

**Local field effects on reorientation in suspensions of anisotropic particles**

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(Received 12 March 2003; published 24 July 2003)

The field-induced reorientation of microellipsoids in suspension depends on particle parameters, e.g., intrinsic dielectric anisotropy, shape, and size, as well as on the concentration of the particles. We study this process and the resulting orientational order parameter of the suspension in fields of arbitrary strength. The mean-field approach presented here provides an explicit link between the particle properties and their orientation distribution, taking into account the electrostatic interaction among the particles at moderate concentrations. It reproduces published experimental observations in the steady state and should be useful for studying reorientation phenomena as well as electro-optical properties in these systems.

DOI: 10.1103/PhysRevE.68.011407

PACS number(s): 82.70.-y, 42.70.-a, 78.20.Jq, 78.67.-n

**I. INTRODUCTION**

Scientists are often interested in determining various properties of microparticles or macromolecules in suspension, such as their size, shape, and dielectric anisotropy. These microscopic properties can be related to measurable transport properties such as translational and rotational diffusion, electric birefringence, and depolarized light scattering [1–3]. In particular, the orientational dynamics of shaped microparticles has attracted considerable interest over the years (see, for example, Ref. [4] and references therein). This orientational dynamics, easily controlled by an externally applied field, leads to the relatively large nonlinear susceptibilities exhibited by liquid suspensions of microparticles. These suspensions are therefore interesting candidates for optical applications such as electro-optic phase modulation of the Kerr type. They have been studied as anisotropic artificial Kerr materials (AKM) for various nonlinear optical applications, e.g., optical birefringence, phase conjugation, and intensity and phase modulation [5–15]. In most of these studies the suspensions are very dilute, with particle volume fraction of 1% or less, and may be considered as random collections of independent particles, since the interaction among the particles is negligible. However, ordering phenomena in these suspensions, and the resulting electro-optical effects, are expected to be influenced by various interactions among the particles, which, in turn, may be significantly enhanced with increasing particle concentration.

In this paper, the orientational order parameter is studied in suspensions with moderate concentrations, taking into account the average electrostatic interaction between the particles. This interaction may already be significant at concentrations so low that excluded volume effects are negligible. An approach is presented, based on calculating the field-dependent macroscopic dielectric properties of the suspension, in which the interaction is estimated using an extension of the well-known Maxwell Garnett approximation to suspensions of anisotropic particles. The orientation distribution of the microparticles is related explicitly to the macroscopic properties and to the magnitude of an externally applied low-frequency field. This approach provides analytic expressions for the orientational order parameter of dilute suspensions and simple numerical procedures for its evaluation in nondi-

lute systems. The order parameter turns out to be quite sensitive to changes in particle properties and concentration. The orientational electro-optical effects are closely related to the order parameter, and may therefore be useful for studying reorientation phenomena in these mixtures.

The rest of the paper is organized as follows. The Maxwell Garnett approximation for suspensions of anisotropic particles is introduced in Sec. II. In Sec. III, we discuss the reorientation of the particles from an initial random orientation distribution to a steady state under thermal fluctuations in the presence of applied field. The dynamics of the reorientation process is discussed in Sec. IV. The electro-optical effects are presented in Sec. V. Finally, some brief conclusions are included in Sec. VI.

**II. MEAN-FIELD CALCULATION OF THE ELECTROSTATIC ENERGY**

An exact calculation of the effective properties of an inhomogeneous medium is in general an intractable problem. The literature on this subject, therefore, includes a wide variety of approximate schemes, each of which is appropriate for different types of composite microgeometries (see, for example, the review papers [16,17] and references therein). One of those, which is particularly useful for microgeometries in which a host material and isolated particles of other materials are clearly identified, is the Maxwell Garnett approximation (MGA). It involves an exact calculation of the field induced in the uniform host by a single spherical or ellipsoidal particle and an approximate treatment of its distortion by the electrostatic interaction between the different particles. The induced dipole moments cause the longest range distortions and their average effect, which results in a uniform field inside the particles, is included in the MGA. This approach has been extensively used for studying the properties of two-component mixtures in which both the host and the particles are isotropic materials with scalar dielectric coefficients. A few variations of the MGA have been adapted for mixtures where the host is an isotropic material and the particles are anisotropic [18–20]. In this section we use this approach to calculate the electrostatic energy of a microellipsoid in a dielectric suspension.

Let us denote the scalar dielectric constant of the host by

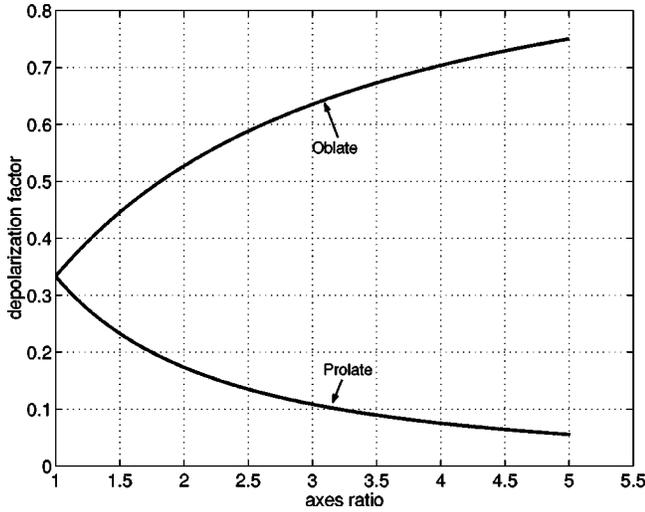


FIG. 1. The principal depolarization factor  $d_{\parallel}$  of Eq. (5) as a function of the axes ratio  $r$  for oblate and  $1/r$  for prolate spheroids.

$\epsilon_h$ . The dielectric tensor of the particles is

$$\epsilon_s = \begin{pmatrix} \epsilon_{\perp} & 0 & 0 \\ 0 & \epsilon_{\perp} & 0 \\ 0 & 0 & \epsilon_{\parallel} \end{pmatrix}. \quad (1)$$

The principal axes of  $\epsilon_s$  are assumed to be parallel to the geometric axes of the ellipsoid. The orientation of the dielectric tensor differs from particle to particle, such that in a

$$d_{\parallel} = \begin{cases} \frac{r^2}{2(1-r^2)^{3/2}} \left( \ln \left[ \frac{1 + \sqrt{1-r^2}}{1 - \sqrt{1-r^2}} \right] - 2\sqrt{1-r^2} \right) & r < 1, \text{ prolate spheroid} \\ \frac{r^2}{(r^2-1)^{3/2}} (\sqrt{r^2-1} - \tan^{-1} \sqrt{r^2-1}) & r > 1, \text{ oblate spheroid,} \end{cases} \quad (5)$$

where  $r = b/a$ .  $d_{\parallel}$  is plotted in Fig. 1.

