MODERN NONLINEAR OPTICS

Part 1

Edited by

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ADVANCES IN CHEMICAL PHYSICS
VOLUME LXXXV

Series Editors

ILYA PRIGOGINI
University of Brusse
Brussels, Belgium
and
University of Texas
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EDITORIAL BOARD

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INTRODUCTION

Few of us can any longer keep up with the flood of scientific literature, even in specialized subfields. Any attempt to do more and be broadly educated with respect to a large domain of science has the appearance of tilting at windmills. Yet the synthesis of ideas drawn from different subjects into new, powerful, general concepts is as valuable as ever, and the desire to remain educated persists in all scientists. This series, *Advances in Chemical Physics*, is devoted to helping the reader obtain general information about a wide variety of topics in chemical physics, a field which we interpret very broadly. Our intent is to have experts present comprehensive analyses of subjects of interest and to encourage the expression of individual points of view. We hope that this approach to the presentation of an overview of a subject will both stimulate new research and serve as a personalized learning text for beginners in a field.

ILYA PRIGOGINE
STUART A. RICE

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PREFACE

Statistical molecular theories of electric, magnetic, and optical saturation phenomena developed by S. Kielich and A. Piekara in several papers in the late 1950s and 1960s clearly foreshadowed the developments of the next thirty years. In these volumes, we as guest editors have been honored by a positive response to our invitations from many of the most eminent contemporaries in the field of nonlinear optics. We have tried to give a comprehensive cross section of the state of the art of this subject. Volume 85 (Part 1) contains review articles by the Poznań School and associated laboratories, and volume 85 (Part 2 and Part 3) contains a selection of reviews contributed from many of the leading laboratories around the world. We thank the editors, Ilya Prigogine and Stuart A. Rice, for the opportunity to produce this topical issue.

The frequency with which the work of the Poznań School has been cited by others in these volumes is significant, especially considering the overwhelming societal difficulties that have faced Prof. Dr. Kielich and his School over the last forty years. Their work is notable for its unfailing rigor and accuracy of development and presentation, its accessibility to experimental testing, the systemic thoroughness of the subject matter, and the fact that it never seems to lag behind developments in the field. This achievement is all the more remarkable in the face of journal shortages and the lack of facilities that would be taken for granted in more fortunate centers of learning.

We hope that readers will agree that the contributors to these volumes have responded with readable and useful review material with which the state of nonlinear optics can be measured in the early 1990s. We believe that many of these articles have been prepared to an excellent standard. Nonlinear optics today is unrecognizably different from the same subject in the 1950s, when lasers were unheard of and linear physics ruled. In these three volumes we have been able to cover only a fraction of the enormous contemporary output in this field, and many of the best laboratories are not represented.

We hope that this topical issue will be seen as a sign of the ability of scientists all over the world to work together, despite the frailties of human society as a whole. In this respect special mention is due to Professor Mansel Davies of Criccieth in Wales, who was among the first in the West to recognize the significance of the output of the Poznań School.

MYRON W. EVANS

Charlotte, North Carolina
August 1993

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RELAXATION THEORY OF NONLINEAR PROCESSES IN THE SMOLUCHOWSKI ROTATIONAL DIFFUSION APPROXIMATION

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CONTENTS

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I. INTRODUCTION

It is our aim to give a review of the results achieved in the relaxation theory of nonlinear electro-optical effects in simple molecular liquids and dilute solutions of macromolecules in the approximation of equations of the Smoluchowski type for orientational molecular diffusion. Equations of this kind were first applied by Debye [1] in his classical theory of dielectric relaxation to elucidate the rotation of dipolar molecules in viscous media. With regard to the fundamental contribution of Smoluchowski's theory of Brownian motion [2–4] to the development of the molecular–kinetic theory of matter, we shall refer to the method used in the present paper as the Smoluchowski rotational diffusion approximation.

The classical theory of nonlinear electro-optical processes of molecular relaxation in intense electric fields of high and low frequency was first proposed by Kasprowicz-Kielich and coworkers [5, 6] and extended by the same authors at the Department of Nonlinear Optics in Poznań [7–14] to the more detailed description of the dispersional and absorptional behavior and time rise of the nonlinear electric polarization of the third order, induced in liquids by different reorienting fields.

The results of Refs. 5 and 6 are especially important. Owing to their high degree of generality, they cover a great variety of nonlinear optical effects [15–17] and can be extended to reorienting fields other than cosine-shaped field.

An extensive review of the present state of the theory concerning rotational Brownian motion has been given in the monograph of Evans et al. [18], the review by Coffey [19], and the monograph of Coffey et al. [20]. Smoluchowski's rotational diffusion equation, which provided the basis for the theory of optical birefringence proposed by Peterlin and Stuart [21] and Benoit [22] has also found applications in the theories of

nonlinear depolarization of scattered light [23] and the optical Kerr effect [24] proposed by Kielich. It has also been applied in the theory of polarization of dipolar liquids by Novikov [25] and in that of dipolar but nonpolarizable liquids by Coffey and Paranjape [26].

