EUROPHYSICS LETTERS 1 August 2002

Europhys. Lett., **59** (3), pp. 337–343 (2002)

Rotational diffusion in a bistable potential

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(received 8 March 2002; accepted 8 May 2002)

PACS. 05.40.Jc – Brownian motion.
PACS. 82.70.Dd – Colloids.
PACS. 61.30.Pq – Microconfined liquid crystals: droplets, cylinders, randomly confined liquid crystals, polymer dispersed liquid crystals, and porous systems.

Abstract. – Using depolarized quasielastic light scattering, we have investigated the rotational diffusion of optically anisotropic colloidal particles in a dilute suspension subject to external electric and magnetic fields ($\boldsymbol{E}_0, \boldsymbol{B}_0$). The particles were produced by the polymerization of nematic liquid crystal droplets, leading to birefringent colloidal spheres whose frozen orientational order is rigidly coupled to the particle orientation. The torque on the droplet director $\boldsymbol{u}(t)$ originating from the coupling of $\boldsymbol{E}_0$ and $\boldsymbol{B}_0$ to the particles' anisotropy in the refractive index and in the diamagnetic susceptibility, respectively, leads to a suppression of the orientational fluctuations about the direction of the external field. We observe a strong dependence of the measured relaxation rates on the field strength and on the orientation of the field relative to the scattering plane. We explain our findings by a solution of the Smoluchowski equation describing rotational diffusion in a bistable potential $V(\boldsymbol{u})$ which has two equivalent minima separated by a potential barrier whose height is proportional to $(E_0, B_0)^2$.

Colloidal particles in a solvent do not only experience random forces due to the collisions with the surrounding molecules, but are also imparted random torques that lead to fluctuating particle orientations described by a unit vector $\boldsymbol{u}(t)$ also called particle director. If the colloids possess optical anisotropy, *e.g.*, due to intrinsic birefringence or shape birefringence, these orientational fluctuations can be probed by depolarized quasielastic light scattering [1]. For isolated, freely rotating spherical particles in the limit of high solvent viscosity η, the rotational part of the field auto-correlation function $g^{(1)}_{\mathrm{VH}}(t) = \langle \boldsymbol{E}^*_{\mathrm{VH}}(0)\boldsymbol{E}_{\mathrm{VH}}(t)\rangle / \langle |\boldsymbol{E}_{\mathrm{VH}}|^2 \rangle$ of the scattered depolarized electric field $\boldsymbol{E}_{\mathrm{VH}}(t)$ decays exponentially with time t; the corresponding decay rate is proportional to the rotational diffusion constant $D_{\mathrm{r}} = k_{\mathrm{B}}T/(8\pi\eta R^3)$, where $k_{\mathrm{B}}T$ is the thermal energy and R is the particle radius.

This simple situation changes completely when the rotational symmetry is broken by an external field (such as an electric or magnetic field) that couples to permanent or induced (electric or magnetic) dipoles localized on the particle. The orientational distribution then develops a peak around the direction of the external field, and, consequently, the amplitudes

of the orientational fluctuations are reduced, leading to reduced fluctuations of $\boldsymbol{E}_{\mathrm{VH}}(t)$. The dynamics of the orientational relaxation, on the other hand, now depends critically on the detailed shape of the external potential $V(\boldsymbol{u})$. For the case of permanent dipoles in an external field, well-known from Debye relaxation [2] in polar fluids, the experimentally accessible time auto-correlation functions of $\boldsymbol{u}(t)$ can be calculated analytically for small field strengths [3]. They show significant departures from exponential behavior, eventually approaching a finite non-zero value at long times which reflects the non-isotropic orientational distribution in thermal equilibrium.

However, the orientational relaxation of *induced* dipoles in an external field has been much less studied. For particles possessing an intrinsic uniaxial symmetry in their dielectric or magnetic properties the potential energy of the induced dipole is equal for both parallel and antiparallel alignment of the particle axis along the field. The two energy minima of such a bistable potential are separated by a barrier which increases with increasing field strength. The theoretical modelling of this problem is identical to the description of the Néel relaxation in single-domain ferromagnetic particles [4] and the dielectric relaxation of electric dipoles in nematic liquid crystals [5]. In the first case, the crystal structure of the particle defines an "easy axis" towards which the magnetization relaxes. In the second case, this easy axis is given by the common direction along which the constituent organic molecules of the liquid crystal align. The main interest of the theoretical work concentrated on calculating the Kramers transition rate or its inverse, the mean-first-passage time, *i.e.*, the time the dipoles need to flip over the potential barrier [4,6–8]. This quantity is equivalent to the slowest decay rate with which a distribution of dipole orientations relaxes towards thermal equilibrium. However, the rotational diffusion in a uniaxial potential shows, apart from the mean-first-passage time, a rich relaxation spectrum which has so far not been addressed. Detailed experimental tests of these theoretical models with magnetic or bulk liquid crystal systems are difficult due to the fact that the potential barrier is not tunable as it is an intrinsic material parameter. Furthermore, the applicability of the idealizing theory to the interpretation of relaxation experiments is still under debate [5, 7, 8].

