ISSN: 2639-0108

Research Article

Advances in Theoretical & Computational Physics

The Dynamic of Rodlike Molecules in a Biaxial Liquid Crystal

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Submitted: 17 March 2021; **Accepted**: 22 March 2021; **Published**: 10 Apr 2021

Citation: *Bachir Ouari (2021) The Dynamic of Rodlike Molecules in a Biaxial Liquid Crystal. Adv Theo Comp Phy 4(2): 98-104.*

Abstract

The relaxation time and the polarizability of molecules with dipole moment parallel to axis in a liquid crystal are considered by a model the Brown model. The solution of this system is obtained by numerical method. Modest analytic equations relaxation is proposed, agreeing one to appreciate the behavior of the system and expecting the polarizability for different value of the barrier and anisotropy parameters, are proposed.

Keywords: Relaxation time, Polarizabilty, Nematic Biaxial Liquid Crystal, Brown's Theory

Introduction

Uniaxial nematic liquid crystals have the feature that the long axes of the molecules tend to be aligned on the average during a particular direction in order that during this phase we've axial symmetry that's the optical properties etc [1]. are cylindrically symmetric about this direction called the director. However, neither the mass centers nor the short axes are ordered [2]. Thus while the long axes of the molecules are aligned parallel to every other, the orientational distribution function is independent of the rotational angle of the molecules about their long axes. The documented Maier-Saupe mean theory of the nematic liquid state with a mean field potential given by the second order Legendre polynomial of the angle between two long molecular axes then predicts a primary order phase change as a function of temperature from the isotropic to the uniaxial nematic state [3-5]. for all circumstances, old theoretical studies based on a generalization of Maier-Saupe theory to particles without an axis of symmetry [2,3,6] and numerous experiments propose that a second phase (with an order one phase transition from the isotropic state to the uniaxial state followed at lower temperatures by a second degree phase transition to a completely different state which is called the biaxial state) exists [7-9]. In this phase, the axes of the short molecules also tend to be directed over long measures (although the centers of gravity remain in any direction unlike in the smectic phase, where the molecules are fixed [10] distributed with the centers of gravity positioned in layers) causing a phase with three directions on which three axes of molecules tend to align [1]. This physical state, can be described by organic molecules [9] extensible, and completely flat, is called [1,6] the biaxial nematic state. Such a biaxial phase has been reported in molecules in the shape of a very elongated bone and in the shape of an elongated bone [11,12]. They are also expected to appear in boomerang class molecules. In addition, a biaxial description has been observed in organic molecules which present in the form of platelets [9]. we know that the existence of the biaxial nematic phase was first theoretically predicted by Freiser from a generalization of Maier-Saupe theory to introduce molecular asymmetry, he did not introduce the famous order parameter to study the transition from uniaxial to biaxial [2]. This was done by Straley for the first time, he introduced no less than four order quantities to describe the global phenomenon of the system by a mean field method where the molecular behavior is in a field potential describing l influence of the anisotropic solvent on such a special molecule [6].

In connection with this article, there is a significant number of theory related to this theme to find a solution of this same problem of the magnetic relaxation of fine ferromagnetic nanoparticles with a lot of potentials, even the biaxial [20, 24]. This solution was studied by Brown using Brownian motion because the underlying dynamic (gyromagnetic) equation for the magnetization inside the particle (Gilbert-Landau-Lifshitz equation augmented by field of shape guaussian) can be translated as Langevin's equation, this equation is very similar to that used to study the relaxation of molecules in liquid crystals [24]. By calculating the mean and solving the gyromagnetic equation on its by solving the Fokker-Planck equation which translates it for the density function of the orientations of the moment of the sphere, we can extract the statistical recurrence equations.

Langevin and Fokker-Planck equations

The orientation of a molecule in liquid crystals is translated by the non-inertial Debye model of a macromolecule in a field potential V (eg, [14-20]). The movement of the molecule is studied by the Euler angles [27], which give the position of the coordinate system of the molecule (fixed body) xyz with respect to the benchmark of the laboratory XYZ. In relaxation problems, the quantities of interest are the means of the Wigner D functions defined as [27]

$$D^J_{M,M'}(\Omega) = e^{-iM\alpha} d^J_{MM'}(\beta) e^{-iM'\gamma}$$

where $d^J_{MM}(\beta)$ is a function with different form, in Ref. [27].