We shall be considering a statistical assembly of mutually noninteracting, axially symmetric molecules, linearly and nonlinearly polarizable in an electric field and possessing a permanent dipole moment along their axis of symmetry. The potential energy of the molecule in the external reorienting field is then dependent on the polar angle ϑ only and, as shown by Morita [27], the rotational diffusion model leads to a scalar coefficient of rotational diffusion.

As shown by Perrin [28], if the potential energy of the molecule in the reorienting field $E(t)$ is moreover dependent on the azimuth angle ϕ, an asymmetry of the diffusion coefficients appears in the rotational diffusion equation leading to three different rotational relaxation times along the principal axes of symmetry of the ellipsoidal molecule [27–31]. It should be noted that the Smoluchowski equation in the form of Eq. 22 does not take into account molecular interactions, which play an essential role in liquids, and thus is applicable only to sufficiently dilute solutions of axial molecules and not excessively big macromolecules in spherical solvents.

The first attempt to include intermolecular interactions was made by Debye and Ramm [33], though the problem is by no means simple, as proved by the work of Frenkel [34]. The next step was taken by Budo [35], to whom is due the inclusion of intramolecular interactions between internally rotating dipolar assemblages in his treatment of dielectric relaxation. The theory was extended by Coffey et al. [36, 37] to comprise the influence of the moment of inertia. Quite recently, Morita and Watanabe [38] have shown that interactions of intramolecular rotating dipolar groups can lead to important divergences from the well-known Debye semicircle on the Cole–Cole graphs [39–41].

The equation of orientational diffusion has been used by Bloembergen and Lallemand [42] to explain the widening of the wings in induced Rayleigh and Raman scattering spectra from solutions of cyclohexane in carbon disulfide. The optical reorientation of molecules in liquids due to birefringence induced by the field of a light wave can also be applied in the synchronization if longitudinal laser modes [43]. Rotational molecular diffusion also plays an essential role in the depolarization of fluorescence from solutions of dipolar liquids as proved, for example, by the theory of Pierov [44]. Tolles [45] found a numerical solution of the Smoluchowski equation for a system of noninteracting nondipolar molecules showing that for high intensities of the electric field when the parameter of polarizabil-

ity anisotropy reorientation takes values $q > 2$ (see Eq. (24)) the effective relaxation time becomes shorter.

Noteworthy is the so-called model of restricted rotational diffusion proposed by Warchol and Vaughan [46], who restricted the variability of the angle of rotation ϑ to the interval $(0 < \omega_0 < \pi/2)$ in the equation of rotational diffusion for noninteracting cylindrical molecules, for which $a_{33} - a_{11} > 0$. Their model was applied by Wang and Pecora [47] to calculate the time correlation functions of the spherical harmonics of the first and second order essential in dielectric relaxation, light scattering, and fluorescence depolarization. Kühle and Rapp [48], having recourse to the properties of coupled differential equations, solved the Smoluchowski equation for noninteracting, nonpolarizable dipolar molecules in a dc electric field with high jumpwise changes in field strength and showed that the averaged Legendre polynomials $\langle P_1(\cos \vartheta) \rangle$ and $\langle P_2(\cos \vartheta) \rangle$ are dependent on the effective relaxation times, which decrease with growing electric field strength.

Attention should be drawn to the extensive theoretical paper of Watanabe and Morita [49] on Kerr effect relaxation in strong electric fields of different shapes, which however, does not take into consideration the effect of nonlinear polarizability of the molecules. Their general method of solving the Smoluchowski equation (22) has recourse to the formalism of Laplace transforms.

Molecular light scattering (LS) is on its own a vast field of science where use is made of the equations of rotational and translational molecular diffusion in liquids. Extensive discussions of linear Rayleigh LS are to be found in the monographs of Berne and Pecora [50] and Chu [51]. Nonlinear LS has been dealt with in full detail by Kielich and his coworkers [52–55]. The earliest and by no means easy measurements of the spectral broadening of second-harmonic Rayleigh LS in different liquids due to rotational molecular diffusion were carried out by Maker [56]. His work has acted as a stimulus for further spectral theories of hyper-Raman [57] and hyper-Rayleigh [58–60] LS in liquids.

Smoluchowski-type equations modeling Brownian motion of molecules in the presence of external forces consistently play an important role in modern physics [19, 61]. Examples of their application are to be found in the theory of the spectral linewidth of nuclear magnetic resonance [62], in the theoretical description of incoherent scattering of slow neutrons in liquids [63, 64] and of current–voltage characteristics of the Josephson junction [65], in calculations of the influence of quantum noise on the mean frequency of ring laser gyroscopes [66], in the theory of harmonic frequency mixing by a Brownian particle in a cosine potential [67] and of the lineshape of single-mode semiconductor lasers [19], and in the descrip-

tion of the slowing down of electrons in gaseous moderators [19]. Further examples of their applications are given in Refs. 3, 19, and 61.

II. DISPERSION AND ABSORPTION OF MOLECULAR NONLINEAR POLARIZABILITIES IN THE APPROACH OF CLASSICAL ELECTRON THEORY

The classical theory of electron dispersion reaches back to Lorentz [68] and has been extended to nonlinear electron dispersion by Voigt [69]. Voigt's ideas concerning nonlinear distortion of molecular systems have stimulated numerous, repeatedly reviewed investigations [70–73].