Non-interacting colloidal particles could thus provide a model system for studying rotational diffusion in external fields, allowing to study more complicated situations such as the dielectric relaxation in bulk or polymer-dispersed liquid crystals or the rotational diffusion in concentrated colloids [9, 10] where the genuine rotational dynamics is strongly influenced by the coupling to translational degrees of freedom via hydrodynamic and potential interactions.

In this paper we present light scattering experiments on the rotational dynamics of optically anisotropic colloids which are aligned either with a magnetic or with an electric field. This constitutes an ideal system to study rotational diffusion in a bistable potential whose barrier is conveniently tuned by the external field. We show that the analysis of the field auto-correlation functions of the depolarized scattered field $\boldsymbol{E}_{\mathrm{VH}}(t)$ in different scattering geometries yields detailed information on the rotational dynamics of the particles with increasing field strength. We demonstrate that we are able to probe different characteristic relaxation rates by choosing different orientations of the aligning field with respect to the scattering plane. This interesting behavior has never been investigated experimentally. In particular, our data provide experimental evidence for an unexpected non-monotonic dependence of one relaxation rate on field strength. Our observations are consistent with a theoretical description on the basis of the orientational Smoluchowski equation which we solve both by a perturbation approach and by a numerical treatment.

Optically anisotropic colloidal particles were prepared by dissolving reactive monomer RM257 (Merck) and small amounts of photoinitiator Darocur 1173 (Ciba) in ethanol at room temperature. Dispersions of liquid crystalline droplets were formed by addition of water at a

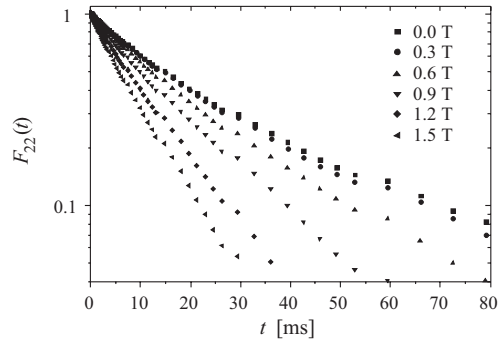

Fig. 1 – Rotational correlation functions $F_{22}(t) = \langle Y_{22}[\boldsymbol{u}(0)]Y_{22}^*[\boldsymbol{u}(t)]\rangle$ for particles with mean radius $R = 304\,\mathrm{nm}$ measured at $B_0 = (0.0\text{–}1.5)\,\mathrm{T}$. The temperature was 16 °C, the solvent was water with a viscosity $\eta = 1.1 \times 10^{-3}\,\mathrm{Pa\,s}$. The slight deviation of the zero-field data from the expected single exponential $F_{22}(t) = \exp[-6D_\mathrm{r}t]$ at short times is due to the fact that the particles are not true Rayleigh scatterers, as discussed in the text.

temperature of about 66 °C, slightly above the crystal-nematic phase transition of the reactive monomer [11]. In order to avoid subsequent coalescence, the droplets were polymerized by irradiation with ultraviolet light. This procedure has the effect of freezing the nematic order in the droplet whose anisotropy axis defines the particle director $\boldsymbol{u}(t)$. Although average particle sizes did vary somewhat from batch to batch, characterization of the droplets using scanning electron microscopy and quasielastic light scattering showed that the polydispersity in particle radius within a single batch could be kept as low as 10%.

