$ goes linearly from finite negative to positive values along the contour of each submolecule in turn. This behavior is represented by the Fourier series

$$e(r) = (3N m_0 / \pi b) \sum_{n \geq 1} (-1)^{n+1} \sin(n\pi N r) / n \quad (15)$$

in which a constant m_0 with the dimensions of a dipole moment is introduced for later convenience. The matrix elements of even k vanish, and for the odd ones the use of $\alpha_k(r) = (2/N)^{1/2} \sin(k\pi r/2)$ leads to

$$\langle p^2 \rangle_k = b^2 \epsilon_k^2 / \mu_k = 8N m_0^2 / k^2 \pi^2 \quad (k \text{ odd}) \quad (16)$$

The dispersion thus exactly resembles model (i), a single region being found at low frequencies, essentially at τ_1' .

(iv) If two chains of the type just described are joined head-to-head, the charge density $e(r)$ is now an even function of contour distance from the chain midpoint. In this case ϵ_k vanishes for all odd k and yields a constant value independent of k for all even k , which corresponds to a single dispersion region near τ_2' . Another model giving exactly the same result would consist of just three discrete charges on the chain, two

of like sign at the ends and one of opposite sign and twice the magnitude at the midpoint.

The foregoing examples should suffice to indicate the conditions under which low-frequency dispersions arise: each repeating unit of the polymer chain must have a component of its dipole moment lying along the direction of the chain contour, and the direction of this component must be the same for long successions of units. In other words, when the chain structure provides a sense of direction, so that one can "tell north from south," one may expect low-frequency dispersion, in which the relaxation time is a strong function of molecular weight; e.g.¹¹

$$\tau_1' = 1.21 M [\eta] \eta_0 / RT \quad (\text{free draining}) \quad (17a)$$

$$\tau_1' = 0.85 M [\eta] \eta_0 / RT \quad (\text{nondraining}) \quad (17b)$$

where $[\eta]$ is the intrinsic viscosity and η_0 is the viscosity of the solvent. Note that all special characteristics of the ball-and-spring model have been eliminated from eq. 17, so that prediction of the relaxation time from other macroscopic quantities is feasible and essentially independent of the model. Such low-frequency dispersions have been observed in cellulose derivatives,^{20,21} which satisfy the above structural condition. Of course these substances also display higher-frequency peaks, which may be ascribed to relaxation of dipoles not correlated with long-range chain motions, such as dipoles on flexible side chains. Low-frequency dispersion would be expected for polypeptides in their random-coil form, and also in 6-nylon, $[-(\text{CH}_2)_6 \text{CONH-}]_x$, but not in 66-nylon, $[-\text{CONH}(\text{CH}_2)_6 \text{NHCO}(\text{CH}_2)_4-]_x$. A small low-frequency molecular-weight-dependent peak in polypropylene oxide²² is also to be ascribed to a similar cause. These examples and our calculations should suffice to confirm in every way the statement made by Zimm in 1956.

Extension of the above treatment to branched molecules with appropriate charge distributions is straightforward, and some calculations of relaxation times are available.^{23,24} Low-frequency dispersions have been observed in trifunctional star polymers of propylene oxide,²⁵ at frequencies which agree well with the theoretical predictions.

Applications of ball-and-spring models to a discussion of high-frequency dispersion are, as has been said earlier, without great significance from a molecular point of view. Thus, for example, the studies of Van Beek and Hermans¹⁹ on the effect of an internal viscosity or of Kästner²⁶ on the effects of flexible side groups are very interesting from a qualitative standpoint, but do not offer the possibility of deducing meaningful molecular parameters from experimental data.

It remains for us to make a few remarks about the work of Kuhn.²⁷ He makes the strong statement, quite incompatible with the calculation of Zimm or of this

(20) P. C. Scherer, D. W. Levi, and M. C. Hawkins, *ibid.*, **24**, 19 (1957).

(21) A. Kheir, Doctoral Dissertation, Leiden, 1959.

(22) M. E. Baur and W. H. Stockmayer, paper presented at the 135th National Meeting of the American Chemical Society, Boston, Mass., April, 1959; also M. E. Baur, Ph.D. Thesis, Massachusetts Institute of Technology.

(23) J. S. Ham, *J. Chem. Phys.*, **26**, 625 (1957).

(24) B. H. Zimm and R. W. Kilb, *J. Polymer Sci.*, **37**, 19 (1959).

(25) J. J. Burke, Ph.D. Thesis, Massachusetts Institute of Technology, 1962.