Here, we discuss the classical results of Kasprowicz-Kielich and Kielich [6] for the effect of nonlinear electronic dispersion on the polarizability of molecules in liquids. To this aim, we consider a molecular system, composed of n electrons, the sth electron having the mass m, electric charge e, and radius vector $\mathbf{r}_s$. In the classical theory of Lorentz, the equation of motion of the electron is of the form [68]

$$m\frac{d^2\mathbf{r}_s(t)}{dt^2} + m\Gamma_s\frac{d\mathbf{r}_s(t)}{dt} = \mathbf{f}_s^L + \mathbf{f}_s^B \tag{1}$$

Quite generally, the electron is acted on by a Lorentz force

$$\mathbf{f}_s^L(\mathbf{r}, t) = e\left[\mathbf{E}(\mathbf{r}, t) + \frac{1}{c}\frac{d\mathbf{r}_s(t)}{dt} \times \mathbf{H}(\mathbf{r}, t)\right] \tag{2}$$

with $\mathbf{E}(\mathbf{r}, t)$ and $\mathbf{H}(\mathbf{r}, t)$ denoting the electric and magnetic electromagnetic field vectors in the space–time point $(\mathbf{r}, t)$.

In accordance with Voigt's hypothesis [69], the electron is bound to the center of the microsystem by the anharmonic force

$$f_{si}^B(\mathbf{r}, t) = -\alpha_{ij}^{(s)}r_{si}(t) - \tfrac{1}{2}\beta_{ijk}^{(s)}r_{si}(t)r_{sk}(t)$$
$$- \tfrac{1}{6}\gamma_{ijkl}^{(s)}r_{si}(t)r_{sk}(t)r_{sl}(t) - \cdots \tag{3}$$

where the coefficients $\alpha_{ij}^{(s)}$ describe the harmonic vibrations and $\beta_{ijk}^{(s)}$ and $\gamma_{ijkl}^{(s)}$ the anharmonic vibrations of the sth electron.

In Eq. (2), Γ_s is a coefficient of the damping force acting on the sth electron. In the absence of the Lorentz force (2) if all damping forces are zero ($\Gamma = 0$), and in the absence of anharmonic force coefficients $\beta_{ijk}^{(s)}, \gamma_{ijkl}^{(s)}$,

the electrons perform harmonic vibrations at the circular frequencies

$$\omega_m^2 = \frac{\alpha_{ij}^{(s)}}{m} \tag{4}$$

In the presence of a Lorentz force (2) with a time dependence of the form

$$E(t) = \sum_a E_a \exp(-i\omega_a t) \tag{5}$$

the electron performs forced vibrations with the fundamental frequency ω_a and sum frequencies $\omega_{ab}, \omega_{abc}$:

$$\omega_{ab} = \omega_a + \omega_b \qquad \omega_{abc} = \omega_a + \omega_b + \omega_c \tag{6}$$

described by

$$\begin{aligned}
r_{si}(t) = &\sum_a r_{si}(\omega_a)\exp(-i\omega_a t) + \sum_{ab} r_{si}(\omega_{ab})\exp(-i\omega_{ab}t) \\
&+ \sum_{abc} r_{si}(\omega_{abc})\exp(-i\omega_{abc}t) + \cdots
\end{aligned} \tag{7}$$

The solution of the problem in Ref. 6 is restricted to the electric part of the Lorentz force (the magnetic field has been considered in Refs. 74 and 75). Hence, by Eqs. (1)–(7), the final result is

$$\begin{aligned}
r_{si}(\omega_a) &= e\alpha_{ij}^{(s)}D_s(\omega_a)E_j(\omega_a) \\
r_{si}(\omega_{ab}) &= \tfrac{1}{2}e^2\beta_{ijk}^{(s)}D_s(\omega_a)D_s(\omega_b)D_s(\omega_{ab})E_j(\omega_a)E_k(\omega_b) \\
r_{si}(\omega_{abc}) &= \tfrac{1}{6}\big\{3e^2\beta_{ijk}^{(s)}\big[D_s(\omega_a)D_s(\omega_{bc})E_j(\omega_a)E_k(\omega_{bc}) \\
&\qquad + D_s(\omega_{ab})D_s(\omega_c)E_j(\omega_{ab})E_k(\omega_c)\big] \\
&\quad + e^3\gamma_{ijkl}^{(s)}D_s(\omega_a)D_s(\omega_b)D_s(\omega_c)E_j(\omega_a)E_k(\omega_b)E_l(\omega_c)\big\} \\
&\quad \times D_s(\omega_{abc})
\end{aligned} \tag{8}$$

In Eq. (8) the complex electron dispersion functions are of the form

$$\begin{aligned}
D_s^{-1}(\omega_a) &= m(\omega_s^2 - \omega_a^2 - i\omega_a\Gamma_s) \\
D_s^{-1}(\omega_{ab}) &= m\big[\omega_s^2 - (\omega_a + \omega_b)^2 - i(\omega_a + \omega_b)\Gamma_s\big] \\
D_s^{-1}(\omega_{abc}) &= m\big[\omega_s^2 - (\omega_a + \omega_b + \omega_c)^2 - i(\omega_a + \omega_b + \omega_c)\Gamma_s\big]
\end{aligned} \tag{9}$$