In a mixture of well separated particles, which is not too dense,  $\mathbf{E}_L$ , the average field acting on each particle, may be calculated by the excluded volume approach discussed by Landauer [16].  $\mathbf{E}_L$  is the average field in the host medium. Therefore,

$$f\langle \bar{\mathbf{E}}_s \rangle + (1-f)\bar{\mathbf{E}}_L = \bar{\mathbf{E}}_0, \quad (6)$$

where the angular brackets denote a volume average over the particles and  $f$  is their volume fraction. Substituting  $\bar{\mathbf{E}}_s$ , we solve for  $\bar{\mathbf{E}}_L$  and find

$$\bar{\mathbf{E}}_L = \frac{\bar{\mathbf{E}}_0}{(1-f) + f\langle \tilde{\kappa} \rangle}. \quad (7)$$

common coordinate system it is  $\tilde{\epsilon}_s = R\epsilon_s R^T$ , where  $R$  is the particle dependent rotation. A voltage difference  $V_0$  is applied on the suspension. The volume averaged field in the system is  $E_0 = V_0/d$ , where  $d$  is the film's thickness. The uniform field inside the particle is  $\bar{\mathbf{E}}_s = \tilde{\kappa} \bar{\mathbf{E}}_L$ , and the induced dipole moment is  $p_s = (v_s/4\pi) \tilde{\alpha} \bar{\mathbf{E}}_L$ , where  $v_s$  is the volume of the particle,  $\tilde{\kappa} = R\kappa R^T$ ,  $\tilde{\alpha} = R\alpha R^T$ , and  $\bar{\mathbf{E}}_L$  is the local field in the vicinity of the particle. For spherical particles, with either a tensor or scalar dielectric coefficient,  $\bar{\mathbf{E}}_L$  is the well-known Lorentz local field. The tensor  $\kappa$  is uniaxial with principal elements

$$\kappa_{\parallel} = \frac{\epsilon_h}{d_{\parallel}\epsilon_{\parallel} + (1-d_{\parallel})\epsilon_h} \quad (2)$$

and

$$\kappa_{\perp} = \frac{\epsilon_h}{d_{\perp}\epsilon_{\perp} + (1-d_{\perp})\epsilon_h}, \quad (3)$$

where  $d_{\parallel}$  and  $d_{\perp} = \frac{1}{2}(1-d_{\parallel})$  are the depolarization coefficients of the ellipsoidal particle along its principal axes [21]. The tensor  $\alpha$  is the polarizability per unit volume of the particle. Its principal elements are

$$\alpha_{\parallel} = \kappa_{\parallel}(\epsilon_{\parallel} - \epsilon_h) \quad \text{and} \quad \alpha_{\perp} = \kappa_{\perp}(\epsilon_{\perp} - \epsilon_h). \quad (4)$$

The principal depolarization coefficient of a microellipsoid with major semiaxes  $[a, b, b]$  is [21]

The denominators, here and in the following equations, should be interpreted as inverse matrices. The induced dipole moment of a single particle is

$$p_s = \frac{v_s}{4\pi} \frac{\tilde{\alpha} \bar{\mathbf{E}}_0}{(1-f) + f\langle \tilde{\kappa} \rangle}. \quad (8)$$

The bulk effective dielectric tensor can be defined by the ratio between the volume averaged displacement field  $D_0 = \langle D \rangle = \epsilon_h \bar{\mathbf{E}}_0 + 4\pi \langle P \rangle$  and the volume averaged electric field  $\bar{\mathbf{E}}_0 = \langle E \rangle$ . This leads to the bulk effective dielectric tensor

$$\epsilon_{eff} = \epsilon_h I + \frac{f\langle \tilde{\alpha} \rangle}{1-f + f\langle \tilde{\kappa} \rangle}, \quad (9)$$

which is the Maxwell Garnett result for mixtures of aniso-

tropic particles. It is valid in the static case and in the quasistatic regime, where the wavelength of the applied field is much larger than the particles.

For a suspension of many particles, it is convenient to define the coordinate system such that the external field  $\bar{E}_0$  is applied in the positive  $z$  direction. In the absence of applied field the particle axes are uniformly distributed in all possible

orientations  $\theta \in [0, \pi]$  and  $\varphi \in [0, 2\pi]$ , where  $\theta$  and  $\varphi$  are the polar and azimuthal orientation angles, respectively. The application of an external field in the  $z$  direction does not change the distribution of the azimuthal angle  $\varphi$ . The angle  $\theta$ , on the other hand, decreases as the field is increased. The average tensors  $\langle \kappa \rangle$  and  $\langle \alpha \rangle$  are, therefore, uniaxial with elements

$$\langle \tilde{\kappa} \rangle_{xx} = \langle \tilde{\kappa} \rangle_{yy} = \frac{1}{2} [\kappa_{\parallel} + \kappa_{\perp} - (\kappa_{\parallel} - \kappa_{\perp}) \langle \cos^2 \theta \rangle] \quad \text{and} \quad \langle \tilde{\kappa} \rangle_{zz} = \kappa_{\perp} + (\kappa_{\parallel} - \kappa_{\perp}) \langle \cos^2 \theta \rangle \quad (10)$$

and

$$\langle \tilde{\alpha} \rangle_{xx} = \langle \tilde{\alpha} \rangle_{yy} = \frac{1}{2} [\alpha_{\parallel} + \alpha_{\perp} - (\alpha_{\parallel} - \alpha_{\perp}) \langle \cos^2 \theta \rangle] \quad \text{and} \quad \langle \tilde{\alpha} \rangle_{zz} = \alpha_{\perp} + (\alpha_{\parallel} - \alpha_{\perp}) \langle \cos^2 \theta \rangle, \quad (11)$$

respectively. The electrostatic energy of a single particle is

$$\mathcal{E} = -\frac{1}{2} p_s \bar{E}_L = -\frac{v_s \tilde{\alpha}_{zz} E_0^2}{8\pi(1-f+f\langle \tilde{\kappa} \rangle_{zz})^2}. \quad (12)$$

This mean-field calculation, via the MGA, thus leads to an explicit dependence of the energy on the average induced polarization of all the particles in the system.

### III. THE STEADY STATE ORIENTATIONAL ORDER PARAMETER

The orientational order parameter of the suspension is

$$S = \frac{1}{2} (3\langle \cos^2 \theta \rangle - 1). \quad (13)$$

It varies from zero at  $E_0 = 0$ , where the orientation distribution is random, to 1 at large fields where all the ellipsoids are aligned with their principal axis parallel to the field. At intermediate situations,  $S$  is determined by a thermal average of the electrostatic energy that seeks to orient the particles in the direction of the applied field.

