Step 9. This is the thermal hydrolysis equilibrium spoken of earlier and in argument 5. The amount of impurity H_2O in the solvent acetic acid and not the product H_2O from step 7 is the critical factor in determining the importance of this reaction.

In summary, we believe that the general photochemical mechanism by which Ce(IV) nitrate efficiently decarboxylates glacial acetic acid without utilizing intermediate NO_3 radicals is clearly established. In so doing the concept of *ligand sensitization* was defined and its usefulness demonstrated whenever a ligand actively participates in an elementary step. In the second paper of this series, we shall prove that the concept is not limited to photoinitiated oxidation–reduction reactions as seen in this study, but can be applied to interpret the unexpected chemistry of spontaneous thermal oxidation–reduction processes as well.

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Transient Electric Birefringence of Suspensions of Asymmetric Ellipsoids

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Abstract: The analysis of the time dependence of the birefringence transient in the Kerr cell following sudden removal of the field is extended to include most important cases of a suspension of a monodisperse polymer representable as a rigid ellipsoid. This requires removal of two restrictions made in previous theory: the assumption of a spheroid, which excludes the ellipsoid having three unequal axes, and the condition that the applied field is everywhere normal to the axis of the Kerr cell, which neglects field end effects of importance particularly in small cells. Expressions are obtained for the birefringence of a suspension in a nonuniform field of arbitrary direction, the relaxation times for the decay in birefringence in the general case, the explicit dependence of the birefringence on the angle through which the axis of the distribution function for angular orientation of the polymer is rotated away from the normal to the cell axis in the case of the spheroid, and the correction for field nonuniformity in previous results for the case of the spheroid.

The rate of disappearance of birefringence of a solution of a polymer in the Kerr cell following sudden removal of the orienting electric field is determined by the rotational diffusion properties of the polymer. If the particular polymer can be represented in a satisfactory fashion by a model structure for which theory is available relating the optical and diffusion behavior of the model to the parameters specifying its shape, then the values of these parameters corresponding to the polymer can be estimated from birefringence data. The simplicity of the model depends on two initial decisions. First, it is necessary to determine whether the molecule behaves in orientation and diffusion as a rigid body or whether it is deformable. Second, one must specify a size range for the model, since this will determine the approximations made in the analysis of its optical and viscous properties. The present investigation is concerned with suspensions of rigid dielectric particles which are very small with respect to the wavelength of light but of sufficient size to permit introduction of macroscopic quantities, like the capacitivity, in the analysis of their polarization and rotational diffusion.

The elements of theory required to describe the variation in birefringence of a suspension following removal of an orienting field are threefold: (1) a theory of Brownian motion applicable to the shape class of the model, which introduces the rate of dissipation of energy or the time scale into the diffusion problem and which relates the macroscopic diffusion constants to the frictional constants of individual particles; (2) expressions for the frictional constants for the model, which introduce the dependence of the diffusion rate on the parameters specifying size and shape within the general shape class of the model; and (3) a theory for the birefringence of a suspension of particles of given orientation which relates the observed quantity, the retardation, to the probability density function for orientation at a given point.

The most general shape class for which all three elements of theory are available is that of the asymmetric ellipsoid. (In the following, the terms symmetric and asymmetric ellipsoid are employed to designate the spheroid of rotation and the ellipsoid possessing three unequal axes, respectively.) The theory of Brownian motion of ellipsoids has been given by Perrin,[1,2] who obtained the rotational diffusion equation for a suspension of such particles, its general

(1) F. Perrin, *J. Phys. Radium*, [7] **5**, 497 (1934).
(2) F. Perrin, *ibid.*, [7] **7**, 1 (1936).

solution in the case of the spheroid, and expressions for the time variations of several mean quantities which appear in the analysis of the behavior of the asymmetric ellipsoid. A recent, independent analysis has been given by Favro.[3] The expressions for the frictional drag experienced in steady rotation about each of the axes of the asymmetric ellipsoid have been derived in terms of the axial lengths of the ellipsoid by Edwardes.[4] Theories of Brownian motion relate the macroscopic constants of the diffusion equation to these expressions. The analysis of the static electric properties of the dielectric ellipsoid in a uniform field is a classical problem of potential theory employing ellipsoidal harmonics and is given by Stratton.[5] The theory of Peterlin and Stuart[6] of the birefringence of ordered suspensions applies the results of the static case to the optical problem, thus treating the problem as one of the polarization of macroscopic dielectrics. Recently, Taylor and Cramer[7] have rederived the Peterlin–Stuart result as a problem of Rayleigh–Gans scattering, for which the underlying assumptions are better understood. The results obtained in these theories suffice to calculate the birefringence of a suspension of asymmetric ellipsoids following removal of an orienting field.

Almost all recent studies of the birefringence transient of solutions of biological polymers (proteins and nucleic acids) in the Kerr cell have employed the carefully elaborated treatment of Benoit[8] of the rotational diffusion equation for ellipsoids. Two of the assumptions made in this study form important restrictions to its application, however. The first is that the analysis is confined to the case of the spheroid possessing optical and electric as well as geometric symmetry about its axis of rotation. Thus, molecules requiring representation as asymmetric ellipsoids, those with permanent dipole moments of nonaxial orientation, and those with intrinsic biaxial birefringence, all three of which probably form important classes in protein structure, are excluded from treatment. Second, Benoit assumes that the applied electric field orienting the particles is perpendicular to the optic axis of the Kerr cell. This requires that the field lines of the orienting field be paralleled throughout the cell and that the field end effects at the edges of the Kerr-cell electrodes be neglected.