Since, by definition, the total induced electric dipole moment of the molecule is

$$\mathbf{p}(t) = \sum_{s=1}^{n} e\mathbf{r}_s(t) \tag{10}$$

by using Eq. 7, we obtain

$$\mathbf{p}(t) = \sum_{a} \mathbf{p}^{(1)}(\omega_a)\exp(-i\omega_a t) + \sum_{ab} \mathbf{p}^{(2)}(\omega_{ab})\exp(-i\omega_{ab}t)$$
$$+ \sum_{abc} \mathbf{p}^{(3)}(\omega_{abc})\exp(-i\omega_{abc}t) + \cdots \tag{11}$$

where the dipole moment components of successive orders are

$$p_i^{(1)}(\omega_a) = a_{ij}^{\omega_a}(\omega_a)E_j^0(\omega_a)$$
$$p_i^{(2)}(\omega_{ab}) = \tfrac{1}{2}b_{ijk}^{\omega_{ab}}(\omega_a, \omega_b)E_j^0(\omega_a)E_k^0(\omega_b) \tag{12}$$
$$p_i^{(3)}(\omega_{abc}) = \tfrac{1}{6}c_{ijkl}^{\omega_{abc}}(\omega_a, \omega_b, \omega_c)E_j^0(\omega_a)E_k^0(\omega_b)E_l^0(\omega_c)$$

The tensors of the linear electron polarizability and nonlinear electron polarizabilities of the molecule are expressed as follows:

$$a_{ij}^{\omega_a}(\omega_a) = \sum_{s=1}^{n} e^2 D_s(\omega_a)\alpha_{ij}^{(s)} \tag{13}$$

$$b_{ijk}^{\omega_{ab}}(\omega_a, \omega_b) = \sum_{s=1}^{n} e^3 D_s(\omega_a) D_s(\omega_b) D_s(\omega_{ab})\beta_{ijk}^{(s)} \tag{14}$$

$$\tag{15}$$
$$c_{ijkl}^{\omega_{abc}}(\omega_a, \omega_b, \omega_c) = \frac{1}{2}\sum_{s=1}^{n} e^4 \Big[3\beta_{iml}^{(s)}\beta_{mjk}^{(s)} D_s(\omega_{ab})$$
$$+ 3\beta_{ijm}^{(s)}\beta_{mkl}^{(s)} D_s(\omega_{bc}) + 2\gamma_{ijkl}^{(s)}\Big]$$
$$\times D_s(\omega_a) D_s(\omega_c) D_s(\omega_{abc})$$

Once we know how these molecular polarizability tensors depend on high (optical) frequencies, we are in a position to determine the electron

dispersion and absorption of the macroscopic polarizability tensors. In fact, high-frequency dispersion, which is due to electron processes practically independent of molecular correlations, can be written, for a medium of N molecules, to a very good approximation, in the form

$$A_{ij}^{\omega_a}(\Gamma, \omega_a) = \sum_{p=1}^{N} a_{ij}^{\omega_a}(\Gamma_p, \omega_a)$$

$$B_{ijk}^{\omega_{ab}}(\Gamma, \omega_a, \omega_b) = \sum_{p=1}^{N} b_{ijk}^{\omega_{ab}}(\Gamma_p, \omega_a, \omega_b) \qquad (16)$$

$$C_{ijkl}^{\omega_{abc}}(\Gamma, \omega_a, \omega_b, \omega_c) = \sum_{p=1}^{N} c_{ijkl}^{\omega_{abc}}(\Gamma_p, \omega_a, \omega_b, \omega_c)$$

On the assumption that all N molecules in V are of one species, the sum of Eq. (16) can simply be replaced by N. Thus, formulae (13) and (14) describe linear and nonlinear electron dispersion and absorption by resolution of the complex functions (9) and their products into real and imaginary parts.

III.   THE RELAXATION FUNCTIONS
WITHIN THE DEBYE–SMOLUCHOWSKI MODEL
OF MOLECULAR ROTATIONAL DIFFUSION

Let us consider an isotropic dielectric of volume V consisting of a great number N of noninteracting molecules possessing a permanent dipole moment m directed along their symmetry 3 axis; components $a_{11} = a_{22} = a_{33}$ of linear electric polarizability; and nonzero components $b_{133} = b_{233}, b_{333}$ as well as $c_{1111}, c_{1133}, c_{3333}$ of their nonlinear polarizabilities.

The change in potential energy of the molecules in an external electric field E_Z applied to the dielectric along the laboratory Z axis can be expressed with sufficient accuracy in the form of the expansion

$$u(\vartheta, E_Z) = -mE_Z P_1(\cos \vartheta) - \tfrac{1}{2}[a_0 + a_2 P_2(\cos\vartheta)]E_Z^2$$

$$- \tfrac{1}{6}[b_1 P_1(\cos \vartheta) + b_3 P_3(\cos \vartheta)]E_Z^3 \qquad (17)$$

$$- \tfrac{1}{24}[c_0 + c_2 P_2(\cos \vartheta) + c_4 P_4(\cos \vartheta)]E_Z^4$$

where we have introduced the irreducible components of linear and

nonlinear polarizabilities equal, respectively, to [17]

$$a_0 = \tfrac{1}{3}(a_{33} + 2a_{11}) \qquad a_2 = \tfrac{2}{3}(a_{33} - a_{11})$$
$$b_1 = \tfrac{3}{5}(b_{333} + 2b_{113}) \qquad b_3 = \tfrac{2}{5}(b_{333} - 3b_{113})$$
$$c_0 = \tfrac{1}{15}(8c_{1111} + 12c_{1133} + 3c_{3333}) \qquad (18)$$
$$c_2 = \tfrac{4}{21}(-4c_{1111} + 3c_{1133} + 3c_{3333})$$
$$c_4 = \tfrac{8}{35}(c_{1111} - 6c_{1133} + c_{3333})$$

