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Mathematical properties of the rotational diffusion equation

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Abstract

An iterative scheme for the approximative solution of the Galerkin system of the linear rotational diffusion equation for the chromophore distribution in nonlinear optical polymers is formulated. Uniformly valid asymptotic steady-state solutions are obtained in terms of power series expansions in the normalized dc field and the convergence properties of the scheme are discussed. Moreover, by neglecting the effect of the ac field, it is proved by means of the Galerkin-system approach that the equilibrium solution of the rotational diffusion equation acts as a global attractor for any initial distributions. In addition, the decay towards this distribution is a purely exponential decay for small and moderate values of the dc-field strength. When the dc-field strength exceeds a certain threshold, this relaxation process is characterized as a damped oscillation.

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1. Introduction

The field of electro-optic (EO) properties of liquids and solids has received increasing attention over the last couple of years due to the interest in nonlinear optical polymers. Several attempts have been made in order to model the EO response of such polymers [1–6]. We refer to these papers for more details concerning the physical implications and limitations of the different modelling approaches.

In [5] and [6] a simple but physically intuitive model of chromophore reorientation in a viscous polymer matrix is presented. Both static (dc) and time-dependent (ac) situations are considered. This model represents an extension of the rotational diffusion equation for the chromophore distribution introduced by Michelotti and Tousseare [4] and Wu [3], who theoretically studied the long-term relaxation behaviour of the induced EO coefficient in terms

of orientational Brownian motion with and without the application of an external electric field [7]. The fundamental assumption underlying this model is that the torque exerted by the polymer matrix can be represented by a microscopic 'molecular' electric field, with a randomly varying orientation throughout the polymer volume. The magnitude of this field is assumed to be temperature dependent but spatially constant. The macroscopic properties of the polymer are obtained by averaging over the fluctuating direction of the field. The results obtained in [6] are shown to compare fairly well with experiments.

Hence, according to [5] and [6], the chromophore distribution denoted by f is governed by the evolution equation

$$\tau_{\text{rot}} \frac{\partial f}{\partial t} = \nabla^2 f + \nabla \cdot (f \nabla U) \tag{1}$$

where the effect of the polymer matrix and applied field is taken care of by a general time- and space-dependent potential energy U (normalized by the thermal energy kT)

$$U = -\vec{\mu} \cdot (\vec{E}_0 + \vec{E}_{\text{M}})/kT.$$

Here $\vec{\mu}$ is the dipole moment, $\vec{E}_0$ the time-independent applied field and $\vec{E}_{\text{M}}$ the molecular field. In addition, τ_{rot} is the rotational diffusion time and $\nabla = \hat{\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin(\theta)}\hat{\varphi}\frac{\partial}{\partial\varphi}$ denotes the angular part of the gradient operator. Note that the inertial effects have been neglected in this description. Solutions of the partial differential equation (1) are not easily obtained due to the coupling between the three variables: θ, φ and t. One approach relies on so-called continued matrix fractions [8,9]. When the angles θ and φ are coupled and U is of the order O(1), this method is not well suited, however. In view of this situation we have considered the following less demanding physical problem: rather than treat the full two-angle problem, we focus on the co-linear case in order to gain some insight into the properties of the full problem. Co-linear fields result whenever the molecular field is either parallel or anti-parallel to the applied field. Hence, only these two relative orientations are considered. Subsequently, approximate values of physical quantities such as angular order parameters are calculated by averaging over these two cases. Though this is clearly a crude approximation to the general case it nevertheless retains the essence of the physical problem. Hence, the present model can be viewed as a toy model designed to illustrate the mathematical properties of the full problem. The consequence of having two co-linear fields is that the φ-dependence of the problem is eliminated. Hence the rotational diffusion equation for the averaged chromophore distribution f reads

$$\tau_{\text{rot}} \frac{\partial f}{\partial t} = \frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \left[\sin(\theta) \left\{ \frac{\partial f}{\partial \theta} + \frac{\partial U}{\partial \theta} f \right\} \right]. \tag{2}$$

We now assume that the potential energy U decomposes into a sum of a time-dependent molecular dc field with normalized amplitude ε and an applied ac field with amplitude $\varepsilon\alpha$ oscillating in time with a fixed frequency ω:

$$U = -\varepsilon \cos(\theta) - \varepsilon\alpha \exp[-\mathrm{i}\omega t] - \varepsilon\alpha^* \exp[\mathrm{i}\omega t]. \tag{3}$$

Here $\varepsilon = |\varepsilon|$ and $\varepsilon = -|\varepsilon|$ account for the parallel and anti-parallel molecular fields, respectively, and α the amplitude of the ac field measured in units of the dc-field amplitude. In [6], approximate solutions of the system equations (2) and (3) are obtained by means of the Galerkin approximation with respect to the Legendre basis $\{P_n(\cos\theta)\}_{n=1}^{\infty}$, and Fourier-series expansion in terms of the Galerkin coefficients. One ends up with an algebraic system of equations. The latter system is truncated both with respect to the Legendre basis and the number of Fourier components. The convergence properties of the solution, however, are not discussed.