Let us define a dimensionless electrostatic energy  $U = [v_s E_0^2 (\alpha_{\parallel} - \alpha_{\perp})] / 8\pi kT$ . We then obtain

$$\langle \cos^2 \theta \rangle = \frac{1}{Q} \int e^{-\mathcal{E}/kT} \cos^2 \theta d\Omega = -\frac{1}{2\tilde{U}} + \frac{e^{\tilde{U}}}{\sqrt{\pi\tilde{U}} \text{Erfi}(\sqrt{\tilde{U}})}, \quad (14)$$

where

$$Q = \int e^{-\mathcal{E}/kT} d\Omega = 2\pi e^{[\tilde{U}\alpha_{\perp}/(\alpha_{\parallel} - \alpha_{\perp})]} \sqrt{(\pi/\tilde{U})} \text{Erfi}(\sqrt{\tilde{U}}), \quad (15)$$

$$\tilde{U} = \frac{U}{(1-f+f\langle \tilde{\kappa} \rangle_{zz})^2}, \quad (16)$$

$\Omega$  is a solid angle,  $k$  is Boltzmann constant, and  $T$  is the temperature.  $\text{Erfi}(x) = (2/\sqrt{\pi}) \int_0^x e^{t^2} dt = -i \text{erf}(ix)$  is the modified error function. For small  $U$  we find  $\langle \cos^2 \theta \rangle = \frac{1}{3} + (4\tilde{U}/45) + \mathcal{O}(\tilde{U}^2)$ .

In the dilute limit  $f \rightarrow 0$ ,  $\tilde{U}$  is reduced to  $U$  and the calculation of the order parameter is straightforward. However, taking into account the electrostatic interaction between particles, we have to consider finite  $f$  and the explicit dependence of  $\tilde{U}$  on the orientation distribution of all the particles in the system. The solution in this case is obtained by a simultaneous numerical solution of Eqs. (14) and (16). The numerical calculation is easy, in principle. The only difficulty arises in the computation of the modified error function  $\text{Erfi}(x)$ , for which we used an algorithm for rapid computation of complex error functions developed by Hui, *et al.* [22].

The dilute-limit result is identical to that obtained by O'Konski, Yoshioka, and Orttung in their study of the steady state birefringence of solutions of polarizable macromolecules [23]. It should be noted, in this context, that most studies of field-induced reorientation consider systems of polar particles with a permanent dipole. This is particularly the case in molecular suspensions where the interaction energy of the permanent dipole with the orienting field is usually greater than that of the induced dipole moments [24,25]. The order parameter in these systems is given by the well-known Langevin function [25]. In the systems considered here, the particles are polarizable but do not possess a permanent dipole moment. This leads to the different result of Eq. (14).

Equation (14) applies for prolate and oblate microparticles. It is assumed here, for simplification, that the suspension is monodispersed, i.e.,  $v_s$  is the same for all particles, however, similar results are obtained for any distribution of  $v_s$ . As expected, when  $E_0 = 0$ ,  $\theta$  is distributed uniformly and  $S = 0$ . It varies sharply at small fields and reaches saturation

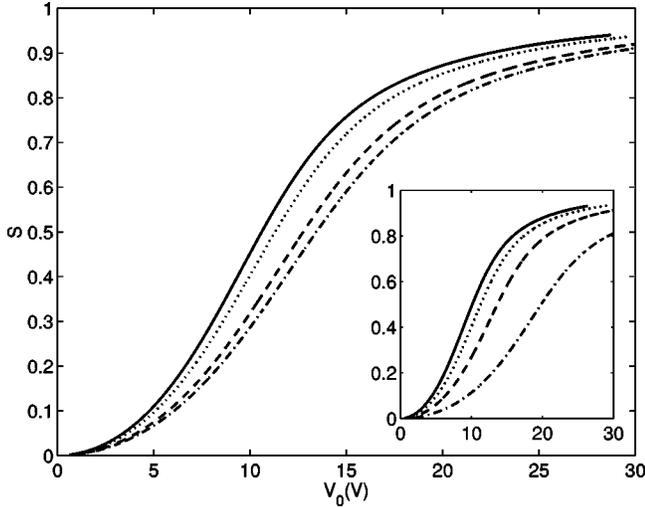


FIG. 2. The order parameter  $S$  as a function of applied voltage  $V_0$  for suspensions of ellipsoids with  $\epsilon_{\parallel}=3$ ,  $\epsilon_{\perp}=2$ ,  $\epsilon_h=1$ ,  $d=20 \mu\text{m}$ . The principal depolarization coefficient is  $d_{\parallel}=0.2$  and the volume fraction varies:  $f=0.4$  (solid line),  $f=0.3$  (dotted),  $f=0.1$  (dashed), and  $f=0.01$  (dash-dotted). In the inset  $f=0.3$  and  $d_{\parallel}=0.1$  (solid line),  $d_{\parallel}=0.2$  (dotted),  $d_{\parallel}=1/3$  (dashed), and  $d_{\parallel}=0.5$  (dash-dotted).

( $S = -1/2$ , and  $1$ , for  $\alpha_{\parallel} - \alpha_{\perp} < 0$ , and  $> 0$ , respectively) at large fields where all the ellipsoids are aligned with the field. The electric fields applied to induce reorientation are low frequency (typically 100 kHz or less) [14,15]. The dielectric coefficients  $\epsilon_{\parallel}$ ,  $\epsilon_{\perp}$ , and  $\epsilon_h$  used in Eq. (14) should therefore be the dielectric coefficients of the particles and liquid host at these low frequencies. The field strength required for saturation may be easily estimated from the definition of  $U$ . For a typical sample with  $\delta\alpha \sim 1$  and  $v_s \approx 10^{-15} \text{ cm}^3$  at  $T = 300 \text{ K}$ ,  $U \sim 10$  leads to  $E_0 \approx 1 \text{ V}/\mu\text{m}$ , i.e., voltages of the order of 20 V are needed to bring a  $20 \mu\text{m}$  thick film to saturation, in excellent agreement with the experimental results of Ref. [15].

Typical results demonstrating the dependence of the order parameter  $S$  on the volume fraction of the particles and their aspect ratio are shown in Fig. 2.  $S$  is plotted as a function of applied voltage  $V_0$  on a  $20 \mu\text{m}$  thick sample. Results are shown for suspensions of particles with axes aspect ratio of 1.7:1, corresponding to a principal depolarization factor  $d_{\parallel}=0.2$ , and four different concentrations. The rise of  $S$  with increasing field is more rapid at higher concentrations. It is evident that although the applied field is strong enough to saturate the rotational degree of freedom of the particles, the concentration effects are modest. This is in agreement with the experimental results of Kralik, Vugmeister, and Malcuit [12], where small concentration effects have been measured in suspensions of ellipsoids with aspect ratios 1.4:1, 1.7:1, and 2.4:1 at volume fractions between 1% and 40%. In the inset, results are shown for suspensions with a fixed concentration  $f=0.3$  and particles with different aspect ratios: prolate spheroids with aspect ratios of 3.2:1 and 1.7:1, perfect spheres, and oblate spheroids with aspect ratio of 1.8:1, corresponding to the principal depolarization factors  $d_{\parallel}=0.1, 0.2, 1/3$ , and  $0.5$ , respectively. The effect of these shape

variations on  $S$  is somewhat stronger than that of the volume fraction variations. This effect has not been examined experimentally yet.