For axially symmetric molecules, the energy (18) is dependent only on the polar angle ϑ between the symmetry axis of the molecule and the Z axis of the laboratory system of coordinates. The $P_i(\cos \vartheta)$ are Legendre polynomials.

An external electric field E_Z applied to the dielectric differs from the mean macroscopic field E_Z^m acting on the molecule. Assuming that the molecule is inside a spherical sample with isotropic electric permittivity ε and if this spherical sample is immersed in an isotropic continuous medium of electric permittivity ε_0, then classical electrostatics leads to

$$E_Z = \frac{\varepsilon + 2\varepsilon_0}{3\varepsilon_0} E_Z^m = L E_Z^m \qquad (19)$$

To gain insight into the influence of molecular rotational diffusion on an arbitrary measured physical quantity $A[\Omega_t, E(t)]$ at a moment of time t subsequent to the application of the time-dependent electric field $E(t)$, we have recourse to a classical statistical averaging procedure defined as follows [3]:

$$\left\langle A[\Omega_t, E(t)] \right\rangle = \frac{1}{V} \int A[\Omega_t, E(t)] f[\Omega_t; t, E(t)] \, d\Omega_t \qquad (20)$$

In Debye's model of dielectric relaxation [1], the time-dependent distribution function $f[\Omega_t; t, E(t)]$ can be determined from the Smoluchowski kinetic equation of diffusion [6, 28, 29]:

$$\frac{\partial f(\Omega_t, t)}{\partial t} = D_{ij} \bigg\{ \nabla_i \nabla_j f(\Omega_t, t)$$
$$+ \frac{1}{kT} \big[\nabla_i f(\Omega_t, t) \nabla_j u(\Omega_t, t) \qquad (21)$$
$$+ f(\Omega_t, t) \nabla_i \nabla_j u(\Omega_t, t) \big] \bigg\}$$

where D_{ij} is the second-rank symmetric diffusion tensor, ∇_i is the operator of spatial differentiation, k is Boltzmann's constant, and T is the absolute temperature. The function $f(\Omega_t, t)$ defines the probability of the molecule having the orientation Ω_t at time t, with Ω denoting the set of Euler angles.

In the present case, the Smoluchowski equation of rotational diffusion takes the form

$$
\frac{1}{D} \frac{\partial f(\vartheta, t)}{\partial t} = \frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left[\sin \vartheta \frac{\partial f(\vartheta, t)}{\partial \vartheta} \right]
$$

$$
+ \frac{1}{kT} \left\{ \frac{\partial u(\vartheta, E_Z)}{\partial \vartheta} - \frac{\partial f(\vartheta, t)}{\partial \vartheta} \right. \tag{22}
$$

$$
\left. + \frac{f(\vartheta, t)}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left[\sin \vartheta \frac{\partial u(\vartheta, E_Z)}{\partial \vartheta} \right] \right\}
$$

$D = I\beta$ denotes the scalar coefficient of rotational diffusion of the molecule, β is the friction constant, and I is the moment of inertia of the molecule.

Equation (22) can be solved by the approximate method of classical statistical perturbation calculus [5–8]. We start by expanding the Maxwell–Boltzmann distribution function $f(\vartheta, E_Z)$ for a time-independent reorienting field E_Z:

$$
f(\vartheta, E_Z) = \frac{\exp[-u(\vartheta, E_Z)/kT]}{\int_0^\pi \exp[-u(\vartheta, E_Z)/kT] \sin \vartheta \, d\vartheta} \tag{23}
$$

$$
= f_0 + f_1(\vartheta, E_Z) + f_2(\vartheta, E_Z) + f_3(\vartheta, E_Z) + \cdots
$$

in a power series in the molecular parameter of dipole moment reorientation p, the parameter of linear polarizability anisotropy q, and the parameters of nonlinear polarizability anisotropy s_1, s_3 defined as follows:

$$
p = \frac{mE_Z}{kT} \qquad q = \frac{|a_{33} - a_{11}|}{2kT} E_Z^2
$$

$$
s_1 = \frac{(3b_{333} + 2b_{113})}{5kT} E_Z^3 \qquad s_3 = \frac{2|b_{333} - b_{113}|}{5kT} E_Z^3 \tag{24}
$$