This serves as the background and motivation for the present work. The main focus in the present paper is the mathematical aspects of the Galerkin system for the rotational

diffusion equation introduced in [6]. In the first part of the paper we analyse the set of differential equations which constitutes the truncated Galerkin system obtained from the rotational diffusion equations (2) and (3). An algorithm for solving this equation iteratively is presented. It is proved that the steady-state part of the solution obtained by means of this iteration scheme converges uniformly to the steady-state part of the exact solution of the truncated Galerkin system. The second part of the paper is devoted to an analysis of the Galerkin system in the absence of any ac effects. In this case the Galerkin system simplifies to a linear, inhomogeneous system of ordinary differential equations with constant coefficients. The equilibrium of this system is identified with the Boltzmann distribution, i.e., the equilibrium solution

$$f_{\mathrm{eq}}(\theta) = f_0 \exp[\varepsilon \cos\theta] \tag{4}$$

of the rotational diffusion equation. It is proved by using the theory of positive stable matrices [10] that the equilibrium of the Galerkin system is asymptotically stable, and hence that the Boltzmann distribution as expected acts as a global attractor for any initial distribution. In addition, it is shown that the equilibrium is an asymptotically stable node for low-dc-field strengths, while it becomes a stable focus when increasing the dc-field strengths above a certain threshold. The location of the eigenvalues of the coefficient matrix can be detected by means of Geršgorin's theorems [11].

This paper can be viewed as a theoretical complement to the paper [6]. In addition, the techniques employed are of interest in their own right. We conjecture that the iteration scheme for the truncated Galerkin system introduced in this paper can easily be adopted to models involving initial value problems of partial differential or integro-differential equations, where it is not possible or practical to obtain the solutions in closed form.

The paper is organized as follows. In section 2 the iteration scheme for solving the truncated Galerkin system is presented in the parameter regime $|\varepsilon| < 1$, and its convergence properties are studied. In section 3 the asymptotic stability of the Boltzmann distribution in the dc case is discussed. The final section contains some concluding remarks. In appendix A the iteration scheme introduced in section 2 is shown to be applicable to the complementary regime $|\varepsilon| \geqslant 1$, while appendix B contains the proof of the positive stability of the coefficient matrix in the dc case, as well as the location of the eigenvalues of this matrix as inferred from Geršgorin's theorems.

2. Iterative method for the truncated Galerkin system of the rotational diffusion equation

The starting point of the analysis is the non-dimensional version of the rotational diffusion equation (2)

$$\frac{\partial f(\theta,t)}{\partial t} = \frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\left\{\sin(\theta)\left[\frac{\partial f(\theta,t)}{\partial\theta} + \frac{\partial U(\theta,t)}{\partial\theta} f(\theta,t)\right]\right\} \tag{5}$$

where

$$U(\theta,t) \equiv -\varepsilon(1 + \alpha \exp[-\mathrm{i}\omega t] + \alpha^* \exp[\mathrm{i}\omega t])\cos(\theta) \tag{6}$$

which is derived from (2) by performing the scalings $t \to t/\tau_{\mathrm{rot}}$ and $\omega \to \tau_{\mathrm{rot}}\omega$.

We expand the solution of the rotational diffusion equation in terms of a Fourier–Legendre series, i.e.

$$f(\theta,t) = \sum_{n=0}^{\infty} a_n(t)\frac{2n+1}{2} P_n(\cos(\theta)) \tag{7}$$

and find that the coefficient functions $a_n(t)$ obey the infinite hierarchy of ordinary differential equations

$$a_0 = 1$$
$$\frac{\mathrm{d}a_n}{\mathrm{d}t} + n(n+1)a_n = \varepsilon F(t;\omega,\alpha)\frac{n(n+1)}{2n+1}(a_{n-1} - a_{n+1}) \qquad n = 1, 2, 3, \ldots. \tag{8}$$

In the process of deriving (8) we have exploited the fact that the total number of chromophores $\mathcal{N} = \int_0^\pi f(\theta, t)\sin(\theta)\,\mathrm{d}\theta$ is a conserved quantity which by means of (7) can be expressed as $\mathcal{N} = a_0$, and that the constant a_0 can be put equal to 1 without loss of generality.