(26) S. Kästner, *Kolloid-Z.*, **184**, 109 (1962); and several earlier papers.

(27) W. Kuhn, *Helv. Chim. Acta*, **33**, 2057 (1950).

(16) B. H. Zimm, G. M. Roe, and L. F. Epstein, *J. Chem. Phys.*, **24**, 279 (1956).

(17) J. E. Hearst, *ibid.*, **37**, 2547 (1962).

(18) N. W. Tschoegl, *ibid.*, **39**, 149 (1963).

(19) L. K. H. Van Beek and J. J. Hermans, *J. Polymer Sci.*, **23**, 211 (1957).

paper, that as long as the dipoles are rigidly fixed to the chain it is immaterial whether they are oriented parallel or perpendicular to the chain direction. He obtains a function for the distribution of relaxation times which depends on no parameter related in any way to the distribution of charges on the chain, *i.e.*, to the relative orientations of the individual dipoles. From our point of view, the recently demonstrated agreement²⁸ of his formula with certain experimental data on methyl cellulose must therefore be regarded as irrelevant.

Birefringence

The birefringence (in excess of that due to solvent) produced by the field is¹³

$$\Delta n = [2\pi(n^2 + 2)^2 c N_A / 9nM] \Delta\Gamma \quad (18)$$

where n is refractive index and $\Delta\Gamma$ is a molecular quantity proportional to the square of the field. The specific Kerr constant²⁹ is then

$$K_{sp} \equiv \Delta n / cnE^2 =$$

$$(2\pi N_A / 81Mn^2)(n^2 + 2)^2(\epsilon_0 + 2)^2(\Delta\Gamma / F^2) \quad (19)$$

If the electric field acts in the x direction and the beam of polarized light travels in the z direction, the desired quantity is given^{11,30} by

$$\begin{aligned} \Delta\Gamma / q' &= \langle \tilde{\mathbf{x}}\mathbf{A}\mathbf{x} \rangle - \langle \tilde{\mathbf{y}}\mathbf{A}\mathbf{y} \rangle \\ &= \langle \tilde{\mathbf{x}}\mathbf{A}\mathbf{x} \rangle - \langle \tilde{\mathbf{x}}\mathbf{A}\mathbf{x} \rangle_0 \end{aligned}$$

with

$$q' = 3(\alpha_1' - \alpha_2') / 5b^2 \quad (20)$$

where the subscript zero denotes a field-free average and the primed polarizabilities are those for optical frequency. The change to normal coordinates gives $\tilde{\mathbf{x}}\mathbf{A}\mathbf{x} = \tilde{\xi}\mathbf{M}\xi = \sum_k \mu_k \xi_k^2$. For the case of transient decay we may now introduce eq. 9, with the result

$$\begin{aligned} \Delta\Gamma / \beta^2 F^2 q' &= (b^4 / 9) \sum_k \epsilon_k^2 \varphi_k^2 \mu_k^{-1} + \\ &\quad (q^2 b^2 / 3) \sum_k \varphi_k^2 \quad (21) \end{aligned}$$

For the static case, setting $\varphi_k = 1$ and invoking eq. 11, we obtain the specific Kerr constant

$$\begin{aligned} K_{sp} &= (2\pi N_A \beta^2 / 1215Mn^2)(n^2 + 2)^2(\epsilon_0 + 2)^2 \times \\ &\quad (\alpha_1' - \alpha_2')(\langle p^2 \rangle_0 + 3Nq^2) \quad (22) \end{aligned}$$

If the mean square permanent moment of the chain is written as $\langle p^2 \rangle_0 = Nm_0^2$, the permanent-dipole term agrees exactly with that given by Stuart and Peterlin,²⁹ but the induced-dipole term disagrees by a constant factor, which we do not trouble to pin down, especially in view of the remoteness of this term from detailed structural interpretation.¹³

The relaxation of the Kerr effect, as seen in eq. 21, shows quite different behavior for the permanent and induced dipoles. The permanent-dipole term is dictated, as in the case of dielectric dispersion, by the matrix elements ϵ_k and must receive a similar structural interpretation. Since the function φ_k appears squared, the relaxation times are each just half as

(28) W. Kuhn and P. Moser, *J. Polymer Sci.*, **A1**, 151 (1963).

(29) A. Peterlin and H. A. Stuart, *ibid.*, **5**, 551 (1950).