If $f(\Omega)$ is function of Euler , the equation of Langevin $f[\Omega(t)]$ in the approximation of Debye is [20]

$$\dot{f} = \dot{\alpha}\frac{\partial f}{\partial \alpha} + \dot{\beta}\frac{\partial f}{\partial \beta} + \dot{\gamma}\frac{\partial f}{\partial \gamma} = (\dot{\mathbf{u}} \cdot \nabla) f \quad \dot{\mathbf{u}}(t) = \hat{D}\left[\ddot{\mathbf{e}}(t) - \nabla V(t)\right]/kT \quad (1)$$

here λ(t) is a torque the white noise forced by the warmth bath, is the direction space, = δ/ δφ is an miniscule rotation vector, **ω**(t) is the angular rate, T is the temperature, k is Boltzmann’s constant, and D is the rotational dispersion tensor. We assume, for easiness, that the diffusion tensor D has only two different mechanisms $D_{xx} = D_{yy} = D\perp$ and $D_{zz} = D_{\parallel}$. This estimate is judicious for molecules, where $D_{xx} \approx D_{yy}$. Thus $D_{\parallel}$ and D⊥ are the rotating diffusion constants about the long and little axes of the molecule, individually. Equation (1) is a stochastic equation for which one must use the Stratonovich explanation [28] (see also [20], Section 2.3) of the average of the multiplicative noise term, as that reading constantly constitutes the mathematical idealism of the physical stochastic process of orientational relaxation in the noninertial limit. The complementary Fokker-Planck equation (in this instance named the Smoluchowski equation) for the function $W(\Omega,t)$ is [20-23].

$$\frac{\partial}{\partial t} W = \nabla \hat{D}\left(\nabla W + \frac{}{kT} W \nabla V\right) \qquad (2)$$

We comment that the Debye (i.e., noninertial rotational diffusion) model undertakes that the molecular dipole reorientation is a Markov process evolving in time as a sequence of small angular steps produced by crashes with the close molecules as well as under the result of torques inventing from the long range order of the liquid crystal. Since the Smoluchowski equation applies to robust dissipative coupling to the heat bath- the Debye theory continually delicately accepts that the dipolar molecule is stuck so strongly to the neighboring molecules (bath) that large jumps of the dipole direction are enormously unlikely. This giving to Fröhlich may be true in a number of cases but others may exist in which the opposite (large jumps) is much more possible [29]. A dipolar molecule resolve then make many fences due to thermal anxiety over the potential barriers unravelling it from another dipole direction through the time obligatory for a significant transformation in direction by sticky flow. Obviously this grips for solids where flow may be measured as totally absent; though it may also be predictable in liquids (such as liquid crystals) where the viscosity is so tall that flow is almost insignificant. Furthermore, together large and small jump transitions may be concurrently charitable rise to occasional large angle reorientations (with corresponding exponential relaxation times) of the dipole over many potential barriers. The large hedges and the longest lived relaxation mode which is associated with them may essentially be labelled by the over damped Kramers leakage rate. We also comment that the mean field estimate has a limited area of applicability, as it ignores native order properties. In malice of this disadvantage, the mean field model is however easily imagined. Besides, it allows quantitative assessment of the dielectric parameters of a liquid crystal.

The classical model of Debye was used in [14-20] for the modest uniaxial anisotropy potential establishing the simplification of the Maier-Saupe theory to comprise dynamical belongings, namely,

$$V(\Omega)/kT = -AD^2_{0,0}(\Omega) = -\frac{A}{2}\left(3\cos^2\beta - 1\right) \qquad (3)$$

where A is the anisotropy constant. Here, the dielectric reply, including an infinity of relaxation modes, may be precisely represented by two styles, one of low frequency ascending from the occasional slow crossing of dipoles over the potential barrier generated by Equation (3) and one of high frequency on behalf of the infinity of fast near-degenerate decay processes associated with the small Markovian steps in each of the two potential wells approached as a single high frequency mode [19].

Though the supposition of an axially symmetric potential (3) radically abridges the analysis, the fallouts so obtained cannot, be practical to non-axially symmetric anisotropy, such as biaxial anisotropy. In command to attain the simplest possible description of the dynamical behavior of uniaxial probes in a biaxial liquid crystal phase, we consider the effective potential [23]

$$\begin{aligned} V(\Omega)/kT &= -A\left\{D^2_{0,0}(\Omega) + \lambda\left[D^2_{2,0}(\Omega) + D^2_{-2,0}(\Omega)\right]\right\} \\ &= (\sigma + \Delta/2)\sin^2\beta + (\Delta/2)\sin^2\beta\cos 2\alpha + \text{Const}, \end{aligned} \qquad (4)$$