The next step consists of truncating system (8), i.e., putting $a_n = 0$ for $n \geqslant N+1$ for some N, which yields a hierarchy of N ordinary differential equations in N unknown functions a_n. We conveniently express the truncated system on a compact vector form as

$$\frac{\mathrm{d}\underline{a}}{\mathrm{d}t} + \mathcal{D}_N \cdot \underline{a} = \varepsilon F(t;\omega,\alpha)(\underline{e} + \mathcal{A}_N \cdot \underline{a} + \mathcal{B}_N \cdot \underline{a}) \tag{9}$$

where

$$\underline{a} = \begin{bmatrix} a_1 \\ a_2 \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ a_{N-1} \\ a_N \end{bmatrix} \qquad \underline{e} = \begin{bmatrix} \frac{2}{3} \\ 0 \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ 0 \\ 0 \end{bmatrix}$$

$$\mathcal{D}_N = \begin{bmatrix} 2 & 0 & \cdot & \cdot & \cdot & \cdot & & & 0 \\ 0 & 6 & 0 & & & & & & \cdot \\ \cdot & 0 & 12 & \cdot & & & & & \cdot \\ \cdot & & \cdot & \cdot & \cdot & & & & \cdot \\ \cdot & & & \cdot & \cdot & \cdot & & & \cdot \\ \cdot & & & & \cdot & \cdot & \cdot & & \cdot \\ & & & & & \cdot & (N-1)N & & 0 \\ 0 & \cdot & \cdot & \cdot & \cdot & \cdot & 0 & & N(N+1) \end{bmatrix}$$

$$\mathcal{A}_N = \begin{bmatrix} 0 & \cdot & \cdot & \cdot & \cdot & \cdot & & & 0 \\ \frac{6}{5} & 0 & \cdot & & & & & & \cdot \\ \cdot & \frac{12}{7} & 0 & \cdot & & & & & \cdot \\ \cdot & & \cdot & \cdot & \cdot & & & & \cdot \\ \cdot & & \cdot & \cdot & \cdot & \cdot & & & \cdot \\ \cdot & & & \cdot & \cdot & \cdot & \cdot & & \cdot \\ & & & & \cdot & \frac{(N-1)N}{2N-1} & 0 & & 0 \\ 0 & \cdot & \cdot & \cdot & \cdot & \cdot & \frac{N(N+1)}{2N+1} & & 0 \end{bmatrix}$$

$$\mathcal{B}_N = \begin{bmatrix} 0 & -\frac{2}{3} & \cdot & \cdot & \cdot & \cdot & & 0 \\ 0 & 0 & -\frac{6}{5} & & & & & \cdot \\ \cdot & 0 & \cdot & \cdot & & & & \cdot \\ \cdot & & \cdot & \cdot & \cdot & & & \cdot \\ \cdot & & & \cdot & \cdot & \cdot & & \cdot \\ \cdot & & & & \cdot & \cdot & \cdot & \cdot \\ & & & & & \cdot & 0 & -\frac{(N-1)N}{2N-1} \\ 0 & \cdot & \cdot & \cdot & \cdot & \cdot & 0 & 0 \end{bmatrix}.$$

The standard theory for ordinary differential equations implies that the initial-value problem of system (9) is well posed, i.e. the solution exists, is unique and depends continuously on the initial data. But due to the implicit form of this system, expressions for exact solutions are not available. However, it is possible to work out an iterative scheme which enables us to construct approximative solutions to system (9). We proceed in the following way: let $\underline{a}^{(k)}$ denote the kth iterated state vector given by

$$\underline{a}^{(k)} = \begin{bmatrix} a_1^{(k)} \\ a_2^{(k)} \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ a_{N-1}^{(k)} \\ a_N^{(k)} \end{bmatrix} \qquad k = 1, 2, 3, \ldots$$

which satisfies the hierarchy of ordinary differential equations

$$\frac{\mathrm{d}\underline{a}^{(k)}}{\mathrm{d}t} + \mathcal{D}_N \cdot \underline{a}^{(k)} = \varepsilon F(t; \omega, \alpha)(\underline{e} + \mathcal{A}_N \cdot \underline{a}^{(k)} + \mathcal{B}_N \cdot \underline{a}^{(k-1)}) \tag{10}$$

with

$$\underline{a}^{(0)} = \underline{0}.$$

Notice that the initial-value problem of system (10) is a well posed system where the iterate $\underline{a}^{(k-1)}$ plays the role of a source effect on the dynamical evolution of $\underline{a}^{(k)}$. By carefully analysing this system one finds that the solutions $a_i^{(k)}$ of this system decompose uniquely into an exponentially decaying transient part denoted by $a_{i,\mathrm{tr}}^{(k)}$ and an oscillatory steady-state part called $a_{i,\mathrm{s}}^{(k)}$ as follows:

$$a_i^{(k)} = a_{i,\mathrm{tr}}^{(k)} + a_{i,\mathrm{s}}^{(k)} \qquad i = 1, 2, \ldots, N.$$