The fundamental nature of these assumptions in the analysis is shown by examination of their effects on the differential equation for diffusion. We let ϑ, ϕ, and ψ be the Eulerian angles describing the orientation of the electric axes a_1, a_2, and a_3 of the particle with respect to a laboratory coordinate system, with ϑ and ϕ being the colatitude and azimuthal angles of, *e.g.*, axis a_3, and with ψ describing the rotation of the ellipsoid about axis a_3. The differential equation for rotational diffusion of ellipsoids, derived from the theory of Brownian motion given by Perrin[2] in terms of the Eulerian angles, is

$$\frac{\partial \rho}{\partial t} = (\Re_1 \cos^2 \psi + \Re_2 \sin^2 \psi)\frac{\partial^2 \rho}{\partial \vartheta^2} + (\Re_1 \sin^2 \psi + \Re_2 \cos^2 \psi)\left(\cot \vartheta \frac{\partial \rho}{\partial \vartheta} + \frac{1}{\sin^2 \vartheta}\frac{\partial^2 \rho}{\partial \phi^2} + \cot^2 \vartheta \frac{\partial^2 \rho}{\partial \psi^2} - \frac{2 \cot \vartheta}{\sin \vartheta}\frac{\partial^2 \rho}{\partial \phi \partial \psi}\right) + \Re_3 \frac{\partial^2 \rho}{\partial \psi^2} + 2(\Re_1 - \Re_2)\frac{\cos \psi \sin \psi}{\sin \vartheta}\left(\frac{\partial^2 \rho}{\partial \vartheta \partial \phi} - \cos \vartheta \frac{\partial^2 \phi}{\partial \vartheta \partial \psi} + \frac{1 + \cos^2 \vartheta}{2 \sin \vartheta}\frac{\partial \rho}{\partial \psi} - \cot \vartheta \frac{\partial \rho}{\partial \phi}\right) \quad (1)$$

where $\rho = \rho(\vartheta, \phi, \psi, t)$ is the probability density function for orientation. The diffusion constants $\Re_i$ are

$$\Re_i = \frac{kT}{C_i} \quad (2)$$

where kT is the thermal energy, and C_i is the frictional couple encountered by the particle in steady rotation at unit angular velocity about its ith axis. The first restriction made by Benoit, requiring rotational symmetry about one of the axes of the particle (*e.g.*, axis a_3), has two effects on the differential equation. First, since $\Re_1 = \Re_2$, the assumption simplifies the coefficients of the first two terms in (1) and eliminates the final bracketed term. The other effect is that, since all orientations about a_3 are physically equivalent, no orientation mechanism can produce a distribution with a probability density function containing a ψ dependence. Taking this as an initial condition on the diffusion, one may eliminate those terms in eq 1 containing differentiation with respect to ψ. The second restriction in the Benoit treatment is that ρ possess a symmetry axis normal to the direction of measurement of the birefringence, *e.g.*, parallel to the fixed axis from which ϑ is measured. This would be the case if the external field were uniform, assuming proper alignment of the Kerr cell. With this restriction, ρ becomes independent of ϕ, and those terms in (1) involving differentiation by ϕ vanish. As a result of the two restrictions together, eq 1 becomes

$$\frac{\partial \rho}{\partial t} = \Re_1\left(\frac{\partial^2 \rho}{\partial \vartheta^2} + \cot \vartheta \frac{\partial \rho}{\partial \vartheta}\right) \quad (3)$$

which may also be written

$$\frac{\partial \rho}{\partial t} = \Re_1 \nabla^2 \rho \quad (4)$$

if the Laplacian operator is specialized to include no ϕ or ψ dependence. This is the equation, although obtained in a different fashion, which is solved by Benoit. Evidently, if the two restrictions are to be removed, then one must return to the full diffusion equation (1).

The present investigation extends the analysis of birefringence in the Kerr cell following removal of the orienting field to include most important cases of the rigid ellipsoid which do not fulfill the Benoit restrictions. We shall state the problem in its general form as follows. Consider a suspension of identical, rigid, anisotropic, nonabsorbing, dielectric, asymmetric ellipsoids, with permanent dipoles, uniformly distributed in a homogeneous, isotropic medium of infinite extent.

(3) L. D. Favro, *Phys. Rev.*, **119**, 53 (1960).
(4) D. Edwardes, *Quart. J. Math.*, **26**, 70 (1893).
(5) J. A. Stratton, "Electromagnetic Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, Sections 3.27 and 3.29.
(6) A. Peterlin and H. A. Stuart, "Doppelbrechung, insbesondere künstliche Doppelbrechung," in "Hand- und Jahrbuch der chemischen Physik," Band 8/13, A. Eucken and K. L. Wolf, Ed., Akademische Verlagsgesellschaft, Leipzig, 1943.
(7) E. W. Taylor and W. Cramer, *Biophys. J.*, **3**, 127 (1963).
(8) H. Benoit, *Ann. Phys.*, [12] **6**, 561 (1951).

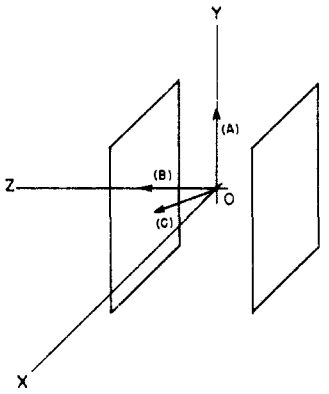

Figure 1. Orientation of electrodes relative to the axial system *OXYZ*: (A) propagation vector of light, (B) applied electric field strength, (C) electric vector of light.

Let the axes of the capacitivity tensor of the material coincide with the geometric axes of the ellipsoids, but assume no restriction on the orientation of the permanent dipole moment. Take the concentration of particles to be sufficiently dilute so that the field arising from the polarization of one particle by an applied electric field is negligible in the vicinity of all other particles; and let the particles be within the size range and possess the optical properties assumed for application of Rayleigh–Gans scattering theory. Let an external field orienting the particles be applied which varies in general in direction, but assume that the field lines always lie in planes parallel to that defined by the predominant field direction in the Kerr cell and the direction along which the retardation is to be measured[9] (the *YOZ* plane in the coordinate system defined below; *cf.* Figure 1). It is desired to calculate the birefringence of the suspension as a function of time following sudden removal of the external field.

The discussion is divided into four sections. In section I, an expression is obtained for the birefringence of an oriented suspension of the defined type in which the symmetry axis of orientation is not perpendicular to the direction of measurement of retardation. The final result is written in the form required for the second section in terms of the distribution function for orientation without evaluation of the distribution. In section II, the solution to the general problem is given, with attention being directed at the expressions for the relaxation times for the decay of birefringence. In section III, the dependence of the measured retardation is written explicitly in terms of the direction of the symmetry axis of the distribution function for a suspension of spheroids. Finally, in section IV, the results of the third section are introduced into Benoit's study to permit evaluation of data on the relaxation of retardation for suspensions of spheroids in cases in which the orienting field is known to be nonuniform.