The series expansion of (23), valid for $p, q, s_1, s_3 \ll 1$, leads to the successive components of the distribution function:

$$f_0 = \tfrac{1}{2}$$

$$f_1(\vartheta, E_Z) = \tfrac{1}{2}pP_1(\cos\vartheta) \pm \tfrac{1}{3}qP_2(\cos\vartheta) + \tfrac{1}{12}s_1P_1(\cos\vartheta)$$
$$+ \tfrac{1}{12}s_3P_3(\cos\vartheta) \tag{25}$$

$$f_2(\vartheta, E_Z) = \tfrac{1}{6}p^2P_2(\cos\vartheta) \pm \tfrac{1}{15}pq\left[P_1(\cos\vartheta) - 6P_3(\cos\vartheta)\right]$$

$$f_3(\vartheta, E_Z) = \tfrac{1}{30}p^3\left[P_3(\cos\vartheta) - P_1(\cos\vartheta)\right]$$

where the $P_i(\cos\vartheta)$ are Legendre polynomials. For a time-variable reorienting field

$$E_Z(t) = \sum_a E_a g_a(t) \tag{26}$$

of the shape $g_a(t)$ we assume the statistical distribution function in the time-dependent form

$$f_1(\vartheta, t) = \tfrac{1}{2}P_1(\cos\vartheta)\left[\sum_a p_a A_{11}^a(t) + \tfrac{1}{6}\sum_{abc} s_{1abc}B_{11}^{abc}(t)\right]$$
$$\pm \tfrac{1}{3}P_2(\cos\vartheta)\sum_{ab} q_{ab}A_{12}^{ab}(t) \tag{27}$$
$$\pm \tfrac{1}{12}P_3(\cos\vartheta)\sum_{abc} s_{3abc}B_{13}^{abc}(t)$$

$$f_2(\vartheta, t) = \pm \tfrac{1}{15}P_1(\cos\vartheta)\sum_a p_a q_{bc}A_{21}^{abc}(t)$$
$$+ \tfrac{1}{6}P_3(\cos\vartheta)\sum_{ab} p_a p_b A_{22}^{ab}(t) \tag{28}$$
$$\pm \tfrac{2}{5}P_3(\cos\vartheta)\sum_{abc} p_a q_{bc}A_{23}^{abc}(t)$$

$$f_3(\vartheta, t) = \tfrac{1}{30}\sum_{ab} p_a p_b\left[P_3(\cos\vartheta)A_{33}^{ab}(t)\right.$$
$$\left. -P_1(\cos\vartheta)A_{31}^{ab}(t)\right] \tag{29}$$

with $p_a = mE_a/kT$, $q_{ab} = (|a_{33} - a_{11}|/2kT)E_a E_b$, and so on.

The unknown reorientation relaxation functions $A_{ij}^a(t)$, $A_{ij}^{ab}(t)$, $A_{ij}^{abc}(t)$, $B_{ij}^{abc}(t)$ introduced above are found on insertion of Eqs. (27)–(29) into the Smoluchowski equation (Eq. 22) and on having recourse to the

orthogonality properties of Legendre polynomials:

$$\frac{1}{2} \int_0^\pi P_i(\cos \vartheta) P_j(\cos \vartheta) \sin \vartheta \, d\vartheta = \frac{\delta_{ij}}{2j + 1} \tag{30}$$

where δ_{ij} is the Kronecker delta. On equating in (22) the terms with the same powers of the reorientation parameters, we get the following equations:

$$\tau_1 \dot{A}_{11}^a + A_{11}^a = g_a(t) \tag{31}$$

$$\tau_2 \dot{A}_{12}^{ab} + A_{12}^{ab} = g_a(t) g_b(t) \tag{32}$$

$$\tau_2 \dot{A}_{22}^{ab} + A_{22}^{ab} = A_{11}^a g_b(t) \tag{33}$$

$$\tau_1 \dot{A}_{21}^{abc} + A_{21}^{abc} = \tfrac{1}{2} [3 A_{11}^a g_b(t) - A_{12}^{ab}] g_c(t) \tag{34}$$

$$\tau_1 \dot{A}_{31}^{abc} + A_{31}^{abc} = A_{22}^{ab} g_c(t) \tag{35}$$

$$\tau_1 \dot{B}_{11}^{abc} + B_{11}^{abc} = g_a(t) g_b(t) g_c(t) \tag{36}$$

where the dots denote time derivatives. Equations (31)–(36) with appropriate initial conditions permit the calculation of the respective shapes of the orientational relaxation rise functions for different shapes of the reorienting pulses $g_a(t)$. The τ_k are rotational relaxation times, related simply with the rotational diffusion coefficient D as follows:

$$\tau_k = [k(k + 1)D]^{-1} = 2\tau_1 [k(k + 1)]^{-1} \tag{37}$$

It is worth noting that for $g_a(t) = g_b(t) = g_c(t) = 0$, the simplified equations (31)–(36) describe the shape of the polarization decay relaxation functions on switching off the electric reorienting fields.