Both the transient part $a_{i,\mathrm{tr}}^{(k)}$ and the steady-state part $a_{i,\mathrm{s}}^{(k)}$ can be expressed in terms of power series in ε with smooth coefficient functions being uniformly bounded in t. Hence, the series representations for $a_i^{(k)}$ and $\frac{\mathrm{d}a_i^{(k)}}{\mathrm{d}t}$ can be majorized by geometric series in ε. The latter series converge as $k \to \infty$ provided $0 < |\varepsilon| < 1$ and hence both $\lim_{k\to\infty} \underline{a}^{(k)}$ and $\lim_{k\to\infty} \frac{\mathrm{d}\underline{a}^{(k)}}{\mathrm{d}t}$ exist in this case. One readily shows that the limit function obeys the truncated Galerkin system (9).

A detailed study of the steady-state part $a_{i,\mathrm{s}}^{(k)}$ reveals that

$$a_{i,\mathrm{s}}^{(k)} = \sum_{j=1}^{k} F_i^{(2j-2+i)}(t; \omega, \alpha)\varepsilon^{2j-2+i} \qquad i = 1, 2, 3, \ldots, N. \tag{11}$$

For example, the explicit expressions for the lowest-order steady-state iterates are obtained as

$$a_{1,\mathrm{s}}^{(1)} = \frac{1}{3}\varepsilon \left\{ 1 + 2\alpha \frac{\mathrm{e}^{-\mathrm{i}\omega t}}{1 - \mathrm{i}\omega} + \mathrm{c.c.} \right\}$$

$$a_{2,\mathrm{s}}^{(1)} = \frac{2}{5}\varepsilon^2 \left(\frac{1}{6} + \frac{4|\alpha|^2}{3(1+\omega^2)} + \left(\frac{\alpha(4 - \mathrm{i}\omega)}{(6 - \mathrm{i}\omega)(1 - \mathrm{i}\omega)} \mathrm{e}^{-\mathrm{i}\omega t} + \frac{\alpha^2}{(2 - \mathrm{i}\omega)(3 - \mathrm{i}\omega)} \mathrm{e}^{-\mathrm{i}2\omega t} + \mathrm{c.c.} \right) \right).$$

From the expansions (11), we find that the iterates obey the convergence property

$$\left| a_{i,\mathrm{s}}^{(k)} - a_{i,\mathrm{s}}^{(k-1)} \right| = \mathrm{O}(\varepsilon^{2k-2+i}) \qquad i = 1, 2, \ldots, N \tag{12}$$

from which it follows that the iterates (11) represent uniformly valid asymptotic approximations to the steady-state part of the exact solutions of the truncated Galerkin system as $\varepsilon \to 0$. Hence,

the iterates $a_{1,s}^{(1)}$ and $a_{2,s}^{(1)}$ yield correct steady-state solutions to the Galerkin system up to order ε^2. In general, the expansions (11) together with the convergence property (12) tell which terms to retain in the Fourier–Legendre series approximation of the exact solution to the rotational diffusion equation in powers of ε in order to achieve the desired accuracy.

One can also solve the truncated Galerkin system (9) for the complementary parameter regime $|\varepsilon| \geqslant 1$ approximately by means of an iteration algorithm which is identical to the one introduced in this section. The crucial point is to make an appropriate rescaling of the truncated Galerkin system (9) and the corresponding iteration scheme (10). The details of the description of this algorithm can be found in Appendix A.

3. The Boltzmann distribution as a global attractor

Let us investigate the situation when the effect of the ac field is negligible in comparison with the dc field. In this case the rotational diffusion equation exhibits an equilibrium solution, termed the Boltzmann distribution, given by (4). We will study the stability of this distribution by means of the Galerkin-system approach. Hence, let $\alpha = 0$ in the truncated Galerkin system (9). We obtain the constant-coefficient inhomogeneous system

$$\frac{\mathrm{d}\underline{a}}{\mathrm{d}t} = \varepsilon\underline{e} - \mathcal{C}_N \cdot \underline{a} \tag{13}$$

where

$$\mathcal{C}_N \equiv \mathcal{D} - \varepsilon\mathcal{A} - \varepsilon\mathcal{B}$$

which can be solved in the standard way. The coefficient matrix $\mathcal{C}_N$ is a tridiagonal, invertible matrix of the type

$$\mathcal{C}_N = \begin{bmatrix} x_0 & y_1 & 0 & \cdot & \cdot & \cdot & \cdot & 0 \\ z_1 & x_1 & y_2 & \cdot & & & & \cdot \\ 0 & z_2 & x_2 & y_3 & \cdot & & & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & & \cdot \\ \cdot & & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & & & \cdot & \cdot & \cdot & \cdot & 0 \\ \cdot & & & & \cdot & z_{N-2} & x_{N-2} & y_{N-1} \\ 0 & \cdot & \cdot & \cdot & \cdot & 0 & z_{N-1} & x_{N-1} \end{bmatrix} \tag{14}$$

where

$$\begin{aligned} x_n &= (n+1)(n+2) && n = 0, 1, 2, \ldots, N-1 \\ y_n &= \varepsilon\frac{n(n+1)}{2n+1} && n = 1, 2, 3, \ldots, N-1 \\ z_n &= -\varepsilon\frac{(n+1)(n+2)}{2n+3} && n = 1, 2, 3, \ldots, N-1. \end{aligned} \tag{15}$$