It should be noted that at higher concentrations, excluded volume effects that might cause the particles to order (a liquid crystal-like isotropic-nematic transition) would have to be taken into account. The threshold concentration for such ordering, and the coexistence of the isotropic suspension with a nematic phase, depends on the aspect ratio of the ellipsoids. For slightly aspherical spheroids (with axes ratios between 0.3 and 3) this threshold is close to the hard sphere freezing volume fraction  $f=0.49$  [26]. It is reduced as the eccentricity of the spheroids increases, e.g., for axes ratios 0.2 or 5 it is reduced to about 0.3. No evidence of excluded volume induced ordering has been observed in suspensions with the aspect ratios shown in Fig. 2, up to  $f=0.4$  [12]. These examples are thus well within the isotropic phase in the absence of field.

#### IV. TRANSIENT BEHAVIOR OF THE ORIENTATIONAL ORDER PARAMETER

The orientational order parameter, and many other macroscopic properties of a suspension, are determined by averages over the orientation distribution function of the particles  $\rho(\Omega, t)$ . In the absence of field this function is constant,  $\rho(\Omega, t) = 1/4\pi$ , over the entire range of orientations  $\theta \in [0, \pi]$  and  $\varphi \in [0, 2\pi]$ . The dependence on the azimuthal angle  $\varphi$  may be omitted since it is uniformly distributed and does not depend on the applied field. The distribution in the absence of field is then  $\rho(\theta, t) = 2\pi\rho(\Omega, t) = 1/2$ . On the application of a low-frequency field the particles undergo rotational diffusion, reaching a steady state where their free energy is a minimum. In the steady state,  $\rho(\theta, t)$  reduces to the Maxwell-Boltzmann distribution which leads to result (14). The dynamics of microellipsoids in solution, driven by an electrostatic torque, is governed by the rotational diffusion equation (sometimes also referred to as the Debye equation or the Planck-Nernst equation) [25]:

$$\frac{\partial \rho(\theta, t)}{\partial t} = \frac{\Theta}{\sin(\theta)} \frac{\partial}{\partial \theta} \left[ \sin(\theta) \left( \frac{\partial \rho(\theta, t)}{\partial \theta} + \frac{1}{kT} M \rho(\theta, t) \right) \right], \quad (17)$$

where  $\Theta$  is the rotational diffusion coefficient of the particle and

$$M = -\frac{\partial \mathcal{E}}{\partial \theta} = -kT \tilde{U} \sin(2\theta) \quad (18)$$

is the electrostatic torque. It is clear that at the steady state, Eq. (17) can be trivially solved to reproduce the Maxwell-Boltzmann distribution  $\rho(\theta, t) \propto \exp(-\mathcal{E}/kT)$ . It should be noted that, in general,  $\rho$  may be a function of both orientation angles  $\theta$  and  $\phi$  and the rotational diffusion coefficient is a uniaxial tensor [27]. However, the case we discuss here, spheroids in the presence of an orienting field, is axisymmetric with a distribution function and electrostatic torque independent of  $\phi$ . Modifications in the orientation distribution of

the spheroids due to rotations produced by Brownian movement depend, in this case only, on  $\theta$  [25]. The reorientation of the particles is thus carried out by rotation about an axis normal to the applied field and the diffusion coefficient in Eq. (17) is the corresponding diagonal element of the diffusion tensor [25,27,28].

The rotational diffusion coefficient of a microellipsoid

with major semiaxes  $[a,b,b]$  is [27]

$$\Theta = \frac{3}{2} \Theta_s^0 \left[ \frac{(2-r^2)G(r)-1}{1-r^4} \right], \quad (19)$$

where  $\Theta_s^0 = kT/8\pi\eta a^3$  is the rotational diffusion coefficient of a sphere of radius  $a$  in a liquid of viscosity  $\eta$ ,  $r=b/a$ , and

$$G(r) = \begin{cases} (1-r^2)^{-1/2} \ln \left[ \frac{(1-r^2)^{1/2} + 1}{r} \right] & r < 1, \text{ prolate spheroid} \\ (r^2-1)^{-1/2} \tan^{-1} [(r^2-1)^{1/2}] & r > 1, \text{ oblate spheroid.} \end{cases} \quad (20)$$

The function (19) is plotted in Fig. 3. The dependence of  $\Theta$  on the volume fraction of the particles has been recently studied, both experimentally and theoretically, in suspensions of hard spheres [29,30]. It was found that an expansion up to second order in  $f$ ,

$$\Theta_s = \Theta_s^0 (1 - 0.63f - 0.68f^2), \quad (21)$$

compares well with experimental and simulation results up to quite high volume fractions ( $f \sim 0.4$ ) below the hard sphere freezing volume fraction  $f = 0.49$  [30]. This formula represents the effect of hydrodynamic interactions among the particles on the rotational diffusion coefficient. Numerical calculations by Claeys and Brady [31], for prolate spheroids with aspect ratio of six, also indicate significant reduction of the rotational diffusion coefficient with increasing volume fraction up to the isotropic-nematic transition ( $f \sim 0.3$ ). However, general results, similar to Eq. (21), for ellipsoidal particles are not available yet.

Since the symmetry of the suspension in the presence of applied field is cylindrical, we may look for a general solu-

tion of the diffusion equation (17) by expanding  $\rho(\theta,t)$  in terms of Legendre polynomials [28]:

$$\rho(\theta,t) = \sum_{l=0}^{\infty} c_l(t) P_l(\cos \theta). \quad (22)$$

The solution for  $S$  is then obtained by recognizing that  $S$  is equal to the average of the second Legendre polynomial

$$S(t) = \langle P_2(\cos \theta) \rangle = \int P_2(\cos \theta) \rho(\Omega,t) d\Omega = \frac{2}{5} c_2(t). \quad (23)$$

The initial conditions are

$$\begin{aligned} c_l(t=0) &= 0 \quad \text{for } l \neq 0, \\ c_0(t=0) &= \frac{1}{2}. \end{aligned} \quad (24)$$

Substituting expansion (22) into the diffusion equation and using the properties of the Legendre polynomials we find the differential equation satisfied by the coefficients  $c_l(t)$  (see Appendix):

$$\begin{aligned} \frac{dc_l(t)}{dt} &= -\Theta l(l+1)c_l(t) + 2\Theta \tilde{U} \left[ \frac{l(l-1)(l+1)}{(2l-1)(2l-3)} c_{l-2}(t) \right. \\ &\quad \left. + \frac{l(l+1)}{(2l-1)(2l+3)} c_l(t) - \frac{l(l+1)(l+2)}{(2l+3)(2l+5)} c_{l+2}(t) \right]. \end{aligned} \quad (25)$$

The temporal behavior of the  $l$ th Legendre component is coupled to that of the  $(l-2)$ th and  $(l+2)$ th components. In the absence of field,  $\tilde{U} = 0$ , the equations decouple and the order parameter  $S$  of Eq. (23) exhibits a simple exponential decay with time constant equal to  $6\Theta$ . For  $l=0$ , we find that  $c_0(t) = 1/2$  for all  $t$ . A complete solution for the other components at finite fields requires solving simultaneously this infinite set of coupled equations.