IV.   THIRD-ORDER ELECTRIC POLARIZATION IN LIQUIDS

On neglecting intermolecular interactions, the Z component of the total dipole moment of the liquid dielectric system $M_Z[E_Z(t)]$, induced by the time-variable field $E_Z(t)$, is given by the expansion [15, 17, 32]

$$\begin{aligned}
\frac{1}{N} M_Z[E_Z(t)] &= m P_1(\cos \vartheta) + [a_0 + a_2 P_2(\cos \vartheta)] E_Z(t) \\
&\quad + \tfrac{1}{2} [b_1 P_1(\cos \vartheta) + b_3 P_3(\cos \vartheta)] E_Z^2(t) \\
&\quad + \tfrac{1}{6} [c_0 + c_2 P_2(\cos \vartheta) + c_4 P_4(\cos \vartheta)] E_Z^3(t) + \cdots
\end{aligned} \tag{38}$$

whereas the electric polarization of the system, acted on by the field $E_Z(t)$, is given by the statistical mean value

$$\langle P_Z(t) \rangle = \langle P_Z[E_Z(t), t] \rangle_{\vartheta, t}$$

$$= \frac{1}{V} \int_0^\pi M_Z[E_Z(t)] f[\vartheta, E_Z(t)] \sin \vartheta \, d\vartheta. \qquad (39)$$

The isotropically averaged electric polarization (38) splits into two components, proportional to the first and third power of $E_Z(t)$:

$$\langle P_Z(t) \rangle = \langle P_Z^{(1)}(t) \rangle + \langle P_Z^{(3)}(t) \rangle \qquad (40)$$

By Eqs. (38), (39) and (27)–(30) these components take the form

$$\langle P_Z^{(1)}(t) \rangle = \frac{\rho m^2}{kT} \sum_a A_{11}^a(t) E_a \qquad (41)$$

$$\langle P_Z^{(3)}(t) \rangle = \rho \sum_{abc} \{ \theta_1 A_{12}^{ab}(t) g_c(t) + \theta_2 [A_{21}^{abc}(t) + A_{21}^{ab}(t) g_c(t)]$$

$$- \theta_3 A_{31}^{abc}(t)$$

$$+ \theta_4 [3 A_{11}^a(t) g_b(t) g_c(t) + B_{11}^{abc}(t)]$$

$$+ \tfrac{1}{6} c_0 g_a(t) g_b(t) g_c(t) \} E_a E_b E_c \qquad (42)$$

with $\theta_1, \theta_2, \theta_3$ denoting the parameters of axially symmetric molecules.

$$\theta_1 = \frac{2}{45kT} (a_{33} - a_{11})^2$$

$$\theta_2 = \frac{2m^2}{45k^2T^2} (a_{33} - a_{11}) \qquad (43)$$

$$\theta_3 = \frac{m^4}{45k^3T^3}$$

intervening in the theory of dielectrics [17, 39–41].

In Eq. (42), the term in θ_1 is related with the process of Langevin reorientation of the polarizability ellipsoid of the molecule. That in θ_2 is

the so-called Debye–Born term; it can take positive as well as negative values, and plays an essential role in Kerr's effect. The negative term involving θ_3, referred to as the Debye term, is related with reorientation of the permanent dipole moment of the molecule. In Eq. (42) a new term appears involving a parameter θ_4 related with the contribution from nonlinear molecular polarizability

$$\theta_4 = \frac{3m}{50kT}(b_{333} + 2b_{113}) \tag{44}$$

introduced by Piekara and Kielich [76, 77] in their theory of changes in the electric susceptibility of dielectrics in strong electric fields and denoted by them as Δ_2^{ee}.

Equations (41) and (42), which represent the essential results of this section, describe the electric polarization of liquids, induced by a reorienting electric field, as a function of time. Assuming that the dielectric experiences the action of three electric fields with frequencies $\omega_a, \omega_b, \omega_c$

$$\begin{aligned}
E_Z(t) &= \tfrac{1}{2} \sum_a E(\omega_a)\exp(-i\omega_a t) \\
&= \tfrac{1}{2} \sum_a L(\omega_a) E_m(\omega_a)\exp(-i\omega_a t)
\end{aligned} \tag{45}$$

where summation over a extends over positive as well as negative values of the ω_a, with $\omega_{-a} = -\omega_a$, its nonlinear electric polarization $\langle P_Z^{(3)}(\omega_{abc}, t)\rangle$ at the frequency $\omega_{abc} = \omega_a + \omega_b + \omega_c$ can be expressed by

$$\begin{aligned}
\langle P_Z^{(3)}(\omega_{abc}, t)\rangle &= \chi(-\omega_{abc}; \omega_a, \omega_b, \omega_c; t) E_m(\omega_a) E_m(\omega_b) E_m(\omega_c) \\
&\quad \times \exp(-i\omega_{abc} t)
\end{aligned} \tag{46}$$

In Eq. (46) the scalar electric susceptibility of order 3 of the isotropic medium is the sum of two parts:

$$\begin{aligned}
\chi(-\omega_{abc}; \omega_a, \omega_b, \omega_c; t) &= \chi(-\omega_{abc}; \omega_a, \omega_b, \omega_c) \\
&\quad + \delta\chi(-\omega_{abc}; \omega_a, \omega_b, \omega_c; t)
\end{aligned} \tag{47}$$

the first part being independent of time and describing the steady-state behavior of the medium (a long time after switching on the fields (45)), and another, transient part, describing the rise in time of the polarization (46) after switching on the reorienting electric fields. The scalar suscepti-bility may also be written in the form [6]

$$\chi(-\omega_{abc}; \omega_a, \omega_b, \omega_c) = \frac{1}{6V} L(\omega_{abc}) L_m(\omega_a) L_m(\omega_b) L_m(\omega_c)$$

$$\times \langle C(-\omega_{abc}; \omega_a, \omega_b, \omega_c) \rangle \tag{48}$$

where $C(-\omega_{abc}; \omega_a, \omega_b, \omega_c)$ denotes the scalar nonlinear polarizability of order 3 of the isotropic dielectric medium. Moreover, we have for the mean field, the relation

$$L(\omega) = \frac{\varepsilon(\omega) + 2\varepsilon_0}{3\varepsilon_0} \tag{49}$$