The equilibrium solution $\underline{a}_{\mathrm{eq}}^{(N)}$ of (13) corresponding to the Boltzmann distribution through the truncated Fourier–Legendre expansion (7) is given by

$$\underline{a}_{\mathrm{eq}}^{(N)} = \varepsilon\mathcal{C}_N^{-1} \cdot \underline{e}. \tag{16}$$

In the case $N = 2$ we have

$$\mathcal{C}_2 = \begin{bmatrix} 2 & \frac{2}{3}\varepsilon \\ -\frac{6}{5}\varepsilon & 6 \end{bmatrix} \qquad \underline{a}_{\mathrm{eq}}^{(2)} = \begin{bmatrix} \frac{5}{15+\varepsilon^2}\varepsilon \\ \frac{\varepsilon^2}{15+\varepsilon^2} \end{bmatrix} \tag{17}$$

from which it follows that

$$\underline{a}_{\mathrm{eq}}^{(2)} = \begin{bmatrix} \frac{1}{3}\varepsilon - \frac{1}{45}\varepsilon^3 + \mathrm{O}(\varepsilon^5) \\ \frac{1}{15}\varepsilon^2 - \frac{1}{225}\varepsilon^4 + \mathrm{O}(\varepsilon^6) \end{bmatrix}$$

by Taylor expansion in ε. On increasing N, i.e. the number of scalar equations in the truncated Galerkin system, the number of scalar components in the equilibrium solution is increased. Increasing N also means that the equilibrium solution is updated. The latter process can be described in the following way: we compare the scalar components of the system $\underline{a}_{\rm eq}^{(N)} = \varepsilon \mathcal{C}_N^{-1} \cdot \underline{e}$ and $\underline{a}_{\rm eq}^{(N-1)} = \varepsilon \mathcal{C}_{N-1}^{-1} \cdot \underline{e}$. Then one can show by Taylor expansion about $\varepsilon = 0$ and the induction principle that

$$\begin{vmatrix} a_1^{(N)} - a_1^{(N-1)} \\ a_2^{(N)} - a_2^{(N-1)} \end{vmatrix} = \mathrm{O}(\varepsilon^{2N-1}) = \mathrm{O}(\varepsilon^{2N-2})$$

$$\vdots$$

$$| a_k^{(N)} - a_k^{(N-1)} | = \mathrm{O}(\varepsilon^{2N-k})$$

$$\vdots$$

$$| a_{N-1}^{(N)} - a_{N-1}^{(N-1)} | = \mathrm{O}(\varepsilon^{N+1}).$$

Here

$$\underline{a}_{\rm eq}^{(N)} = \begin{bmatrix} a_1^{(N)} \\ a_2^{(N)} \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ a_{N-1}^{(N)} \\ a_N^{(N)} \end{bmatrix} \qquad \underline{a}_{\rm eq}^{(N-1)} = \begin{bmatrix} a_1^{(N-1)} \\ a_2^{(N-1)} \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ a_{N-2}^{(N-1)} \\ a_{N-1}^{(N-1)} \end{bmatrix}$$

and

$$\underline{a}_{\rm eq}^{(0)} = 0$$

by definition. Next, we investigate the stability of this equilibrium within the framework of the model. We first decompose the solution of (13) as

$$\underline{a} = \underline{a}_{\rm eq}^{(N)} + \underline{\xi}$$

and find that

$$\frac{\mathrm{d}\underline{\xi}}{\mathrm{d}t} = -\mathcal{C}_N \cdot \underline{\xi}.$$

It can be proved that the matrix $\mathcal{C}_N$ is positively stable, i.e., that the real part of each eigenvalue of $\mathcal{C}_N$ is positive, from which it follows that the equilibrium $\underline{a}_{\rm eq}^{(N)}$ is asymptotically stable. Moreover, the location of the eigenvalues of $\mathcal{C}_N$ can be studied by means of Geršgorin's theorems. The details of this analysis can be found in Appendix B.