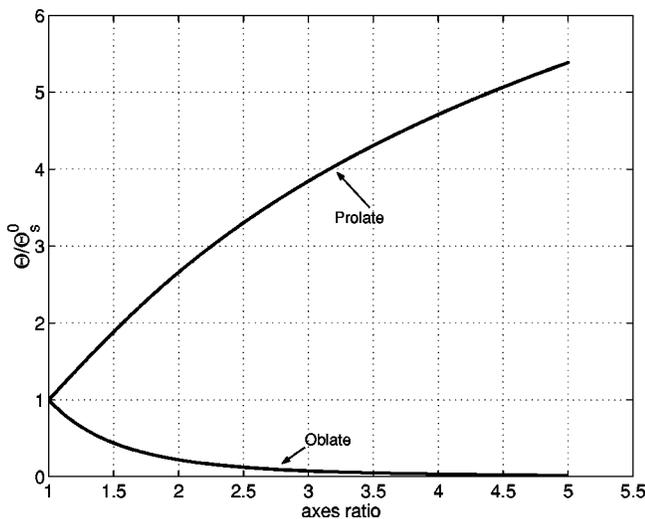


FIG. 3. The ratio  $\Theta/\Theta_s^0$  of Eq. (19) as a function of the axes ratio  $r$  for oblate and  $1/r$  for prolate spheroids.

### A. The low field limit

At low fields,  $U \ll 1$ , we may consider only some low orders of Legendre polynomials. Truncating the full set of equations (25) at the fourth order we obtain a system of two coupled equations for  $c_2(t)$  and  $c_4(t)$ . In the dilute case  $\tilde{U} = U$ , this set may be solved to give an analytical solution (see the Appendix). Up to second order in  $U$  the solution for  $c_2(t)$  is

$$c_2(t) = \frac{U}{3}(1 - e^{-6\Theta t}) + \frac{2U^2}{63}[1 - e^{-6\Theta t}(1 + 6\Theta t)] + O(U^3). \quad (26)$$

At very small fields the transition to steady state is purely exponential with a time constant  $6\Theta$ . At slightly higher fields the behavior is somewhat more complicated but is still dominated by an exponential transition with the same time constant. It is shown in the Appendix that at higher fields the coupling of different Legendre components complicates the reorientation process. The third order term in the expansion of  $c_2(t)$  includes an exponential with time constant  $20\Theta$ , characteristic of  $c_4(t)$ .

The first-order solution may also be obtained in the non-dilute case by substituting  $\rho(\theta, t) = \rho(\theta, t=0)$  in the dielectric torque term of Eq. (17) and noting that the electrostatic energy  $\mathcal{E}$  is a simple function of  $P_2(\cos \theta)$ . The equations for the different Legendre polynomials are then decoupled and the equation for  $c_2(t)$  is

$$\frac{dc_2(t)}{dt} = -6\Theta c_2(t) + 2\Theta \tilde{U}, \quad (27)$$

where  $\tilde{U}$  of Eq. (16) is itself a function of  $c_2(t)$ . A few examples of numerical solutions of this equation, for the order parameter  $S$  as a function of  $t$ , are shown in Figs. 4 and 5. In Fig. 4 we consider suspensions of prolate [Fig. 4(a)] and oblate [Fig. 4(b)] spheroids with aspect ratio equal to 2 and minor axis of  $0.05 \mu\text{m}$  in a liquid of viscosity  $\eta = 1$  cP. The corresponding rotational diffusion coefficients are  $\Theta = 420 \text{ s}^{-1}$  and  $35 \text{ s}^{-1}$ , respectively. As expected,  $S$  increases (decreases) with time for the prolate (oblate) spheroids. It also does not reach its saturation value of 1 (or  $-1/2$ ) since  $U \ll 1$  is not large enough to saturate the orientational degree of freedom of the spheroids. The rate of change of  $S$  with time is more rapid at higher concentrations and the saturation value is also higher. The time constant of the process is, however, identical at all concentrations. This can be easily checked by normalizing all the curves to the same saturation value. Under this scaling they are identical. This means that in the low-field limit, the electrostatic interaction among the particles at moderate concentrations is not large enough to affect the time constant of the transient behavior in the suspension. However, the dependence of  $\Theta$  on  $f$  does affect this transient behavior. This is demonstrated in Fig. 5, for a suspension of spheres with intrinsic anisotropy. The sphere radius is  $0.1 \mu\text{m}$  and the corresponding rotational diffusion coefficient is  $\Theta_s^0 = 165 \text{ s}^{-1}$ . In Fig. 5(a) results are shown neglecting the dependence of  $\Theta_s$  on the volume fraction. As

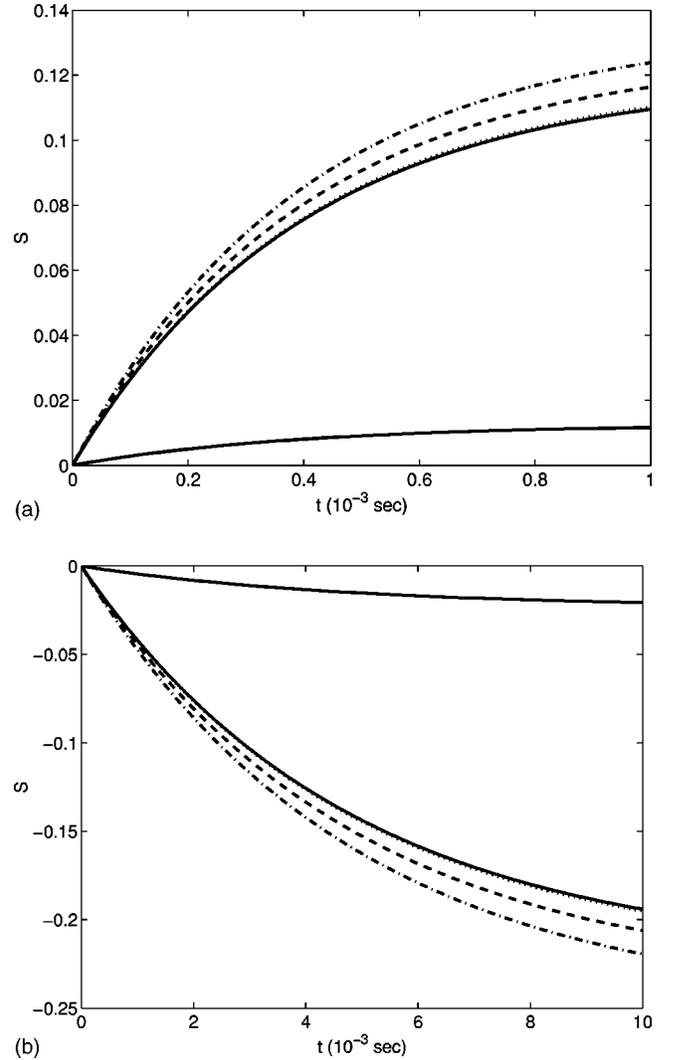


FIG. 4. The order parameter  $S$  as a function of time in suspensions with  $\epsilon_{\parallel} = 3$ ,  $\epsilon_{\perp} = 2$ , and  $\epsilon_h = 1$ . (a) Prolate spheroids with  $\Theta = 420 \text{ s}^{-1}$  at applied fields  $E_0 = 10 \text{ V/m}$  (upper curves) and  $E_0 = 1 \text{ V/m}$  (lower curve). Upper curves:  $f = 0$  (solid),  $f = 0.01$  (dotted),  $f = 0.1$  (dashed), and  $f = 0.2$  (dash dot). Lower curve:  $f = 0.1$ . (b) Oblate spheroids with  $\Theta = 35 \text{ s}^{-1}$  at applied fields  $E_0 = 10 \text{ V/m}$  (upper curves), and  $E_0 = 1 \text{ V/m}$  (lower curve) and volume fractions as in (a).