Light scattering experiments were performed using an Ar ion laser at a wavelength $\lambda_0 = 514.5\,\mathrm{nm}$. Using a superconducting 7 T magnet, the particles at low volume fractions $\phi \approx 10^{-3}$ were oriented in the magnetic field due to the anisotropy of their diamagnetic susceptibility; in these experiments, the magnetic field $\boldsymbol{B}_0$ was aligned parallel to the wave vector $\boldsymbol{k}_\mathrm{i}$ of the excitation beam; its polarization was parallel to the scattering plane Σ, while the outgoing polarization was perpendicular to Σ. Scattered light at a scattering angle $\theta = 4°$ was collected with a single-mode fiber and detected by two photomultipliers (Hamamatsu). The amplified and discriminated photomultiplier signals were fed into an ALV-5000/FAST correlator operating in pseudo–cross-correlation mode in order to suppress detector afterpulsing. At small scattering angles the measured intensity-intensity cross-correlation function $g^{(2)}_\mathrm{VH}(t)$ then showed two well-separated relaxations: a decay at long times which is due to the translational motion of the particles, and a decay at shorter times which reflects rotational motion. The decay time of the translational correlation function $F_\mathrm{t}(q,t) = \exp[-q^2 D_\mathrm{t} t]$ (where q is the magnitude of the scattering vector and $D_\mathrm{t} = k_\mathrm{B}T/(6\pi\eta R)$ is the translational diffusion coefficient) is independent of the magnetic field strength B_0, indicating that rotation and translation are indeed decoupled. Correcting $g^{(2)}_\mathrm{VH}(t)$ for static scattering [12] and Faraday rotation of VV scattered light by the cell walls yields the rotational correlation function $g^{(1)}_\mathrm{VH}(t)/F_\mathrm{t}(q,t)$ which is, in this specific geometry, given by $F_{22}(t) = \langle Y_{22}[\boldsymbol{u}(0)]Y_{22}^*[\boldsymbol{u}(t)]\rangle$, where $Y_{22}[\boldsymbol{u}(t)]$ denotes the $(l = 2, m = 2)$ spherical harmonics for the particle director $\boldsymbol{u}(t) = (\varphi(t), \vartheta(t))$ [1].

As shown by fig. 1, the decay of $F_{22}(t)$ is strongly accelerated, even at the shortest correlation times measurable, by the presence of the magnetic torque which tends to suppress the thermally excited excursions of $\boldsymbol{u}(t)$ from the orientation of lowest energy along the magnetic field. The relaxation rate of the zero-field data at 40.7 kHz is in good agreement with the

theoretical value $6D_{\rm r} = 3k_{\rm B}T/(4\pi\eta R^3)$. A CONTIN analysis [13] shows that the slight deviations in $F_{22}(t)$ from a single exponential decay can be attributed to decay rates of about $20\,D_{\rm r}$ and $42\,D_{\rm r}$, originating from the time correlation functions of the $l = 4$ and $l = 6$ spherical harmonics which contribute to the quasielastic light scattering since our particles are not true Rayleigh scatterers [14, 15].

In order to understand our observations, we describe the rotational diffusion of an isolated particle in an external field by the Smoluchowski equation

$$\frac{\partial W(\boldsymbol{u},t)}{\partial t} = \mathcal{L}W(\boldsymbol{u},t)\,, \tag{1}$$

where $W(\boldsymbol{u},t)$ denotes the probability of finding the particle oriented along the unit vector $\boldsymbol{u}$ at time t. In the Smoluchowski operator

$$\mathcal{L} = D_{\rm r}\left[\nabla_{\rm r}^2 + \frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial V(\vartheta)}{\partial\vartheta}\ldots\right)\right] \tag{2}$$

the angular part of the Laplacian, $\nabla_{\rm r}^2$, *i.e.*, the square of the angular momentum operator of quantum mechanics, describes free rotational diffusion, whereas the drift term reflects the fact that the particle experiences a torque $-\partial V(\vartheta)/\partial\vartheta$ due to the uniaxial potential $V(\vartheta)$ (in units of the thermal energy $k_{\rm B}T$) which restricts free rotation along the azimuthal angle ϑ. The drift term can be derived from the requirement that the equilibrium distribution $W_0(\boldsymbol{u}) \propto \exp[-V(\vartheta)]$ is a stationary solution of eq. (1). For our colloidal particles with an internal nematic order, the potential is calculated from the well-known magnetic-field term in nematics [16]. Assuming a uniaxial director distribution, we arrive at the bistable potential $V(\vartheta) = -\sigma\cos^2\vartheta$ with $\sigma = C\Delta\chi v B_0^2/(2k_{\rm B}T)$, where $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$ is the diamagnetic anisotropy of the nematic phase, and $v = \frac{4\pi}{3}R^3$ is the volume of the particle. The geometrical factor C is unity for a uniform director field in the droplet.