I. Birefringence of Oriented Suspensions

An effect of orientation of ellipsoidal particles in a suspension is to render the suspension birefringent. In a uniform external field, the birefringence must be constant and, by symmetry, uniaxial with the optic axis parallel to the field strength. In a nonuniform field, any volume element small with respect to the variation in the field direction is subjected to an approximately uniform field, and the birefringence over the volume element is constant and uniaxial. Since previous studies of Kerr-cell birefringence have been confined to the uniform-field case, the wave normal has been taken perpendicular to the optic axis of the suspension. In extending the analysis to include the nonuniform field, it is therefore necessary to obtain an expression for the birefringence in cases in which the optic axis is tilted away from the perpendicular. This is the purpose of the present section.

We shall first define some axial systems and the transformations relating them which will facilitate our subsequent description of the initial particle orientation and the effect of diffusion on the orientation. Let *OXYZ* (*cf.* Figure 1) be a set of rectangular coordinates fixed with respect to the Kerr cell, with *OZ* parallel to the predominant external field direction (perpendicular to the electrode faces), *OY* such that the light is propagated parallel to *OY* from negative values of *Y*, and with *OX* completing the right-handed system. To each particle, assign two sets of coordinates. Let one of them, *OX'Y'Z'*, be fixed with respect to *OXYZ*, with its axes parallel to the geometric axes of the particle at the instant the field is removed. Let the other, *OX''Y''Z''*, move with the particle, with its axes parallel to those of the particle at all times. Relating the three systems of coordinates for a particle, we define two transformations, with matrices $A = (a_{ij})$ and $C = (c_{ij})$, such that

$$l_j' = \sum_k c_{jk} l_k''$$

$$l_i = \sum_j a_{ij} l_j' = \sum_j \sum_k a_{ij} c_{jk} l_k'' \qquad (5)$$

(Throughout the following, sums are over the three axes, with the sum indices referring to the appropriate *x*th, *y*th, and *z*th axes, respectively.) The quantities l_j'', l_j', and l_j are the direction cosines of any given vector fixed within the particle with the *j*th axes of the systems of coordinates *OX''Y''Z''*, *OX'Y'Z'*, and *OXYZ*, respectively. Evidently, the elements a_{ij} are independent of time and describe the initial distribution of particle orientations, whereas the c_{ij}'s are in general time dependent and describe the Brownian motion of the particles following removal of the field. Since in the absence of the field the motion of a particle is independent of its orientation (in the assumed dilute suspension), the elements of *C* are independent of *A*. The elements of *A* are obviously independent of *C*.

The most concise derivation of the birefringence of a suspension is that of Taylor and Cramer[7] employing a method described especially by van de Hulst.[10] In applying this method, we shall restrict discussion largely to the immediate application here and refer to these sources for its justification and elaboration. We wish to calculate the effect of a layer of a dilute oriented suspension of very small particles of the assumed type, continuous at its two faces with semi-infinite layers of suspending medium, upon light propagated through it as seen at a point *P* far removed from the layer. In the Rayleigh–Gans approximation,

(9) In a Kerr cell, the electrodes are standardly rectangular, and the edges producing the disturbing end effects in the field are normal to the *YOZ* plane. Consequently, this assumption is sufficiently general to include the types of nonuniform fields usually encountered.

(10) H. C. van de Hulst, "Light Scattering by Small Particles," John Wiley and Sons, Inc., New York, N. Y., 1957.

which is assumed to apply in the present case, the light at P is a superposition of the primary wave and of dipole radiation (scattering) arising from polarization of the individual particles by the primary wave. The expression for the total scattered amplitude represents the sum over all particles contributing to the scattered light at P. This summation, which will be replaced by an integration, is simplified by two factors. First, the amplitude of the scattered wave from a given particle depends on particle orientation relative to the primary beam because of the anisotropy of the particle, *i.e.*, the dependence on direction of the particle polarizability. It should be noted that an ellipsoidal particle is anisotropic as a result of its shape, even in the case that it consists of a material which is itself isotropic. Second, if the suspension is only slightly turbid, as we assume in taking the concentration of particles to be dilute, then the only particles which contribute to the scattering intensity at a point P far from the layer are those contained in the small cylindrical volume about the layer normal through P. For these particles, one need consider only expressions for zero-angle scattering (parallel to the direction of propagation of the primary beam). In performing the integration over contributing particles, let $d\Omega$ designate an infinitesimal range about the orientation Ω in some configuration space for the particles; $dn(\Omega)$, the number of particles with orientation Ω, $\Omega + d\Omega$; and $\rho(\Omega)$, the probability density function for particle orientation. If N is the number of particles per unit volume in the suspension and V the volume contributing to scattered light at P, then $dn = NV\rho(\Omega)\, d\Omega$; and if $u_i'(\Omega)$ is the zero-angle scattering amplitude at P for light polarized parallel to i from a particle of orientation Ω, then the total scattered amplitude at P from all particles is $\int u_i'(\Omega)\, dn(\Omega) = NV\int u_i'(\Omega)\rho(\Omega)\, d\Omega = NV\langle u_i'\rangle$, where the integration extends over all possible orientations. The integral is thus simply proportional to the averaged expression for zero-angle scattering from a single particle.

We shall describe polarized light in terms of two linearly polarized components of amplitudes u_Z and u_X with their electric vectors parallel and perpendicular, respectively, to the YOZ plane in the coordinate system defined earlier. Let $\{i\}$ be a column vector with elements u_Z and u_X, with $\{0\}$ and $\{1\}$ being associated with incident and scattered light, respectively. The average zero-angle scattering amplitude of radiation for a single particle may be written in the form

$$\{1\} = \frac{\mathbf{S}e^{-ik(r-y)}}{ikr}\{0\} \tag{6}$$

where $\{0\}$ characterizes the primary polarizing wave, $k = 2\pi/\lambda$ is the wave number of the light in the suspending medium, y the vertical distance from the layer to P, and r the distance from the scattering particle to P. The light-scattering problem is solved by calculation of the four elements of the scattering matrix $\mathbf{S}$ of the transformation defined by (6).