(30) This equation means that each submolecule is considered to contribute independently to the birefringence.

long as in the dielectric case, and are thus exactly those which appear in the viscosity theory.¹¹ Inspection of the induced-dipole term predicted by the present theory shows that it cannot be taken seriously, for the short relaxation times play the leading role, as already remarked by Kirkwood,⁸ and as could have been anticipated on physical grounds.

Light Scattering

Although the effect of an electric field on light scattering had been known for some time in the case of colloidal suspensions of rigid particles, it seems to have been first studied for solutions of chain molecules about 10 years ago by Wippler and Benoit.³¹ Experimental results exist for both equilibrium³² and dynamic³³ situations, but thus far the published theory has dealt only with equilibrium^{31,34} except for rigid rods where the relaxation problem is obvious. The relaxation for flexible chains is easily treated by the methods of the present paper.

The well-known single-particle scattering function³⁵ is given by

$$P(\vartheta) = 1 - (2\pi/\lambda)^2 s^2 N^{-2} \sum_{i>j} \langle x_{ij}^2 \rangle + \dots \quad (23)$$

where x_{ij} is the component of the distance between chain elements i and j in the direction of the scattering vector \mathbf{s} whose magnitude s is $2 \sin(\vartheta/2)$. We shall not concern ourselves with higher terms in $P(\vartheta)$, which are known for the equilibrium case,^{31,34} nor do we distinguish here between $N+1$ and N . In matrix notation, the desired quantity is

$$\begin{aligned} \sum_{i>j} x_{ij}^2 &= N \tilde{\mathbf{x}}\mathbf{x} - \tilde{\mathbf{x}}\mathbf{E}\mathbf{x} \\ &= N \tilde{\xi}\xi - \tilde{\xi}(\tilde{\mathbf{Q}}\mathbf{E}\mathbf{Q})\xi \quad (24) \end{aligned}$$

in which \mathbf{E} represents a square matrix of rank $N+1$ with all of its elements equal to unity. Unlike the calculations made earlier, this one requires consideration of the contribution from the translational normal coordinate, $k=0$. However, because the columns of \mathbf{Q} are the orthogonal eigenvectors $\alpha_k(r)$, it transpires that the contribution of the final term in eq. 24 to the *average* value is a constant independent of N and hence negligible compared to the preceding term for long chains. It is then easy to obtain the final result. After subtraction of the zero-field value, the difference $\Delta P(\vartheta)$ is given by

$$\begin{aligned} -\Delta P(\vartheta) / (2\pi\beta\mathbf{s}\cdot\mathbf{F}/\lambda)^2 &= \\ (L^2 q^2 / 3\pi^2) \sum_k k^{-2} \varphi_k^2 + (NL^4 / 9\pi^4) \sum_k k^{-4} \epsilon_k^2 \varphi_k^2 \quad (25) \end{aligned}$$

where the mean square end-to-end length of the chain is written $L^2 = Nb^2$. It is immediately clear that the first term on the right side of this expression is completely negligible compared to the second, in agreement with physical intuition and previous work,³¹ and also that the existence of a charge distribution giving nonzero values of ϵ_k for low k is essential for obtaining an effect of appreciable magnitude even at equilibrium. This

(31) C. Wippler and H. Benoit, *Makromol. Chem.*, **13**, 7 (1954).

(32) C. Wippler, *J. Polymer Sci.*, **23**, 199 (1957), and earlier references therein.

(33) M. L. Wallach and H. Benoit, *ibid.*, **57**, 41 (1962).

(34) A. Ishihara, R. Koyama, N. Yamoda, and A. Nishioka, *ibid.*, **17**, 341 (1955).

(35) See, for example, B. H. Zimm, *J. Chem. Phys.*, **16**, 1093 (1948).

conclusion is in entire accord with experience; for example, the effect is measurable for nitrocellulose but not for poly(methyl methacrylate) even of very high molecular weight.³¹ It can also be shown that for equilibrium eq. 25 is in agreement with special examples treated by Wippler and Benoit³¹ and by Wallach and Benoit.³⁶

Very recently Wallach and Benoit³⁶ have measured the effect in an alternating field for solutions of two nitrocellulose fractions in ethyl acetate, these having weight-average molecular weights of 1.5×10^6 and 4.0×10^6 and intrinsic viscosities of 2.55 and 9.1 dl./g., respectively. The observed relaxation times were about 60 and 200 μ sec., at concentrations of several tenths of a per cent. Since eq. 25 indicates the overwhelming importance of the first chain relaxation mode ($k = 1$) for this type of polymer, the above experimental values may be compared with calculations of π_1' based on eq. 17b, which yield about 6 and 55 μ sec.³⁷ The effects of both concentration and polydispersity would be to augment these figures, so that the agreement between theory and experiment may be considered reasonable.