The Smoluchowski equation governs the time evolution of $W(\boldsymbol{u},t)$ for an initial probability distribution $W(\boldsymbol{u},0)$. Using a relaxational ansatz $W(\boldsymbol{u},t) \propto \varphi(\boldsymbol{u})\exp[-\lambda t]$ in eq. (1), one is led to the eigenvalue problem of the Smoluchowski operator: $\mathcal{L}\varphi_\lambda(\boldsymbol{u}) = -\lambda\varphi_\lambda(\boldsymbol{u})$. Once all the eigenfunctions and eigenvalues are known, the Smoluchowski equation is solved. For example, as is well known from quantum mechanics, the spherical harmonics $Y_{lm}(\boldsymbol{u})$ are the eigenfunctions of the unperturbed diffusion operator $\nabla_{\rm r}^2$, and the eigenvalues of the zero-field Smoluchowski operator are $l(l+1)D_{\rm r}$. The time correlation functions of the spherical harmonics, observable directly for $l = 2$ in a light scattering experiment, are then given by $\langle Y_{lm}[\boldsymbol{u}(0)]Y_{lm'}^*[\boldsymbol{u}(t)]\rangle \propto \exp[-l(l+1)D_{\rm r}]\,\delta_{mm'}$.

For weak coupling to the external field ($\sigma < 1$), the eigenvalues λ_{lm} of the Smoluchowski operator can be calculated by applying standard perturbation theory to the Hermitian operator $\mathcal{L}_{\rm H} = \exp[V/2]\mathcal{L}\exp[-V/2] = D_{\rm r}[\nabla_{\rm r}^2 + (\nabla_{\rm r}^2 V)/2 - (\nabla_{\rm r}^2 V)\cdot(\nabla_{\rm r}^2 V)/4]$ which has the same eigenvalue spectrum as $\mathcal{L}$ [17]. Since the potential $V(\vartheta) = -\sigma\cos^2\vartheta$ possesses uniaxial symmetry, m is still a good "quantum" number, and we can apply perturbation theory for non-degenerate eigenvalues up to second order in σ. Using recursion relations for the associated Legendre polynomials in $Y_{lm}(\boldsymbol{u}) = \exp[im\varphi]P_l^m(\cos\vartheta)$ [18], we arrive at exact expressions for the eigenvalues λ_{lm}, where we keep the index l although it is no longer a good "quantum" number. Specifically for $l = 2$, we obtain

$$\lambda_{2m}(\sigma)/D_{\rm r} = l(l+1) + \begin{cases} -\frac{4}{7}\sigma + \frac{509}{1029}\sigma^2\ , & m = 0, \\ -\frac{2}{7}\sigma + \frac{160}{1029}\sigma^2\ , & |m| = 1, \\ +\frac{4}{7}\sigma + \frac{428}{5145}\sigma^2\ , & |m| = 2. \end{cases} \tag{3}$$

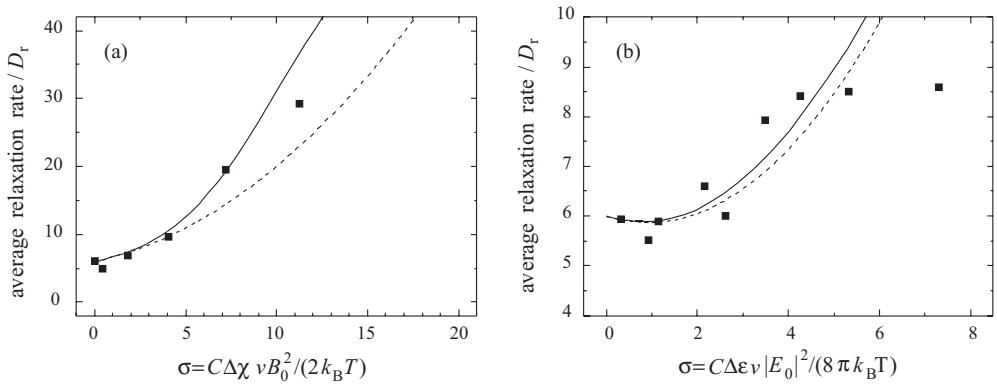

Fig. 2 – (a) Average relaxation rate of the measured correlation function $F_{22}(t)$ as a function of the reduced coupling parameter $\sigma = C\Delta\chi v B_0^2/(2k_BT)$ (squares). The dashed line is the perturbation theory result eq. (3). The value for the anisotropy of the diamagnetic susceptibility $\Delta\chi = 5 \times 10^{-7}$ has been adjusted for optimal agreement with the theoretical prediction. The full line is the average relaxation rate $\overline{\lambda}_{22}(\sigma)$ computed from the numerical solution of eq. (6). (b) Average relaxation rate of the measured correlation function $F_{21}(t)$ as a function of the reduced coupling parameter $\sigma = C\Delta\varepsilon v\,|E_0|^2/(8\pi k_BT)$ (squares). The full line is the average relaxation rate computed from the numerical solution eq. (6). The dashed line is the perturbation theory result eq. (3).