For arbitrary N, the eigenvalues of $-\mathcal{C}_N$ in the purely diffusive case (i.e. $\varepsilon = 0$) are, as expected, real, negative and distinct. Hence, by analysing the characteristic equation of $-\mathcal{C}_N$ in terms of the implicit function theorem, we conclude that all the eigenvalues are real for small but non-zero values of ε^2 which means that $\underline{a}_{\rm eq}^{(N)}$ acts as a stable node at least for low values of the dc-field strengths.

For example, in the case $N = 2$, we find by direct computation that the eigenvalues $\lambda_\pm$ of $-\mathcal{C}_2$ is given as

$$\lambda_\pm = -4 \pm \tfrac{2}{5}\sqrt{25 - 5\varepsilon^2}$$

which shows that $\mathrm{Re}\,[\lambda_\pm] < 0$ for all ε. Moreover, one finds that $\lambda_\pm$ are real for moderate dc-field strengths, i.e. $0 \leqslant \varepsilon^2 \leqslant 5$, and complex for the complementary high dc-field strength regime $\varepsilon^2 > 5$. In the former case the equilibrium $\underline{a}_{\rm eq}^{(2)}$ acts as a stable node, while in the

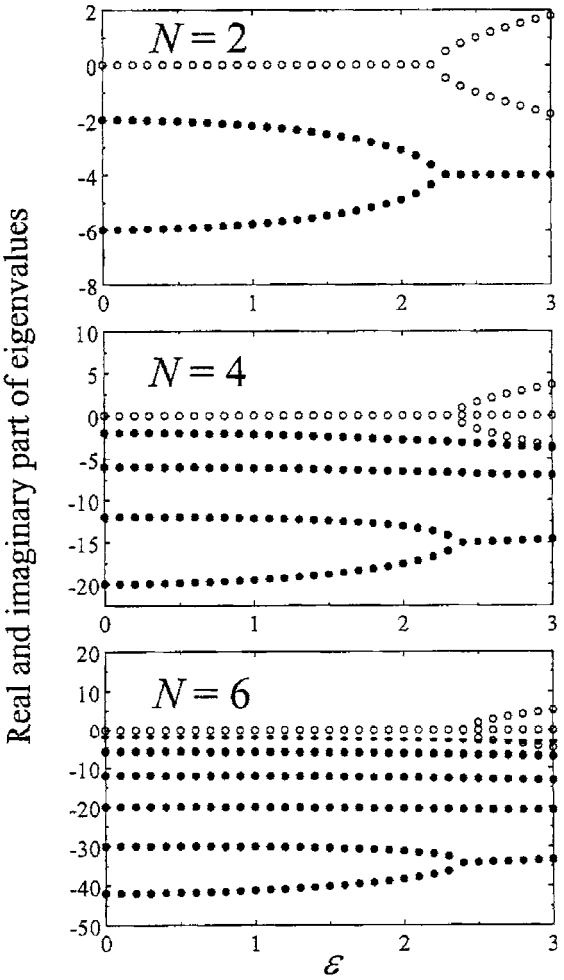

Figure 1. The real and imaginary parts of the eigenvalues of the coefficient matrix $-\mathcal{C}_N$ as functions of the dc amplitude ε for $N = 2, 4, 6$, where $\mathcal{C}_N$ is the matrix defined by (14). The filled circles denote the real parts and the open circles the imaginary parts.

latter situation, it is a stable focus. In figure 1 we have displayed the real and imaginary part of the eigenvalues as a function of the dc-field amplitude ε for $N = 2$, 4 and 6, thus supporting the conjecture that the equilibrium $\underline{a}_{\mathrm{eq}}^{(N)}$ becomes a stable focus when increasing the intensities above a certain threshold. However, one readily observes that the dependence of the eigenvalues on the dc-field strength reveals a more complicated structure as the order of the Galerkin system is increased.

From the asymptotic stability of the equilibrium solution $\underline{a}_{\mathrm{eq}}^{(N)}$ we can conclude by means of the corresponding Fourier–Legendre series (7) that the Boltzmann distribution acts as a global attractor for all initial distributions of the rotational diffusion equation when the ac-field contribution is negligible as compared with the dc effect. Moreover, this attractor is of the stable-node type for small and moderate values of the normalized dc-field intensity ε^2 while it becomes of stable focus type when this intensity increases above a certain threshold.

4. Conclusion

In this paper an iteration scheme for the Galerkin system (8) resulting from the rotational diffusion equations (5) and (6) has been studied. The convergence properties of this scheme is addressed, thus showing the possibility of getting an approximation of the desired accuracy of the steady-state part of the solution to the Galerkin system. It also follows, by appealing to the convergence of the algorithm that the exact solution of the Galerkin system decomposes into a transient part and a purely oscillatory part which consists of harmonics and higher-order harmonics in the fundamental driving frequency. Next, the exact solution of the Galerkin system is analysed in the situation when the ac effects are negligible. In that case the Galerkin system reduces to a linear, inhomogeneous constant-coefficient problem, where the equilibrium corresponds to the Boltzmann distribution. By using the theory of positive stable matrices it is shown that this distribution acts as a global attractor for all initial distributions, as expected. Moreover, it is shown that this process is characterized by a purely exponential decay in time for low and moderate dc-field strengths, while the relaxation behaviour becomes oscillatory when the dc-field strengths exceeds a certain threshold. Finally, the decay towards this equilibrium state is analysed in terms of Geršgorin's theorems for the location of the eigenvalues of the coefficient matrix of the linear problem.