(36) M. L. Wallach and H. Benoit, private communication, 1963.

(37) By using a published viscosity-molecular weight relationship, such as that of M. L. Hunt, S. Newman, H. A. Scheraga, and P. J. Flory, *J. Phys. Chem.*, **60**, 1278 (1956), it is possible to increase the calculated values by a factor of three.

Clearly more experimental results would be welcome, but eq. 25 makes clear that the effects of polydispersity will require great care in the interpretation. Conversely, the effect when observable will according to the present theory yield no molecular information (other than polydispersity) that cannot be more conveniently obtained by less difficult techniques.

An ancient conversation with B. H. Zimm is gratefully recalled.

Appendix

For an alternating applied field of circular frequency ω , the second-order coefficient $c_k(t)$ of the distribution function of eq. 5 is given in real representation by the formula

$$8c_k(t) = P_k + Q_k \cos 2\omega t + R_k \sin 2\omega t$$

with

$$P_k = 2q^2 + a_k[1 + \omega^2(\tau_k')^2]^{-1}$$

$$Q_k = 2q^2[1 + \omega^2(\tau_k')^2]^{-1} +$$

$$a_k[1 - \omega^2(\tau_k')^2][1 + \omega^2(\tau_k')^2]^{-2}$$

$$R_k = 2q^2\omega\tau_k'[1 + \omega^2(\tau_k')^2]^{-1} +$$

$$2a_k\omega\tau_k'[1 + \omega^2(\tau_k')^2]^{-2}$$

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS, WASHINGTON, D. C. 20234]

On the Validity of the Einstein-Smoluchowski Theory of Light Scattering

BY ROBERT ZWANZIG

RECEIVED MARCH 30, 1964

The molecular basis of the Einstein-Smoluchowski macroscopic theory of light scattering is investigated, using a generalization of Frölich's theory of dielectrics. The macroscopic and molecular theories differ by an experimentally negligible quantity, associated with the electric field dependence of the dielectric constant. A slight depolarization, not accounted for by the macroscopic theory, is associated with the same quantity. Because of the method of derivation, the results obtained here are valid only in the limit of long wave length and low frequency.

Introduction

The macroscopic theory of light scattering due to Smoluchowski¹ and Einstein² is based on a certain extremely plausible hypothesis: that the molecular nature of the scattering medium can be ignored, and that one can regard the light as being scattered by local fluctuations in the dielectric constant of a continuous medium.

In applications of this hypothesis, the dielectric constant is usually taken to be a function of local thermodynamic variables, so that the dielectric constant fluctuates solely because the local thermodynamic state fluctuates.³

Several attempts have been made to derive the Einstein-Smoluchowski theory from the principles of molecular physics. The most detailed investigation up to now is due to Fixman⁴ and is a continuation of

earlier work by Yvon.⁵

Fixman restricted his analysis to a system of spherical polarizable atoms. He calculated the intensity of scattered light in the form of a power series expansion in the polarizability α of a single atom, keeping all terms of order α^2 , α^3 , and α^4 , and omitting many terms of higher order.

Previously, Yvon had calculated the dielectric constant of the same system as a power series in α .

Fixman compared his results, found independently of the Einstein-Smoluchowski hypothesis, with the results that are obtained using this hypothesis. It should be noted that in this comparison, fluctuations in the dielectric constant were attributed entirely to fluctuations in density, and fluctuations in temperature (or local energy density) were ignored. Fixman found exact agreement between the two approaches in the α^2 and α^3 terms.

In the α^4 term, however, a certain "completely intractable" integral appeared. Fixman observed that this integral, whatever its magnitude, must give

(1) M. Smoluchowski, *Ann. Physik*, **25**, 205 (1908).

(2) A. Einstein, *ibid.*, **33**, 1275 (1910).

(3) Einstein considered only fluctuations in density and composition. It is customary, however, to refer to the more general theory involving fluctuations in all local thermodynamic variables as the Einstein-Smoluchowski theory.

(4) M. Fixman, *J. Chem. Phys.*, **23**, 2074 (1955).

(5) J. Yvon, "Actualités Scientifiques et Industrielles," No. 548. Hermann et Cie., Paris, 1937.