where $\sigma = A(3-\sqrt{6}\lambda)/2$ is the barrier height parameter,

$\Delta = \sqrt{6}A\lambda$, and λ (or Δ) describes the biaxiality limit (λ= 0 corresponds to a uniaxial nematic). The potential V is now considered by the two angles β and α, and not γ. We comment that the energy scape in uniaxial anisotropy Equation (3) is axially symmetric and is a unchanging equatorial ridge (zone) separating two polar minima and has no saddle points, on the other hand, biaxial anisotropy (4) produces *azimuthally nonuniform* energy deliveries with two saddle points (see Figure 1). A detailed discussion of the coefficients occurring in the biaxial potential and their picture in terms of order limits included of the nasty principles of matrix elements of the Wigner matrices is given in [21,23]. Similar problems such as biaxial molecules in a uniaxial phase [21, 30], where V is also given by Equation (4) with α replaced by γ , viz., [21]

$$\begin{aligned} V(\Omega)/kT &= -A\left\{D^2_{0,0}(\Omega) + \lambda\left[D^2_{0,2}(\Omega) + D^2_{0,-2}(\Omega)\right]\right\} \\ &= (\sigma + \Delta/2)\sin^2\beta + (\Delta/2)\sin^2\beta\cos 2\gamma + \text{Const}, \end{aligned} \qquad (5)$$

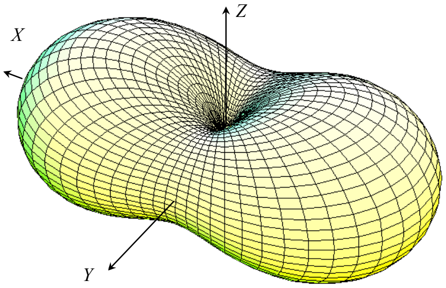

Figure 1: Biax potential in the polar spherical coordinate [Eq. (4), σ = β]. (The azimuthal φ and polar g angles of this system are related to the Euler angles α and β as φ = α + π/2 and g=β).

and biaxial molecules in a biaxial phase [10], where V be contingent on all three angles α, β, and γ, can be preserved in a similar manner. For real liquid crystal compounds the biaxiality parameter λ is of the order of 0.03÷0.2. For example, $\lambda \cong 0.2$ for nematic 4,4'-dimethoxyazoxybenzene (PAA) was projected from NMR data [21]. However, even for small values of $\lambda \approx 0.1$, the dynamics of the probe molecules strikingly depend on λ (see Sect. VI).

For ease, we shall reflect orientational relaxation of a molecule in a biaxial liquid crystal phase. We assume that the dipole moment is **μ** fixed along the long axis of the molecule so that spin of the molecule about this axis does not donate to the dielectric answer. Our object is simply to prove (using the nontrivial which may be comprehensive to the additional case of a dipole at an arbitrary angle to the long axis) how precise solutions for the polarizability of a molecule affecting in the potential of Equation (4) can be got. In order to accomplish this we remark that the Fokker-Planck equation (2) can be explained by expanding W in Wigner's D functions so springy an infinite hierarchy of differential-recurrence equations for the statistical moments [20-23]. The hierarchy of moment equations can also be got by be an average of the Euler equation (1) over its apprehensions without option to the Fokker-Planck equation ([20], Chapter 7). The following system of moment equations can be resolved by direct matrix diagonalization which includes scheming the eigenvalues and eigenvectors of the system matrix (e.g., Ref. 2) or by a computationally efficient matrix continued fraction method [19,20]. Here we practice the latter method to compute the polarizability $x_{\|}(\omega)$ and relaxation time $\boldsymbol{\tau}_{\|}$ of molecules with dipole moment parallel to the long axis in the mean field biaxial potential given by Equation (4). Next we link these exact solutions with asymptotic estimations founded on the high damping Kramers' escape rate theory [26] as adapted to rotation in nonaxially symmetric potentials by Smith and de Rosario [31], Brown [24], and Coffey *et al*. [32] (comprising a particular case of Langer's general theory [33] of the decay of metastable states in multidimensional systems).

Longitudinal dynamic polarizability and relaxation times

Conferring to the theory of linear response (Ref. 20, Chapter 2), the change of the component of the dipole moment $\mu\langle\cos\beta\rangle(t)$ of an assembly of noninteracting polar rodlike molecules, when a minor external field E_1, $(\mu\bullet E_1)/kT \ll 1$, practical along the Z axis has been swapped off at time $t = 0$, is specified by

$$\mu\langle\cos\beta\rangle(t)=\mu\int\cos\beta W(\Omega,t)d\Omega=\chi_{\|}E_1C_{\|}(t) \tag{6}$$

Here

$$C_{\|}(t)=\frac{\langle D^1_{0,0}[\Omega(0)]D^1_{0,0}[\Omega(t)]\rangle_0}{\langle D^1_{0,0}[\Omega(0)]^2\rangle_0}=\frac{\langle\cos\beta(0)\cos\beta(t)\rangle_0}{\langle\cos^2\beta(0)\rangle_0} \tag{7}$$

is the regularized equilibrium autocorrelation function of the component of the dipol, $\chi_{\|}=\mu^2\left\langle\cos^2\beta\right\rangle_0/kT$ is the polarizability, and the brackets $\langle\ \rangle_0$ entitle the equilibrium average distinct as

$$\left\langle A\right\rangle_0=\frac{1}{Z}\int A(\Omega)\,e^{-\beta V(\Omega)}d\Omega \tag{8}$$