In future papers we aim to address the question of the applicability of iteration schemes to other truncated Galerkin systems. With this in mind it should be mentioned that the theoretical model for photoinduced anisotropy in liquid-crystalline azobenzene side-chain polyesters consists of rate equations for *trans* and *cis* chromophore distributions, which assume the form of linear integro-differential equations. Thus, when applying the Galerkin procedure (7), we find an infinite set of linear ordinary differential equations for the time evolution of the Legendre–Fourier coefficients [12], where closed-form expressions for the exact solutions cannot be obtained.

We also aim to extend the present model for the chromophore distribution by incorporating inertial terms and time-delay effects. Such effects are believed to play an important role in certain experiments, and it is important to clarify both the physical implications and limitations as well as the mathematical aspects of such modelling approaches.

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Appendix A. The Galerkin scheme for $|\varepsilon| \geqslant 1$

The iteration scheme for the Galerkin system also works in the case $|\varepsilon| \geqslant 1$. Introduce the parameter δ defined by

$$\delta = \frac{1}{\varepsilon} \tag{18}$$

i.e. the inverse normalized dc field, and the new timescale

$$\tau = \frac{t}{\delta^2}. \tag{19}$$

Then the system (9) can be transformed to

$$\frac{\mathrm{d}\underline{a}}{\mathrm{d}\tau} + \delta^2 \mathcal{D}_N \cdot \underline{a} = \delta F(\tau; \omega_\delta, \alpha)(\underline{e} + \mathcal{A}_N \cdot \underline{a} + \mathcal{B}_N \cdot \underline{a}) \tag{20}$$

where the scaled frequency ω_δ is defined as

$$\omega_\delta \equiv \omega\delta^2. \tag{21}$$

The structure of (21) enables us to formulate an iteration algorithm for this system in a way analogous to (10)

$$\begin{aligned} &\frac{\mathrm{d}\underline{a}^{(k)}}{\mathrm{d}\tau} + \delta^2 \mathcal{D}_N \cdot \underline{a}^{(k)} = \delta F(\tau; \omega_\delta, \alpha)(\underline{e} + \mathcal{A}_N \cdot \underline{a}^{(k)} + \mathcal{B}_N \cdot \underline{a}^{(k-1)}) \\ &\underline{a}^{(0)} = 0. \end{aligned} \tag{22}$$

This system is equivalent to (10) through the transformations (18)–(21). One readily shows that the steady state part $a_{i,\mathrm{s}}^{(k)}$ of the component functions of the kth iterate $\underline{a}^{(k)}$ of (22) can be expanded as a power series of δ which is formally identical to (11)

$$a_{i,\mathrm{s}}^{(k)} = \sum_{j=1}^{k} F_i^{(2j-2+i)}(\tau; \omega_\delta, \alpha)\delta^{(2j-2+i)} \qquad i = 1, 2, 3, \ldots, N$$

with the coefficient functions being uniformly bounded in τ. Now, since $|\varepsilon| > 1$ by assumption, $|\delta| < 1$ and hence by exactly the same argument as above we can conclude that the steady-state limit of $\underline{a}^{(k)}$ exists as $k \to \infty$ and the limit function of $\underline{a}^{(k)}$ obeys system (22). By restoration to the original variables it is concluded that the power-series expansion (11) yields a uniformly valid asymptotic approximation to the steady-state part of the exact solution.

Finally, let us investigate the non-generic case $|\varepsilon| = 1$. By introducing a change of timescale

$$\tau = \frac{t}{|\delta|}$$

where δ is a free parameter designed to fulfil the condition $|\delta| < 1$, systems (9) and (10) are transformed into

$$\begin{aligned} &\frac{\mathrm{d}\underline{a}}{\mathrm{d}\tau} + |\delta|\mathcal{D}_N \cdot \underline{a} = |\delta| F(\tau; \omega_\delta, \alpha)(\underline{e} + \mathcal{A}_N \cdot \underline{a} + \mathcal{B}_N \cdot \underline{a}) \\ &\frac{\mathrm{d}\underline{a}^{(k)}}{\mathrm{d}\tau} + |\delta|\mathcal{D}_N \cdot \underline{a}^{(k)} = |\delta| F(\tau; \omega_\delta, \alpha)(\underline{e} + \mathcal{A}_N \cdot \underline{a}^{(k)} + \mathcal{B}_N \cdot \underline{a}^{(k-1)}) \\ &\underline{a}^{(0)} = 0 \end{aligned}$$

with

$$\omega_\delta \equiv \omega|\delta|$$

and by the same type of arguments as in the case $|\varepsilon| > 1$ we conclude that the iterative scheme (10) is also applicable in the case $|\varepsilon| = 1$ with uniform convergence to the exact solution of the Galerkin system (9).