Unlike free rotation where all modes (l, m) decay with a degenerate rate $l(l+1)D_r$ independent of m, the presence of the external field now lifts this degeneracy. In particular, the relaxation of modes with $m = 2$ (as observed in our specific geometry with the alignment along $\boldsymbol{k}_i$) is predicted to start with a positive slope at $\sigma = 0$, confirming the experiment at low values of σ (see fig. 2a).

For increasing coupling strengths ($\sigma > 1$) the perturbation theory loses its validity. Furthermore, the new eigenfunctions deviate more and more from the spherical harmonics $Y_{lm}(\boldsymbol{u})$. As a result, the correlation functions $F_{lm}(t) = \langle Y_{lm}[\boldsymbol{u}(0)]Y^*_{lm}[\boldsymbol{u}(t)]\rangle$, observable for $l = 2$ in the light scattering experiment, will no longer be single exponentials. In order to understand the orientational relaxation, we can, in principle, calculate $F_{lm}(t)$ from a full solution of the eigenvalue problem. Here we take a more direct approach. Via the conditional probability $P(\boldsymbol{u}, t \mid \boldsymbol{u}', t' = 0)$, which gives the probability of finding the particle with orientation $\boldsymbol{u}$ at time t when it had with certainty the orientation $\boldsymbol{u}'$ at $t' = 0$, we rigorously define the time correlation function

$$F_{lm}(t) = \int \mathrm{d}\boldsymbol{u} \int \mathrm{d}\boldsymbol{u}'\, Y^*_{lm}(\boldsymbol{u}) P(\boldsymbol{u}, t \mid \boldsymbol{u}', t' = 0)\, W(\boldsymbol{u}', t' = 0) Y_{lm}(\boldsymbol{u}'), \tag{4}$$

where $W(\boldsymbol{u}', t' = 0)$ is the initial distribution. Note that correlations between different m are zero by symmetry. Taking the time derivative of the last equation and using $\partial P/\partial t = \mathcal{L}P$, we obtain the evolution equation

$$\frac{\partial}{\partial t} F_{lm}(t) = \int \mathrm{d}\boldsymbol{u} \int \mathrm{d}\boldsymbol{u}'\, [\mathcal{L}^\dagger Y^*_{lm}(\boldsymbol{u})] P(\boldsymbol{u}, t \mid \boldsymbol{u}', t' = 0) W(\boldsymbol{u}', t' = 0) Y_{lm}(\boldsymbol{u}'), \tag{5}$$

where $\mathcal{L}^\dagger = D_r[\nabla_r^2 - (\nabla_r V)\cdot\nabla_r]$ is the adjoint of $\mathcal{L}$. Noting again that $Y_{lm}(\boldsymbol{u}) = \exp[im\varphi]P_l^m \cdot$ $\cdot(\cos\vartheta)$ and using recursion relations for $P_l^m(\cos\vartheta)$ to evaluate $\mathcal{L}^\dagger Y^*_{lm}(\boldsymbol{u})$, eq. (5) is converted

into a recursion of ordinary differential equations for the correlation functions $F_{lm}(t)$:

$$\frac{1}{D_\mathrm{r}}\frac{\partial}{\partial t}F_{lm}(t) = [-l(l+1) + 2\sigma A_{lm}]F_{lm}(t) + 2\sigma[B_{lm}F_{l-2,m}(t) + C_{lm}F_{l+2,m}(t)]\,, \qquad (6)$$

$A_{lm} = \frac{l(l+1)-3m^2}{(2l+3)(2l-1)}$, $B_{lm} = \frac{(l+1)(l+|m|)(l-1+|m|)}{(2l+1)(2l-1)}$, and $C_{lm} = -\frac{l(l+1-|m|)(l+2-|m|)}{(2l+1)(2l+3)}$ being the coupling coefficients. Our result agrees with a derivation in ref. [19] based on the Langevin equation.