In general, the particle dipole moment $\mathbf{p}$ induced by an external field E is

$$\mathbf{p} = \epsilon_0\sum_i \alpha_i(\mathbf{E}\cdot\mathbf{e}_i)\mathbf{e}_i \tag{7}$$

(the dimensions here and throughout are in the rationalized mks system; ϵ_0 is the capacitivity of free space), where $\mathbf{e}_i$ is a unit vector parallel to the ith electric axis of the particle, and α_i is the polarizability along that axis. For an alternating field, such as that associated with the light wave, α_i is dispersive. Since we are interested in scattered light in the direction OY only, we wish expressions for the transverse polarizations, p_x and p_z. The component p_x of the induced dipole moment in the OX direction is

$$p_x = \epsilon_0 E_x\sum_i \alpha_i(\mathbf{e}_i\cdot\mathbf{e}_x)^2 + \epsilon_0 E_z\sum_i \alpha_i(\mathbf{e}_i\cdot\mathbf{e}_x)(\mathbf{e}_i\cdot\mathbf{e}_z) \tag{8}$$

and the analogous expression for p_z is formed by mutual exchange of x and z. The scalar products in (8) are the direction cosines, which can be written in terms of the elements of matrices A and C in eq 5, one observing that the subscript of p_i is the same as that of l_i and that of α_i fixes l_k'' to δ_{ik}.

If $p_\nu^{(i)}$ is the magnitude of the dipole moment in the νth direction induced in a particle by the primary plane wave u_{0i}

$$u_{0i} = e^{i(\omega t - kr)} \tag{9}$$

polarized parallel to the ith direction, then the amplitude $u_{1\nu}^{(i)}$ of the spherical wave radiated in directions normal to ν by the dipole, at distances far from the dipole, is[11]

$$u_{1\nu}^{(i)} = \frac{k^2}{4\pi\epsilon_l}\frac{p_\nu^{(i)}}{r}e^{i(\omega t - kr)} = \frac{ik^3 p_\nu^{(i)}}{4\pi\epsilon_l}\frac{e^{-ik(r-y)}}{ikr}\cdot u_{0i} \tag{10}$$

where ϵ_l is the capacitivity for the frequency ω of pure solvent. Substituting eq 8 into 10 and comparing with eq 6, one obtains[12] after conversion of the direction cosines as indicated

$$\begin{aligned} S_{11} &= q\,\langle\sum_i \alpha_i(\sum_j a_{3j}c_{ji})^2\rangle \\ S_{22} &= q\langle\sum_i \alpha_i(\sum_j a_{1j}c_{ji})^2\rangle \\ S_{12} = S_{21} &= q\langle\sum_i \alpha_i(\sum_j a_{1j}a_{3j}c_{ji}^2 + 2\sum_{j>k}\sum a_{1j}a_{3k}c_{ji}c_{ki})\rangle \end{aligned} \tag{11}$$

where $q = ik^3/4\pi n_l^2$ ($\epsilon_l/\epsilon_0 = n_l^2$). The expressions indicate averages over particle orientations.

We can show that the off-diagonal elements S_{12} and S_{21} vanish in the mean. Since matrices A and C are independent, we may write $\langle a_{1j}a_{3j}c_{ji}c_{ki}\rangle = \langle a_{1j}a_{3j}\rangle\langle c_{ji}c_{ki}\rangle$. The double sum in S_{12} vanishes because $\langle c_{ji}c_{ki}\rangle = 0$ if $j \neq k$, as discussed below. The averages of the squares of elements of C do not in general vanish. The quantities a_{1j} and a_{3j} are the direction cosines of the jth axis of the ellipsoid with the coordinates OX and OZ, respectively, at the instant the field is removed. Because of the rotational symmetry of the angular distribution of particles about the orienting field direction, which, lying by assumption in the YOZ plane, is always normal to OX, and the bilateral symmetry of the distribution about the YOZ plane, this product and thus the first sum in S_{12} must evidently also vanish in the mean. It follows that $S_{12} = S_{21} = 0$. The scattering matrix is therefore diagonal, and one may write for the total scattered amplitudes

(11) Reference 5, Section 8.5 (27).

(12) If $E_x = E_z$, this is the usual case in the Kerr cell, in which the light is polarized at 45° to the applied field.

$$u_{1z} = S_{11}\frac{e^{-ik(r-y)}}{ikr}u_{0Z}$$

$$u_{1x} = S_{22}\frac{e^{-ik(r-y)}}{ikr}u_{0X} \quad (12)$$

so that the two waves are scattered as if independent with scalar scattering functions. Integration of these expressions over the volume contributing to the forward scattering yields[13] as the total amplitude u_ν, primary and scattered[14]

$$u_\nu = u_{0\nu}\left(1 - \frac{2\pi}{k^2}NlS_\nu\right) \quad (13)$$

$$\nu = Z, X$$

where N is the number of particles per unit volume, l the thickness of the layer, and $S_Z \equiv S_{11}$ and $S_X \equiv S_{22}$.

In order to find the refractive index corresponding to each wave, we formally replace the layer of suspension with a slab of homogeneous material and adjust its refractive index until it produces the same effect on the light at P as that produced by the suspension. We then accept this value of the refractive index as that of the suspension. The effect of the slab on $u_{0\nu}$ is to retard it by the amount of time $\Delta t = l[(1/v_\nu) - (1/v_l)] = l(n_\nu - n_l)/c$, where n_ν and n_l are the refractive indices of the slab and adjacent semi-infinite dielectric (suspending medium), respectively. The difference $(n_\nu - n_l)$ is assumed to be close to unity in the Rayleigh–Gans approximation. The retarded wave becomes ($k = \omega n_l/c$)

$$u_\nu = e^{-ikl(n_\nu - n_l)/n_l}u_{0\nu} = u_{0\nu}\left[1 - \frac{ikl}{n_l}(n_\nu - n_l)\right] \quad (14)$$

In the general case, n_ν is complex, its real part determining the phase lag of the light upon transmission and the imaginary part absorption effects. Since the suspension is assumed to be nonabsorbing, n_ν here is purely real. If the effects of the suspension and slab on the light at P are to be identical, then we may equate the amplitudes in the two cases and thus obtain

$$\frac{n_\nu}{n_l} = 1 - i\frac{2\pi N}{k^3}S_\nu \quad (15)$$

the subscript in n_ν denoting the case under comparison. The desired expression for the birefringence Γ is obtained as the difference $n_z - n_x (= n_p - n_s)$

$$\Gamma = \frac{N}{2n_l}\langle\sum_i \alpha_i[\sum_j (a_{3j}^2 - a_{ij}^2)c_{ji}^2 + 2\sum_{j>k}\sum(a_{3j}a_{3k} - a_{1j}a_{1k})c_{ji}c_{ki}]\rangle \quad (16)$$