In our further discussion it will prove convenient to expand the nonlin-ear susceptibility in a power series in the inverse energy $(kT)^{-1}$, permit-ting an elegant separation of the various molecular contributions to the nonlinear electric polarization of order 3:

$$\chi(-\omega_{abc}; \omega_a, \omega_b, \omega_c; t) = \chi^{(0)}(-\omega_{abc}; \omega_a, \omega_b, \omega_c; t)$$

$$+ \frac{1}{kT} \chi^{(1)}(-\omega_{abc}; \omega_a, \omega_b, \omega_c; t)$$

$$+ \frac{1}{k^2 T^2} \chi^{(2)}(-\omega_{abc}; \omega_a, \omega_b, \omega_c; t) \tag{50}$$

$$+ \frac{1}{k^3 T^3} \chi^{(3)}(-\omega_{abc}; \omega_a, \omega_b, \omega_c; t)$$

In the zeroth approximation, for the fields (45) we obtain

$$\chi^{(0)}(-\omega_{abc}; \omega_a, \omega_b, \omega_c; t) = \tfrac{1}{6} c_0 \tag{51}$$

Thus, in the approximation of Smoluchowski rotational diffusion, nonlin-ear third-order polarizability contributes nothing to the process of rise in polarization, where the essential contributions come from fast electron processes of absorption and dispersion of the Lorentz type.

Further contributions to the susceptibility (50) are given by [8]

$$
\begin{aligned}
\chi^{(1)}&(-\omega_{abc}; \omega_a, \omega_b, \omega_c; t) \\
&= \mathop{\mathbf{S}}_{abc} \left[\tfrac{2}{45}\gamma(-\omega_{abc}, \omega_a)\gamma(\omega_b, \omega_c)Q_{20}(\omega_{bc}; t)\exp(-i\omega_a t) \right. \\
&\qquad + \tfrac{1}{10}m(-\omega_{abc})b(\omega_a, \omega_b, \omega_c)Q_{10}(\omega_{abc}; t) \\
&\qquad \left. + \tfrac{3}{10}b(-\omega_{abc}, \omega_a, \omega_b)m(\omega_c)Q_{10}(\omega_c; t)\exp(-i\omega_a t) \right]
\end{aligned}
$$
(52)

$$
\begin{aligned}
\chi^{(2)}&(-\omega_{abc}; \omega_a, \omega_b, \omega_c; t) \\
&= \tfrac{2}{45} \mathop{\mathbf{S}}_{abc} \left(\tfrac{1}{2}m(-\omega_{abc})m(\omega_a)\gamma(\omega_b, \omega_c) \right. \\
&\qquad\times \{ 3R_{10}(\omega_a)[Q_{10}(\omega_{abc}; t) - Q_{11}(\omega_{bc}; t)] \\
&\qquad\quad - R_{20}(\omega_{bc})[Q_{10}(\omega_{abc}; t) - Q_{12}(\omega_a; t)] \} \\
&\qquad + \gamma(-\omega_{abc}, \omega_a)m(\omega_b)m(\omega_c)R_{10}(\omega_c) \\
&\qquad\quad \times [Q_{20}(\omega_{bc}; t) - Q_{21}(\omega_b; t)] \\
&\qquad \left. \times \exp(-i\omega_a t) \right)
\end{aligned}
$$
(53)

$$
\begin{aligned}
\chi^{(3)}&(-\omega_{abc}; \omega_a, \omega_b, \omega_c; t) \\
&= -\tfrac{1}{45} \mathop{\mathbf{S}}_{abc} m(-\omega_{abc})m(\omega_a)m(\omega_b)m(\omega_c) \\
&\quad R_{10}(\omega_c)\{R_{20}(\omega_{bc})[Q_{10}(\omega_{abc}; t) - Q_{12}(\omega_a; t)] \\
&\qquad\quad - R_{21}(\omega_b)[Q_{11}(\omega_{ab}; t) - Q_{12}(\omega_a; t)]\}
\end{aligned}
$$
(54)

In Eqs. (52)–(54) we have introduced the time-dependent relaxational functions

$$
Q_{km}(\omega_{abc}; t) = R_{km}(\omega_{abc})\left[\exp\left(-i\omega_{abc}t - \frac{t}{\tau_m}\right) - \exp\left(-\frac{t}{\tau_k}\right) \right]
$$
(55)

where $\mathbf{S}_{abc}$ is the operator of symmetrization over all permutations of the frequencies $\omega_a, \omega_b, \omega_c$.

Equations (50)–(55) represent the chief result of our investigation. They describe the evolution in time of the process leading, in liquids, to a steady state of third-order polarization under the action of three, in general, time-variable electric fields (45).