To compute the experimentally relevant correlation functions $F_{2m}(t)$, we have numerically diagonalized the coefficient matrix of the system of linear differential equations (6) for sufficiently large l. The correlation functions $F_{2m}(t)$ are then computed using the initial value $F_{lm}(0) = \int \mathrm{d}\boldsymbol{u}\, Y^*_{lm}(\boldsymbol{u})W_0(\boldsymbol{u})Y_{lm}(\boldsymbol{u})$ obtained with the help of the equilibrium distribution function $W_0(\boldsymbol{u}) \propto \exp[-V(\vartheta)]$ for a given value of the coupling strength σ. As already mentioned above, due to the fact that the coefficient matrix of eqs. (6) is not diagonal in l, the observable correlation functions $F_{2m}(t)$ are not normal modes and therefore their decay is a sum of exponentials. For a quantitative comparison with experimental data, it is therefore convenient to define the average relaxation rate

$$\overline{\lambda}_{2m} = F_{2m}(0) \,/ \int_0^\infty \mathrm{d}t\, F_{2m}(t), \qquad (7)$$

which reproduces the relaxation rate for a single exponential decay. The quantity $\overline{\lambda}_{2m}$ is shown for the case of alignment along $\boldsymbol{k}_\mathrm{i}$ ($m = 2$) in fig. 2a (full line). It is monotonously increasing with σ, in good agreement with the experimental data and the result (3) of the perturbation theory. At higher fields, $\sigma > 2$, both the experimental data and the numerical solution of eq. (6) deviate from the perturbation theory.

A critical test of the theory outlined above is the comparison of the prediction for $F_{21}(t)$ with experiment. The correlation function $F_{21}(t)$ can be observed by choosing the scattering plane perpendicular to the aligning field. We have realized this geometry by illuminating the sample with a V-polarized laser beam having a $1/e$ width at the focus of about $50\,\mu$m which produces a much higher electric field strength E_0 than in our first experiment. As a result, the particles experience a torque originating from the anisotropy of their dielectric constant. The magnitude of the torque is completely equivalent to the magnetic-field case, *i.e.*, $\sigma \sin 2\vartheta$ with $\sigma = C\Delta\varepsilon v\,|E_0|^2/(8\pi k_\mathrm{B}T)$ [16], where $\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp$ is the dielectric anisotropy of the nematic phase. Quite unlike the situation for ($l = 2$, $m = 2$) observed above, the average relaxation rate $\overline{\lambda}_{21}(\sigma)$ as a function of the external field strength now first decreases from $6D_\mathrm{r}$ to a shallow minimum at an incident laser power of about 40 mW after which the relaxation rate increases again as illustrated in fig. 2b. This unexpected decrease is indeed predicted by the second-order perturbation theory for $|m| = 1$ in eq. (3).

As in the case of magnetic alignment, the average relaxation rate $\overline{\lambda}_{21}(\sigma)$ computed from the numerical solution of eq. (6) closely follows the result from perturbation theory (3) up to a coupling strength $\sigma \approx 2$ (see fig. 2b). In contrast to the theoretical predictions, the experimental relaxation rate does not continuously increase at larger laser powers, but rather reaches a plateau at about $8.5D_\mathrm{r}$. This behavior might be due to depolarization fields within the particle and is the subject of further investigation. The peculiar minimum in the relaxation rate at $\sigma \approx 1$ indicates the competition of the enhanced restoring torque tending to accelerate the relaxation of $\boldsymbol{u}(t)$ back to the equilibrium direction and the increasingly slow exchange between parallel and antiparallel particle orientations over the potential barrier.

In summary, we have introduced frozen nematic particles as an ideal model system to study rotational diffusion in external fields. Specifically, we have investigated, both experimentally

and theoretically, rotational diffusion in a bistable potential. The relaxation rates of the particle orientations measured as a function of field strength are in excellent agreement with the theoretical predictions from a solution of the orientational Smoluchowski equation; in particular our theoretical treatment explains the surprising finding that a non-zero torque on a spherical particle may slow down its relaxation back to the equilibrium orientation.

The sensitivity of orientational dynamics of these particles to external fields makes them useful as model systems for gaining detailed insight into the orientational relaxation in more complex potential landscapes [20, 21], such as when the particles interact via collective hydrodynamic forces, or as local probes for near-field light forces. In addition, their strong birefringence offers exciting perspectives for applications such as electro-optical switching [22] or microfluidic devices.

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AM and JLA-L gratefully acknowledge generous support by the Alexander-von-Humboldt Foundation. HS is supported by a Heisenberg Fellowship of the Deutsche Forschungsgemeinschaft.

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