in the previous examples, the rise of  $S$  with time is more rapid at higher concentrations and the saturation value is also higher. The time constant of the process is, however, identical at all concentrations. In Fig. 5(b) the dependence of  $\Theta_s$  on  $f$ , Eq. (21), is taken into account. In contrast to Fig. 5(a), the different curves now overlap at short times. This means that, as expected, the initial rate at which  $S$  increases with time is reduced with increasing  $f$ . The order parameter still reaches higher saturation values at more concentrated suspensions, but the time constant of the process is increased.

### B. The high-field limit

At sufficiently high-field strength, the effect of the rotational diffusion may be neglected and the particles may be

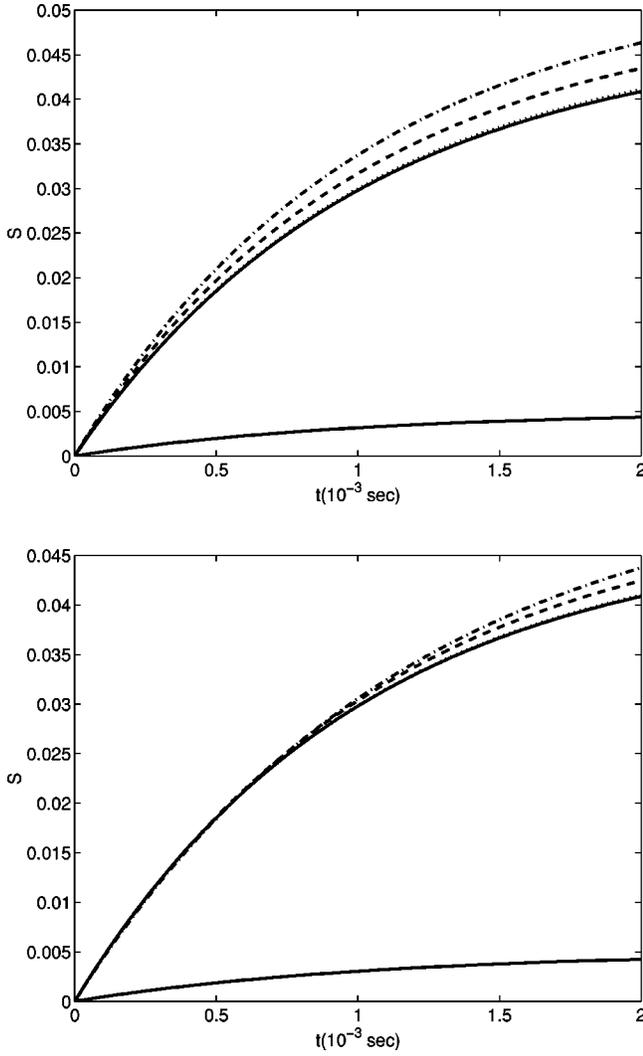


FIG. 5. The order parameter  $S$  as a function of time in suspensions of spherical particles with the same intrinsic anisotropy as in Fig. 4 and  $\Theta_s^0 = 165 \text{ s}^{-1}$ . (a) Constant  $\Theta = \Theta_s^0$ . (b)  $\Theta$  depends on the volume fraction, as in Eq. (21). The different curves are as in Fig. 4.

considered as rotating at an angular velocity proportional to the torque [25]:

$$\frac{d\theta}{dt} = \frac{\Theta}{kT} M = -\Theta \tilde{U} \sin(2\theta). \quad (28)$$

This case has been discussed by O'Konski, Yoshioka, and Orttung [23] in the analogous problem of the reorientation of polarizable macromolecules. Integrating this equation we find

$$\cos \theta_0 = (1 + e^{\tau} \tan^2 \theta)^{-1/2}, \quad (29)$$

where  $\tau = 4\Theta \tilde{U} t$ . The particles at orientation  $\theta_0$  at  $t=0$  rotate to  $\theta$  at time  $t$ . In the absence of electric field the orientation distribution is uniform, therefore

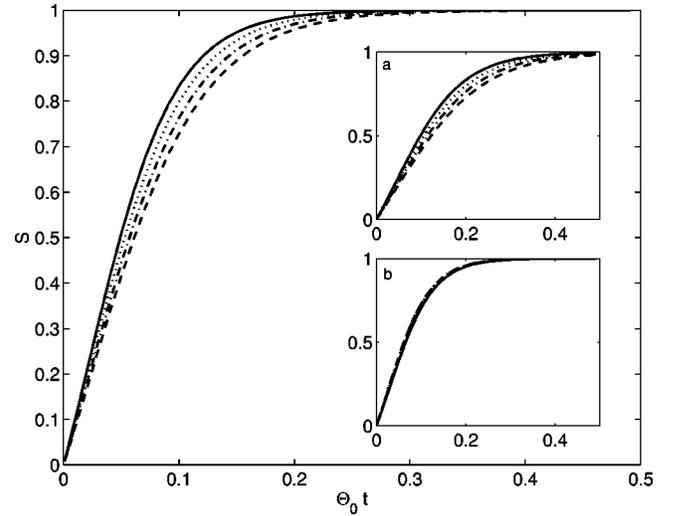


FIG. 6. The orientational order parameter  $S$  at the high-field limit as a function of dimensionless time  $\Theta_0 t$ , for two values of normalized energy  $\Theta U = 10$  and  $\Theta U = 5$  [inset (a)] and volume fractions  $f = 0.3$  (solid lines),  $f = 0.2$  (dotted lines),  $f = 0.1$  (dash-dotted lines) and  $f = 0$  (dashed lines). In inset (b),  $\Theta_0 U = 10$  and the dependence of the rotational diffusion coefficient  $\Theta_s$  on the volume fraction  $f$  is taken into account.

$$\rho(\theta, t) = 2\pi \rho(\Omega, t) = \frac{d(\cos \theta_0)}{2d(\cos \theta)} = \frac{e^\tau}{2(\cos^2 \theta + e^\tau \sin^2 \theta)^{3/2}} \quad (30)$$

and

$$\langle \cos^2 \theta \rangle = \int_0^\pi \rho(\theta, t) \cos^2 \theta \sin \theta d\theta = \frac{e^\tau}{e^\tau - 1} + \frac{e^\tau}{(e^\tau - 1)^{3/2}} \left[ \tan^{-1} \frac{1}{\sqrt{e^\tau - 1}} - \frac{\pi}{2} \right]. \quad (31)$$

Truncating to second order in  $\tau$  we find  $\langle \cos^2 \theta \rangle = \frac{1}{3} + \frac{2}{15} \tau + \frac{1}{105} \tau^2 + O(\tau^3)$ .