II. Relaxation Times in Anisotropic Diffusion

We shall now evaluate eq 16 for the general conditions set forth in the problem as stated in the introductory section. The equation consists of sums of averages of products of an element of the polarizability tensor of the typical particle: two elements (which may be the same or different) of matrix A and two elements of matrix C. As before, since A and C are independent, the mean of the product of an element of A with one of C is the product of the individual means. The elements of A, first, describing the orientation of the particles at the instant the field is removed, *e.g.*, at time zero, will not be evaluated as such. It will be found that they are not contained in the expressions for the relaxation times and that they occur in the equation for the birefringence in such a fashion that it would be exceedingly difficult either to estimate them individually or to obtain information from them about the particles. With respect to the elements of C, expressions for the time-dependent averages of all pairwise products of direction cosines are given by Perrin[2] in terms of the frictional constants of the particles. They are derived from the general diffusion equation (1) with the initial condition that, in the mean, the axes of the particles coincide at time zero with their respective Kerr-cell axes. This condition is not fulfilled by the initial distribution of particles, *i.e.*, $\langle a_{ij}\rangle \neq \delta_{ij}$, except in the trivial case of the infinite orienting field. Since it is fulfilled, as is the more rigorous condition $c_{ij} = \delta_{ij}$ itself, by the elements of matrix C initially, Perrin's results do give us the quantities $\langle c_{ij}c_{kl}\rangle$. This is the reason for the introduction of the separate matrices. The device, which is applied, for example, by Einstein,[15] in his theory of translational Brownian motion, has the effect formally of assigning to all particles identical initial orientations in a single common axial system and identifying concentrations here with probability densities in random diffusion. It is valid if the subsequent motions of the individual particles are independent, *i.e.*, if the matrices A and C are uncorrelated.

Perrin obtains, first, that the means of all double products in which any index value occurs only once vanish. This result eliminates all terms in the second sum in the brackets in eq 16. For the squared elements, Perrin finds (his eq 32 and 33)

$$\langle c_{ii}^2\rangle = \frac{1}{3} + \frac{1}{3}(1 + \Theta_i)e^{-6\Theta_- t} + \frac{1}{3}(1 - \Theta_i)e^{-6\Theta_+ t}$$

$$\langle c_{ij}^2\rangle = \frac{1}{3} - \frac{1}{6}(1 - 2\Theta_k)e^{-6\Theta_- t} - \frac{1}{6}(1 + 2\Theta_k)e^{-6\Theta_+ t} \quad (17)$$

where i, j, and k are all different, where

$$\Re = \frac{1}{3}\Sigma\Re_i$$

$$\wp^2 = \frac{1}{3}\sum_{i>j}\sum\Re_i\Re_j \quad (18)$$

$$\Theta_i = \frac{\Re_i - \Re}{2\sqrt{\Re^2 - \wp^2}}$$

and where

$$\Theta_\pm = \Re \pm \sqrt{\Re^2 - \wp^2} \quad (19)$$

The quantities $\Re_i$ are the rotational diffusion constants defined in eq 1 which are related to the particle properties as $\Re_i = kT/C_i$ (eq 2). The equations of the frictional constants C_i for an ellipsoid of axial lengths $2a$, $2b$, and $2c$ corresponding to the subscripts 1, 2,

(13) There are typographical errors in the analogous expressions in Taylor and Cramer.

(14) Reference 10, p 32.

(15) A. Einstein, *Ann. Phys.*, 17, 549 (1905), Section 4.

and 3, respectively, are derived by Edwardes,[4] to be[16]

$$C_1 = \frac{16\pi\eta}{3}\frac{a_2^2 + a_3^2}{a_2^2P_2 + a_3^2P_3}$$
$$C_2 = \frac{16\pi\eta}{3}\frac{a_1^2 + a_3^2}{a_1^2P_1 + a_3^2P_3} \qquad (20)$$
$$C_3 = \frac{16\pi\eta}{3}\frac{a_1^2 + a_2^2}{a_1^2P_1 + a_2^2P_2}$$

where η is the viscosity of the suspending liquid. The constants P_1, P_2, and P_3 are the definite integrals

$$P_i = \int_0^\infty \frac{d\lambda}{(a_i^2 + \lambda)K} \qquad (21)$$

where $K^2 = (a_1^2 + \lambda)(a_2^2 + \lambda)(a_3^2 + \lambda)$. The integrals in (21) cannot be solved in closed form unless at least two of the axes are of equal length, *i.e.*, in the case of the spheroid.

For convenience of computation, eq 19 and 21 may be written in the following forms

$$\Theta_\pm = \frac{kT}{3}\left[\sum_i \frac{1}{C_i} \pm \left(\sum_i \frac{1}{C_i^2} - \sum_{i>j}\sum \frac{1}{C_iC_j}\right)^{1/2}\right] \qquad (19')$$

$$P_a = \frac{p}{\sin^2\alpha}[F(\beta) - E(\beta)]$$

$$P_b = \frac{P}{\sin^2\alpha\cos^2\alpha}\left[E(\beta) - \cos^2\alpha F(\beta) - \frac{\sin^2\alpha\sin\beta\cos\beta}{\cos\gamma}\right] \qquad (21')$$

$$P_c = \frac{p}{\cos^2\alpha}\left[\frac{\sin\beta\cos\gamma}{\cos\beta} - E(\beta)\right]$$

where $\cos\beta = c/a$, $\cos\gamma = b/a$, $\sin\alpha = \sin\gamma/\sin\beta$, and $p = (2\cos\gamma\cos\beta)/(abc\sin^3\beta)$. $F(\beta)$ and $E(\beta)$ are Legendre's elliptic integrals of the first and second kinds, respectively, of modulus $\sin\alpha$ and amplitude β. Equation 19′ is obtained from substitution of the definitions (eq 18) and rearrangement, and eq 21′ are the forms given by Osborn.[17] P_a, P_b, and P_c are identified as P_1, P_2, and P_3 by ordering the three axes 1, 2, and 3 from largest to smallest and labeling them, in this order, as a, b, and c, respectively (so that, *e.g.*, the axis of rotation a_3 is a for the prolate ellipsoid and c for the oblate, and P_3 is P_a and P_c, respectively).