Appendix B. Asymptotic stability of the equilibrium in the dc case

We prove the positive stability of $\mathcal{C}_N$ given as (14) and (15) by appealing to the following general theorem [10]: *let $\mathcal{C}_N$ be an $N \times N$ matrix and E_N an $N \times N$ matrix which is positive*

definite and diagonal. If $F_N + F_N^t$ is positive definite, where $F_N = E_N^{-1} \cdot \mathcal{C}_N \cdot E_N$, then $\mathcal{C}_N$ is positive stable. In our case, let $\mathcal{E}_N$ be the positive definite diagonal matrix defined as

$$\mathcal{E}_N = \begin{bmatrix} 1 & 0 & 0 & \cdot & \cdot & \cdot & \cdot & 0 \\ 0 & k_1 & 0 & 0 & & & & \cdot \\ 0 & 0 & k_1k_2 & \cdot & \cdot & & & \cdot \\ \cdot & \cdot & \cdot & k_1k_2k_3 & \cdot & \cdot & & \cdot \\ \cdot & & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & & & \cdot & \cdot & \cdot & \cdot & 0 \\ \cdot & & & & \cdot & \cdot & \cdot & 0 \\ 0 & \cdot & \cdot & \cdot & \cdot & 0 & 0 & k_1k_2 \ldots k_{N-1} \end{bmatrix}$$

where $k_i = \sqrt{-\frac{z_i}{y_i}}$, $i = 1, 2, 3, \ldots, N-1$, where y_i and z_i are given by (15). Let $\mathcal{F}_N$ be the matrix

$$\mathcal{F}_N = \mathcal{E}_N^{-1} \cdot \mathcal{C}_N \cdot \mathcal{E}_N$$

where $\mathcal{C}_N$ is given as (14) and (15). Then we find that

$$\mathcal{F}_N + \mathcal{F}_N^t = \begin{bmatrix} 2x_0 & 0 & 0 & \cdot & \cdot & \cdot & \cdot & 0 \\ 0 & 2x_1 & 0 & 0 & & & & \cdot \\ 0 & 0 & 2x_2 & \cdot & \cdot & & & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & & \cdot \\ \cdot & & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & & & \cdot & \cdot & \cdot & \cdot & 0 \\ \cdot & & & & \cdot & \cdot & \cdot & 0 \\ 0 & \cdot & \cdot & \cdot & \cdot & 0 & 0 & 2x_{N-1} \end{bmatrix}$$

i.e. a diagonal matrix which is positive definite. Hence, it follows that $\mathcal{C}_N$ is positive stable.

It is also possible to extract information about the location of the eigenvalues by means of Geršgorin's theorems [11]. According to the first theorem of Geršgorin [11], it follows that the eigenvalues must also be located in the subset Ω of the complex λ-plane given as

$$\Omega = \Omega_1 \cup \Omega_2 \cup \Omega_3 \cup \cdots \cup \Omega_{N-1} \cup \Omega_N$$

where the sets $\Omega_n (n = 0, 1, 2, \ldots, N-1)$ are the closed discs

$$\Omega_0 = \{\lambda; |\lambda + 2| \leqslant \tfrac{2}{3}|\varepsilon|\}$$

$$\Omega_n = \left\{\lambda; |\lambda + n(n+1)| \leqslant \frac{2n(n+1)}{2n+1}|\varepsilon|, n = 2, 3, \ldots, N-1\right\}$$

$$\Omega_N = \left\{\lambda; |\lambda + N(N+1)| \leqslant \frac{N(N+1)}{2N+1}|\varepsilon|\right\}.$$

Hence we can conclude that the eigenvalues of $-\mathcal{C}_N$ are located in the subset

$$\Delta \equiv \Omega \cap \{\lambda; \mathrm{Re}\,(\lambda) < 0\}$$

of the complex λ-plane. Notice that the radius of each Geršgorin disc $\Omega_n (n = 0, 1, 2, \ldots, N-1)$ is proportional to dc-field amplitude $|\varepsilon|$. For small and moderate values of $|\varepsilon|$, we expect, according to Geršgorins second theorem [11], that each disc Ω_n contains one and only one eigenvalue of $-\mathcal{C}_N$ of the left complex λ-halfplane.

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