In the dilute limit  $f \rightarrow 0$ ,  $\tilde{U}$  is reduced to  $U$ ,  $\tau$  is independent of  $f$  and the calculation of the order parameter is straightforward. At finite  $f$ , the solution is again obtained by a simultaneous numerical solution of Eqs. (31) and (16). In Fig. 6,  $S$  is plotted as a function of the dimensionless time  $\Theta_0 t$  [ $\Theta_0 = \Theta(f=0)$ ]. Results are shown for suspensions of spheres with four different concentrations. In the main figure,  $\Theta U = 10$  and the dependence of  $\Theta$  on  $f$  is neglected. The rise of  $S$  with time is more rapid at higher concentrations. In inset (a),  $\Theta U = 5$ , which leads to longer rise times of  $S$  for all concentrations. In inset (b),  $\Theta_0 U = 10$  and the dependence of  $\Theta_s$  on  $f$ , Eq. (21), is taken into account. The rate of increase of  $S$  with time is reduced with increasing  $f$  and the curves overlap.

## V. FIELD-INDUCED BIREFRINGENCE AND OPTICAL PHASE SHIFT

Once the order parameter  $S$  is known, Eq. (9) can be used to calculate the ordinary and extraordinary refractive indices of the AKM. In this calculation, the dielectric coefficients  $\epsilon_{\parallel} = n_{\parallel}^2$ ,  $\epsilon_{\perp} = n_{\perp}^2$ , and  $\epsilon_h = n_h^2$ , substituted in Eqs. (10) and (11), are those of the particles and host at the frequency of light incident on the sample.  $n_{\parallel}$ ,  $n_{\perp}$ , and  $n_h$  are the corresponding refractive indices. The effective dielectric tensor is uniaxial and its principal axis is perpendicular to the film plane. The ordinary refractive index of the AKM is therefore

$$n_o = \sqrt{\epsilon_h + \frac{f\langle\tilde{\alpha}\rangle_{xx}}{1-f+f\langle\tilde{\kappa}\rangle_{xx}}} \quad (32)$$

and the extraordinary index is

$$n_e = \sqrt{\epsilon_h + \frac{f\langle\tilde{\alpha}\rangle_{zz}}{1-f+f\langle\tilde{\kappa}\rangle_{zz}}} \quad (33)$$

The optical phase shift experienced by light of wavelength  $\lambda$  incident at angle  $\vartheta$  on the plane surface of the AKM film is

$$\phi = \frac{2\pi d}{\lambda \cos \vartheta} \delta n, \quad (34)$$

where

$$\delta n = \frac{n_o n_e}{\sqrt{n_e^2 \cos^2 \vartheta + n_o^2 \sin^2 \vartheta}} - n_o. \quad (35)$$

The electric-field-induced birefringence is  $\Delta n = n_e - n_o$ . To first order in the volume fraction we obtain

$$\Delta n = \frac{f(\alpha_{\parallel} - \alpha_{\perp})}{2n_h} S. \quad (36)$$

The electro-optical effects thus reflect the dependence of the orientational order parameter on changes in particle shape, intrinsic anisotropy, and concentration. They may, therefore, be useful for studying reorientation phenomena, overcoming the problems due to light scattering, in these materials.

## VI. CONCLUSIONS

In this paper, the local field effect on the reorientation of microellipsoids in dielectric liquid suspensions is studied using a simple model for the bulk effective dielectric response. The model is an extension of the well-known Maxwell Garnett approximation for the dielectric properties of mixtures of isotropic particles and, similarly, it is exact to second order in the volume fraction of the particles. As in previous studies of this problem, the essential physics involves a balance between the electrostatic energy, which favors alignment with the applied field, and thermal fluctuations. However, the approach presented here gives explicit results for the field-dependent orientation distribution of the ellipsoids and provides a convenient framework for the evaluation of

the electrostatic effects, allowing an explicit consideration of the electrostatic interaction between the particles at moderate concentrations.

Steady state calculations provide analytical results for dilute systems and a very simple numerical scheme for systems with higher concentrations of microellipsoids. They reproduce published experimental observations on artificial Kerr materials. In particular, the calculated order parameter at moderate concentrations ( $f=0.1-0.4$ ) agrees well with the experiments of Kralick, Vugmeister, and Malcuit [12] which are, to the best of our knowledge, the only results published for this regime.

The transient behavior in the dilute limit is purely exponential at low fields, with a time constant  $6\Theta$ . At higher fields, the transition process is more complicated, including exponential terms with longer time constants due to the coupling among different Legendre components, representing different decay modes. In the nondilute case, it is found that the effect of the electrostatic interaction among the particles on the transition times is negligible at low fields. Increasing the concentration affects only the saturation value of  $S$  in this limit. The effect of hydrodynamic interactions, i.e., the reduction of the rotational diffusion coefficient at higher concentrations, is, however, not negligible. The transient behavior at low fields is, therefore, slower at higher concentrations but the saturation value of  $S$  is higher.

Different behavior is observed at very high fields. The electrostatic interactions increase the rate of the transition in this limit, and the hydrodynamic interactions reduce it. The transition rate at high field, thus, depends on a balance between these two effects, increasing at higher concentrations due to the local field electrostatic effects and decreasing due to slowing of the rotational diffusion. In the example presented in Fig. 6 [inset (b)] these two effects cancel and the curves of  $S(t)$  at different concentrations overlap.

The orientational order parameter and the associated electro-optical effects, e.g., the optical phase shift and birefringence, are sensitive to properties of the microparticles. We may select the operation voltage and the magnitude of the effects by varying particle concentration and shape as well as the intrinsic dielectric coefficients of the components. Measurement of these effects may, therefore, offer a convenient method for studying the reorientation process and the physical parameters that influence it.

## ACKNOWLEDGMENTS

I thank N. Argaman, A. Bar-Shalom, and G. Hazak for useful discussions.