Introducing these results into eq 16, one obtains for the birefringence at any time following removal of the field

$$n_z - n_x = \frac{N}{2n_l}\sum_i\sum_j \alpha_i\langle a_{3j}^2 - a_{1j}^2\rangle\langle c_{ji}^2\rangle \qquad (22)$$

In substituting for $\langle c_{ji}^2\rangle$, we observe first that, since $\Sigma a_{3j}^2 = \Sigma a_{1j}^2 = 1$ (as the sums of squares of the direction cosines of a vector), the constant term $^1/_3$ occurring in each of the averages is eliminated. We find finally

$$\Gamma = \frac{N}{2n_l}(A_+e^{-6\Theta_+t} + A_-e^{-6\Theta_-t}) \qquad (23)$$

where

$$6A_\pm = \langle a_{31}^2 - a_{11}^2\rangle[2\alpha_1(1 \mp \Theta_1) - \alpha_2(1 \pm 2\Theta_3) - \alpha_3(1 \pm 2\Theta_2)] + \langle a_{32}^2 - a_{12}^2\rangle[-\alpha_1(1 \pm 2\Theta_3) + 2\alpha_2(1 \mp \Theta_2) - \alpha_3(1 \pm 2\Theta_1)] + \langle a_{33}^2 - a_{13}^2\rangle[-\alpha_1(1 \pm 2\Theta_2) - \alpha_2(1 \pm 2\Theta_1) + 2\alpha_3(1 \mp \Theta_3)] \qquad (24)$$

Equation 23 is the desired solution to the problem. It is seen, first, that the decrease in birefringence for asymmetric ellipsoids is in general a mixed exponential curve which requires for its characterization two relaxation times $^1/_6\Theta_+$ and $^1/_6\Theta_-$ which may be estimated from it. The two values Θ_+ and Θ_- suffice to detemine the quantities $\mathcal{R}$ and $\mathcal{P}$

$$\mathcal{R} = \frac{1}{2}(\Theta_+ + \Theta_-)$$
$$\mathcal{P}^2 = \Theta_+\Theta_- \qquad (25)$$

one of which, $\mathcal{R}$, is seen from its definition (eq 18) to be related to the harmonic mean of the frictional constants C_i as $kT/\mathcal{R}$. Second, one may conclude that Θ_+ and Θ_- do not contain sufficient information to permit estimation of the three C_i's individually. It is necessary to combine rotational diffusion data with some other shape parameter, such as the volume or the radius of gyration, to obtain a unique determination of the axial lengths. Moreover, no generalization can be made about the relative values of Θ_+ and Θ_- which would serve to distinguish a mixed curve of this origin from one which would also be observed with a mixed suspension of two different types of spheroids. Finally, one notes that in the case of random initial orientation, the mean values of all quantities a_{ij}^2 are equal and the two coefficients $A_\pm$ vanish, as required.

It should be noted that the relaxation times depend solely on the axial lengths of the particles and not on the polarizabilities or initial orientation of the suspension. Taylor and Cramer[18] have recently brought into question the validity of the value of the birefringence as obtained from calculations based on representation of the polymer molecule as a uniform dielectric particle of the same shape. The polarizability tensor, which as we have seen is the basis of the birefringence calculation, is derived in macroscopic theory directly from the relationship between the external (applied) electric field strength and the local field strength within the particle. Thus, a failure of the birefringence calculation would show that the local electric field within the molecule is markedly different from that within the model dielectric particle. It follows that since particles in an electric field seek to minimize, in the mean, the magnitude of the local electric field strength within the particles, and since the variance of the distribution is also a function of the value of the local electric field strength, these results have the same significance to theories of orientation of molecules in electric fields as they do to optical theories. Since both the α_i and the a_{ij} are affected by these considerations, it is felt that more must be known about the local field within polymer molecules before it would be use-

(16) To within an arithmetic error in the final result which is corrected by Perrin.[1] The results must reduce to $8\pi\eta a^3$ for a sphere of radius a.

(17) J. A. Osborn, *Phys. Rev.*, **67**, 351 (1945).

(18) E. W. Taylor and W. Cramer, *Biophys. J.*, **3**, 143 (1963).

ful to evaluate eq 24 for the meaning of the coefficients $A_{\pm}$ of the exponential quantities in the decay curve.

III. Dependence of Birefringence on Field Direction

In the preceding section, the dependence of the birefringence on the angle formed by the field direction with the direction of measurement, being contained in the coefficients $A_{\pm}$, was not evaluated as such. We shall now specialize eq 16 to the case of the optically symmetric spheroid, with, in general, a permanent dipole moment of nonaxial orientation, and transform the resulting expressions to obtain explicit evaluation of this dependence. As in section II, the analysis is general in not requiring any assumptions about orientation mechanisms in describing the initial distribution of particles about the field direction. Moreover, the conclusions apply to a system during its response to the orienting field as well as following removal of the field.

In writing the birefringence for any given instantaneous particle distribution, we formally apply to the suspension an orienting field which produces that distribution and prevent diffusion by equating the matrices C to the unit matrix, *i.e.*, $C_{ij} = \delta_{ij}$. The orientation is thus contained in the distribution of elements of the time-independent matrices A. From eq 16, if $\alpha_1 = \alpha_2 \neq \alpha_3$, then the birefringence produced by the assumed distribution is

$$\frac{2n_l}{N}\Gamma = \sum_i \alpha_1\langle a_{3i}^2 - a_{1i}^2\rangle$$
$$= \alpha_1 \sum_i \langle a_{3i}^2 - a_{1i}^2\rangle - \alpha_1\langle a_{33}^2 - a_{13}^2\rangle + \alpha_3\langle a_{33}^2 - a_{13}^2\rangle$$
$$= (\alpha_3 - \alpha_1)\langle a_{33}^2 - a_{13}^2\rangle \quad (26)$$

the difference of sums of direction cosines vanishing as before.