## APPENDIX

The rotational diffusion equation for microellipsoids in solution is

$$\frac{\partial \rho(\theta, t)}{\partial t} = \frac{\Theta}{\sin(\theta)} \frac{\partial}{\partial \theta} \left[ \sin \theta \left( \frac{\partial \rho(\theta, t)}{\partial \theta} + \frac{1}{kT} M \rho(\theta, t) \right) \right], \quad (A1)$$

where  $\Theta$  is the rotational diffusion coefficient of the particle and

$$M = -\frac{\partial \mathcal{E}}{\partial \theta} = -kT\tilde{U} \sin(2\theta) \quad (\text{A2})$$

is the electrostatic torque. Substituting the expansion (22)

$$\rho(\theta, t) = \sum_{m=0}^{\infty} c_m(t) P_m(\cos \theta) \quad (\text{A3})$$

and defining  $x = \cos \theta$  we find

$$\begin{aligned} \frac{1}{\Theta} \sum_m \frac{dc_m(t)}{dt} P_m(x) &= \sum_m c_m(t) \frac{\partial}{\partial x} [(1-x^2)P'_m(x)] \\ &\quad - 2\tilde{U} \sum_m c_m(t) \frac{\partial}{\partial x} [x(1-x^2)P_m(x)]. \end{aligned} \quad (\text{A4})$$

Using the recurrence formulas

$$(1-x^2)P'_m(x) = mP_{m-1}(x) - mxP_m(x),$$

$$mP_m(x) = xP'_m(x) - P'_{m-1}(x),$$

we find

$$\begin{aligned} \frac{1}{\Theta} \sum_m \frac{dc_m(t)}{dt} P_m(x) &= -\sum_m c_m(t) m(m+1)P_m(x) \\ &\quad - 2\tilde{U} \sum_m c_m(t) \{mxP_{m-1}(x) \\ &\quad + [1 - (3+m)x^2]P_m(x)\}. \end{aligned} \quad (\text{A5})$$

Let us now evaluate the integrals

$$I_1 = \int_{-1}^1 x P_n(x) P_m(x) dx \quad (\text{A6})$$

and

$$I_2 = \int_{-1}^1 x^2 P_n(x) P_m(x) dx. \quad (\text{A7})$$

Using the recurrence relation

$$(m+1)P_{m+1}(x) = (2m+1)xP_m(x) - mP_{m-1}(x),$$

we find

$$\begin{aligned} I_1 &= \frac{n+1}{2n+1} \int_{-1}^1 P_{n+1}(x) P_m(x) dx \\ &\quad + \frac{n}{2n+1} \int_{-1}^1 P_{n-1}(x) P_m(x) dx \end{aligned} \quad (\text{A8})$$

and

$$\begin{aligned} I_2 &= \frac{(n+1)(n+2)}{(2n+1)(2n+3)} \int_{-1}^1 P_{n+2}(x) P_m(x) dx \\ &\quad + \frac{(4n^3+6n^2-1)}{(2n-1)(2n+1)(2n+3)} \int_{-1}^1 P_n(x) P_m(x) dx \\ &\quad + \frac{n(n-1)}{(2n+1)(2n-1)} \int_{-1}^1 P_{n-2}(x) P_m(x) dx. \end{aligned} \quad (\text{A9})$$

Using the orthogonality relation

$$\int_{-1}^1 P_n(x) P_m(x) dx = \frac{2}{2n+1} \delta_{mn},$$

this is reduced to

$$I_1 = \frac{2n}{(2n+1)(2n-1)} \delta_{n,m+1} + \frac{2n+2}{(2n+1)(2n+3)} \delta_{n,m-1} \quad (\text{A10})$$

and

$$\begin{aligned} I_2 &= \frac{2n(n-1)}{(2n-3)(2n-1)(2n+1)} \delta_{n,m+2} \\ &\quad + \frac{2(4n^3+6n^2-1)}{(2n-1)(2n+1)^2(2n+3)} \delta_{nm} \\ &\quad + \frac{2(n+1)(n+2)}{(2n+1)(2n+3)(2n+5)} \delta_{n,m-2}. \end{aligned} \quad (\text{A11})$$

Using the orthogonality of the Legendre polynomials and substituting  $I_1$  and  $I_2$  in Eq. (A5) we obtain a set of coupled differential equations for  $c_l(t)$ :

$$\begin{aligned} \frac{1}{\Theta} \frac{dc_l(t)}{dt} &= -l(l+1)c_l(t) + 2\tilde{U} \left[ \frac{l(l-1)(l+1)}{(2l-3)(2l-1)} c_{l-2}(t) \right. \\ &\quad + \frac{l(l+1)}{(2l-1)(2l+3)} c_l(t) \\ &\quad \left. - \frac{l(l+1)(l+2)}{(2l+3)(2l+5)} c_{l+2}(t) \right]. \end{aligned} \quad (\text{A12})$$

The time evolution of each Legendre component  $l$  is thus coupled to that of the  $(l-2)$ th and  $(l+2)$ th components. From the equation for  $l=0$  we deduce that  $c_0(t)$  is constant.

A numerical solution for the other components may, in principle, be found by choosing a cutoff for this infinite system of equations.

A relatively simple analytic solution can be obtained for the low-field limit, assuming that each temporal component  $l$  is completely determined by the lowest order coupling to the  $(l-2)$ th and  $(l+2)$ th components and ignoring higher order couplings. Under this assumption the component  $c_2(t)$ , and the orientational order parameter  $S$ , are given by a set of two equations for  $l=2$  and  $l=4$ :

$$\frac{1}{\Theta} \frac{dc_2(t)}{dt} = -6c_2(t) + 2\tilde{U} \left[ 1 + \frac{2}{7}c_2(t) - \frac{8}{21}c_4(t) \right],$$

$$\frac{1}{\Theta} \frac{dc_4(t)}{dt} = -20c_4(t) + 2\tilde{U} \left[ \frac{12}{7}c_2(t) - \frac{20}{77}c_4(t) \right]. \quad (\text{A13})$$

In the dilute limit  $\tilde{U}=U$  is constant and the solution of this two-equation system, with initial conditions (24), can be obtained using MATHEMATICA. For  $c_2(t)$  we find

$$c_2(t) = \frac{U}{14} \left( \frac{5(2U-77)}{165-20U+4U^2} [-2 + e^{-(1/11)(143-6U+y)\Theta t} (1 + e^{(2/11)y\Theta t})] \right. \\ \left. + \frac{(556U^2+660U-29645)e^{(1/11)(143-6U+y)\Theta t} (e^{-(2/11)y\Theta t} - 1)}{(165-20U+4U^2)y} \right), \quad (\text{A14})$$

where

$$y = (5929 + 44U - 316U^2)^{1/2}. \quad (\text{A15})$$

A series expansion of Eq. (A14) for small  $U$  gives

$$c_2(t) = \frac{U}{3} (1 - e^{-6\Theta t}) + \frac{2U^2}{63} [1 - e^{-6\Theta t} (1 + 6\Theta t)] - \frac{4U^3}{324135} \\ \times [343 - 108e^{-20\Theta t} - e^{-6\Theta t} (235 + 3570\Theta t - 4410\Theta^2 t^2)] + O(U^4). \quad (\text{A16})$$

At small fields the transition to steady state is purely exponential with a time constant  $6\Theta$ . The coupling of different Legendre components complicates the transition process at higher fields. The third-order term in the expansion of  $c_2(t)$  includes an exponential with the characteristic time constant of  $c_4(t)$ ,  $20\Theta$ .

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