We shall describe the orientation of a particle by means of its Eulerian angles referred to the axial system $OXYZ$. Let ϑ and ϕ be the colatitude and azimuthal angles of axis a_3, measured from OZ and the YOZ planes, respectively. The third Eulerian angle, ψ, describing rotation about axis a_3, is arbitrary, since its value cannot occur in the expression for the birefringence of particles optically symmetrical about axis a_3. The standard expressions for a_{13} and a_{33}[19] are $a_{13} = \sin\vartheta \sin\phi$ and $a_{33} = \cos\vartheta$. Substitution into eq 26 yields

$$\Gamma = \frac{N}{2n_l}(\alpha_3 - \alpha_1)\langle\cos^2\vartheta - \sin^2\vartheta \sin^2\phi\rangle$$
$$= \frac{N}{2n_l}(\alpha_3 - \alpha_1)\int_0^{2\pi}\int_0^{\pi}(\cos^2\vartheta - \sin^2\vartheta \sin^2\phi)\rho \sin\vartheta \, d\vartheta d\phi \quad (27)$$

The integral definition of the mean has been introduced for evaluation below. Here, $\rho(\vartheta,\phi,t) \sin\vartheta \, d\vartheta d\phi$ is the instantaneous probability that the orientation of a particle be within an infinitesimal region about the particular values (ϑ,ϕ), ρ being the probability density function as before. The second form of eq 27 is eq 37c in Peterlin and Stuart.[6]

Equation 27 for the birefringence is independent of the form of ρ. We now wish to express ρ in as general a form as possible incorporating the dependence on field direction in an explicit form. Independent of whether the particles of a given small volume element of the suspension are at equilibrium with the field at a particular instant, or whether they have undergone diffusion following removal of a field which has completely or partially aligned them, the angular distribution within the volume element must be symmetrical about the field direction in that element, so long as the particles were randomly arranged before application of the field. Let us define a fixed local coordinate system $OX^*Y^*Z^*$ for a given volume element with OZ^* parallel to the applied field strength in the volume element and OY^* lying in the plane formed by the field strength and the direction along which the birefringence is to be measured (the YOZ plane). Let ϑ^* and ϕ^* be the colatitude and azimuthal angles of the symmetry axis of the particle relative to these coordinates, measured, respectively, from OZ^* and the Y^*OZ^* plane. Under very general conditions[20,21] the probability density function ρ may be expanded in terms of the complete orthogonal set formed by the surface zonal harmonics

$$\rho(\vartheta^*,t) = \sum_n A_n(t)P_n(\mu^*) \quad (28)$$

where $\mu^* = \cos\vartheta^*$, and the coefficients A_n are defined by

$$A_n = \frac{1}{2}(2n + 1)\int_{-1}^{1} P_n(\mu^*)\rho d\mu^* \quad (29)$$

The functions $P_n(\mu^*)$ are the Legendre polynomials of the first kind.

Since the meridional planes Y^*OZ and YOZ coincide, we may transform the Legendre polynomials from the one coordinate system to the other by means of biaxial harmonics.[22] In general, if θ is the angle between OZ and OZ^*, and if the meridional planes coincide, then

$$P_n(\mu^*) = \sum_{m=0}^{n}(2 - \delta_{0m})\frac{(n - m)!}{(n + m)!}P_n^m(\cos\theta)P_n^m(\mu)\cos m\phi \quad (30)$$

where $\mu = \cos\vartheta$ and the $P_n^m(\mu)$ are the associated Legendre polynomials of the first kind. We note that the transformation introduces a ϕ dependence into $P_n(\mu^*)$ and thus ρ as expected, since the distribution is not symmetrical about the new axis OZ. Substitution of eq 28 and 30 into eq 27 for the birefringence yields

$$\Gamma = \frac{N}{2n_l}(\alpha_3 - \alpha_1)\sum_n\sum_m A_n(2 - \delta_{0m})\frac{(n - m)!}{(n + m)!}P_n^m(\cos\theta) \times \int_{-1}^{1}\int_0^{2\pi}[\mu^2 - (1 - \mu^2)\sin^2\phi]P_n^m(\mu)\cos m\phi \, d\phi d\mu \quad (31)$$

(19) *Cf.* H. Goldstein, "Classical Mechanics," Addison-Wesley Publishing Co., Reading, Mass., 1950, p 107 ff.

(20) J. G. Kirkwood, *J. Polymer Sci.*, 12, 1 (1954).

(21) I. Tinoco, *J. Am. Chem. Soc.*, 77, 4486 (1955).

(22) W. R. Smythe, "Static and Dynamic Electricity," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Section 5.24.

Applying the recursion formulas and other properties of the Legendre polynomials,[21] especially

$$\mu^2 = \frac{1}{3}[P_0(\mu) + 2P_2(\mu)]$$
$$(1 - \mu^2) = \frac{2}{3}[P_0(\mu) - P_2(\mu)] = \frac{1}{3}P_2^2(\mu) \quad (32)$$

one obtains for the integrals

$$\int_{-1}^{1}\int_{0}^{2\pi} \mu^2 P_n^m(\mu) \cos m\phi \, d\phi d\mu = \frac{4\pi}{3}\left(\delta_{0m}\delta_{0n} + \frac{2}{5}\delta_{2m}\delta_{2n}\right) \quad (33)$$

$$\int_{-1}^{1}\int_{0}^{2\pi} (1 - \mu^2)(1 - \cos^2\phi) P_n^m(\mu) \cos m\phi \, d\phi d\mu = \frac{4\pi}{3}\left(\delta_{0m}\delta_{0n} - \frac{1}{5}\delta_{0m}\delta_{2n} - \frac{6}{5}\delta_{2m}\delta_{2n}\right)$$

Substitution into eq 31 yields

$$\Gamma = \frac{N}{2n_l}(\alpha_3 - \alpha_1)\frac{2\pi}{15}A_2[6P_2(\cos\theta) + P_2^2(\cos\theta)] \quad (34)$$

Applying the relations

$$P_2(\cos\theta) = \frac{1}{2}(2 - 3\sin^2\theta)$$
$$P_2^2(\cos\theta) = 3\sin^2\theta \quad (35)$$

one obtains finally

$$\Gamma = \frac{2\pi N}{5n_l}(\alpha_3 - \alpha_1)(\cos^2\theta)A_2 \quad (36)$$

This is the desired expression for the birefringence as a function of field direction. It shows that the birefringence characteristic of a particular field strength, as given, for example, by the Kerr law, is weighted by the square of the cosine of the angle through which the field is tilted. One notes that the probability density function for particle orientation is represented in eq 36 solely by the coefficient A_2 of the second term in its expansion in spherical harmonics.

It is appropriate to discuss the necessity of correction for field end effects in Kerr-cell work and the application of eq 36. The integrated intensity at the photomultiplier tube in a Kerr apparatus is given by

$$I = \int g(\delta)\, dxdz \quad (37)$$

the coordinates referring to the axial system $OXYZ$, where $\delta(x,z)$ is the retardation produced by the column of a given cross section $dxdz$, and $g(\delta)$ is the intensity due to a beam of unit cross section propagated through a system producing uniform retardation δ. The integration extends over the total cross-sectional area occupied by the beam in the cell. If the applied field is of uniform strength throughout the sample volume, of length l, then δ is a constant and the intensity is $g(\Gamma,l)a$, where a is the beam cross section and Γ the birefringence of the suspension. Because of end effects, the field strength does not in general have constant magnitude or direction, so that the retardation produced by any given volume element in the suspension is a function of its position. The full integration, or field correction, is evidently necessary whenever a significant fraction of the volume occupied by the beam is in the region of field nonuniformity.

The nature of the correction required depends on the size of the Kerr cell. In large cells, in which the beam cross section is very small relative to the distance between the electrodes, the beam may be taken as approximately confined to the midplane between the electrode faces. By symmetry, the field at the midplane is everywhere perpendicular to the plane, so that no correction for direction is required. A simple correction for the decreasing magnitude of the field strength in the midplane near and beyond the ends of the electrodes has been given by Chaumont[23] which applies if the windows are sufficiently far removed from the ends of the electrodes so that they do not perturb the field. In smaller Kerr cells, such as those now standardly being employed in studies of proteins and nucleic acids, the light beam almost fills the electrode gap and the windows are placed close to the ends of the electrodes. This design is chosen both to maintain maximum light passing through the system and to restrict the required volume of sample. If the field is nonuniform in a significant portion of the sample volume near the windows, direct evaluation of the integral in eq 37 may be needed in careful work concerned with the absolute magnitude (as opposed to its relative time variation; see below) of the birefringence.

IV. Relaxation Time of the Optically Symmetric Spheroid

The important conclusion is obtained from eq 23 that the relaxation times in the decay of birefringence of a suspension of ellipsoids are independent of the field direction within the Kerr cell. If they are the desired quantities in a particular study, then it is not necessary to make a correction for field end effects. In studies requiring the absolute magnitude of the birefringence, an equation derived for the uniform field is corrected for field direction by multiplication with the square of the cosine of the angle through which the field is tilted from the perpendicular, as we have seen. Benoit's results for the optically symmetric spheroid may be corrected directly in this way. Because of the wide application of the Benoit derivation, it is of interest to consider its relation to the present analysis.

The differential equation describing the motion of the particles following removal of the field is, from eq 4

$$\frac{1}{\Re_1}\frac{\partial\rho}{\partial t} = (1 - \mu^{*2})\frac{\partial^2\rho}{\partial\mu^{*2}} - 2\mu^*\frac{\partial\rho}{\partial\mu^*} \quad (38)$$

In Benoit's study, eq 38 is written in terms of the cell coordinates $OXYZ$, since the distribution is symmetric about OZ, whereas in the present case it is necessary to use the local coordinates $OX^*Y^*Z^*$. The usual separation of variables leads to a differential equation in the time with solutions of the form

$$B_n' e^{-n(n+1)\Re_1 t} \quad (39)$$

where $-n(n + 1)$ is the separation constant, n being any positive integer, and an equation $M = M(\mu^*)$ in the

(23) M. L. Chaumont, *Ann. Phys.*, [9] **5**, 17 (1916).

spatial coordinates

$$\frac{d}{d\mu^*}\left[(1 - \mu^{*2})\frac{dM}{d\mu^*}\right] = -n(n + 1)M \qquad (40)$$

Equation 40 is Legendre's equation. Its solutions are the surface zonal harmonics

$$M = \sum_n C_n' P_n(\mu^*) \qquad (41)$$

the Legendre polynomials of the second kind being omitted because the distribution is finite on the axis. Combining eq 39 and 41, we obtain for the general solution for (38)

$$\rho = \sum_n B_n e^{-n(n+1)\Re_1 t} P_n(\mu^*) \qquad (42)$$

In Benoit's case, eq 42 can be introduced directly under the integral in eq 27. In the present case, comparison of eq 42 with eq 28 shows them to be identical if one writes

$$A_n = B_n e^{-n(n+1)\Re_1 t} \qquad (43)$$

The entire subsequent analysis of section III then follows, and we write on inspection, from eq 36

$$\Gamma = \frac{2\pi N}{5n_l}(\alpha_3 - \alpha_1)\cos^2\theta\ B_2 e^{-6\Re_1 t} \qquad (44)$$

This is the same result as that obtained by Benoit except for the factor $\cos^2\theta$.

Equation 44 may also be obtained directly from eq 23. One notes that, in one case, Benoit's derivation or that employed in the first part of the present section, one restricts the differential equation itself to the case of the spheroid and solves the particular boundary-value problem; whereas in the other, by introduction of Perrin's expressions for the means of time-dependent quantities in diffusion, one obtains the solution for the birefringence from the general differential equation for anisotropic diffusion directly and then specializes it to the case of the spheroid. If $C_1 = C_2 \neq C_3$, then it follows from the definitions 18 and 19 that $\Theta_1 = \Theta_2 = {}^1/_2$, $\Theta_3 = -1$ and that $\Theta_+ = \Re_1$ and $\Theta_- = (\Re_1 + 2\Re_3)/3$. We note, first, that if $\alpha_1 \neq \alpha_2 \neq \alpha_3$, then the birefringence of the suspension decays in a mixed exponential fashion after removal of the field with the relaxation times ${}^1/_6\Re_1$ and ${}^1/_2(\Re_1 + 2\Re_3)$. This is the case that the spheroidal particles consist of a material which itself possesses biaxial anisotropy with one of the electric axes coinciding with the particle axis a_3, and we do not consider it further. In order to possess optical as well as geometric symmetry about axis a_3 (the assumption made in section III and elsewhere in the present section), the particle consists either of an isotropic material or a material of uniaxial anisotropy with its optic axis coincident with particle axis a_3, and $\alpha_1 = \alpha_2 \neq \alpha_3$. In this case, the coefficients $A_\pm$ themselves simplify. First, A_- is found to vanish identically. This is an expected result. The decay in birefringence cannot contain a dependence on the frictional constant about the symmetry axis, since rotations about this axis are not manifested optically. The other coefficient A_+ becomes such that

$$\frac{2n_l}{N}\Gamma = \frac{1}{3}(\alpha_3 - \alpha_1)[3\langle a_{33}^2 - a_{13}^2\rangle - \sum_i \langle a_{3i}^2 - a_{1i}^2\rangle]$$

$$= (\alpha_3 - \alpha_1)\langle a_{33}^2 - a_{13}^2\rangle \qquad (45)$$

Substituting these results for the coefficients into eq 23, one obtains eq 26 multiplied by the time-dependent exponential. Application of the analysis of section III to this equation yields eq 45 identically.

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