(Z is the partition function). The correlation function $C_{\|}(t)$ controls the dielectric relaxation and permits one to assess the ac response of the system to a small ac field because the polarizability $\chi_{\|}(\omega)=\chi'_{\|}(\omega)-i\chi''_{\|}(\omega)$ assumed by [20].

$$\chi_{\|}(\omega)/\chi_{\|}=1-i\omega\int_0^\infty e^{-i\omega t}C_{\|}(t)dt \tag{9}$$

Giving to Eq. (9), the behavior of $\chi_{\|}(\omega)$ is strong-minded by the time conduct of $C_{\|}(t)$. In order to describe quantitatively the time performance of $C_{\|}(t)$, one may officially present two time constants. These are the integral relaxation (or correlation) time $\tau_{\|}$ distinct as the area under $C_{\|}(t)$, viz.,

$$\tau_{\|}=\int_0^\infty C_{\|}(t)dt \tag{10}$$

and the relaxation time $\tau_{\|}^{ef}$ defined by

$$\tau_{\|}^{ef}=-1/\dot{C}_{\|}(0) \tag{11}$$

(detailed info on the initial decay of $C_{\|}(t)$ in the time domain). The times $\tau_{\|}$ and $\tau_{\|}^{ef}$ so defined control the low and high-frequency parts of $\chi_{\|}(\omega)$ which may be exemplified by general properties of Fourier transforms. We have in the exciting cases of very low ($\omega\to0$) and very high ($\omega\to\infty$) frequencies:

$$\frac{\chi_{\|}(\omega)}{\chi_{\|}}\sim\begin{cases}1-i\omega\displaystyle\int_0^\infty C_{\|}(t)dt=1-i\omega\tau_{\|}, & \omega\to0,\\[2ex] \dfrac{\dot{C}_{\|}(0)}{i\omega}+\ldots=-\dfrac{i}{\omega\tau_{\|}^{ef}}+\ldots, & \omega\to\infty.\end{cases} \tag{12}$$

The times $\tau_{\|}$ and $\tau_{\|}^{ef}$ may consistently be defined in terms of the eigenvalues (λ_k) of the Fokker-Planck operator L_{FP} from Eq. (2) because $C_{\|}(t)$ may properly be printed as the separate set of reduction modes [20]

$$C_{\|}(t)=\sum_k c_k e^{-\lambda_k t} \tag{13}$$

where $\sum_k c_k=1$, so that from Equations. (10), (11), and (13)

$$\tau_{\|}=\sum_k c_k/\lambda_k \tag{14}$$

and

$$\tau_{\|}^{ef}=\left(\sum_k c_k\lambda_k\right)^{-1} \tag{15}$$

Conferring to Eq. (14), the correlation time $\tau_{\|}$ contains contributions from *all* the eigenvalues λ_k. The least nonvanishing eigenvalue λ_1 is associated with the gentlest overbarrier relaxation mode and so with the long-time behavior of $C_{\|}(t)$; the other eigenvalues λ_k characterize high-frequency intrawell modes. In general, in order to evaluate $\tau_{\|}$ numerically, a knowledge of all the λ_k and C_k is required. However, in the low temperature (high barrier) limit, $\lambda_1\ll|\lambda_k|$ and $c_1\approx1\gg c_k$ $(k\neq1)$ provided the wells of the potential remain equivalent (as is so for biaxial anisotropy) so that

$$\tau_{\|}\approx1/\lambda_1 \tag{16}$$

In other words, the inverse of the smallest nonvanishing eigenvalue closely approximates the correlation time $\tau_\parallel$ in the low temperature limit. The approximate Eq. (16) is not valid for the effective relaxation time $\tau_\parallel^{ef}$ when escape over a potential barrier is involved as the terms $C_k\lambda_k$ with $k \neq 1$ in Eq. (15) may give a significant contribution to $\tau_\parallel^{ef}$ with the result that $\tau_\parallel^{ef}$ differs exponentially from λ_1.

Matrix continued fraction solution

We compute numerically $\tau_\parallel$ and $\chi_\parallel(\omega)$ using matrix continued fractions as developed in Refs. 19 and 20. Since only two Euler angles β and α are complicated, we can shorten the solution by noticing that $D^l_{m,0}(\alpha,\beta,\gamma)=\sqrt{4\pi/(2l+1)}\,Y^*_{l,m}(\beta,\alpha)$ where $Y_{l,m}(\vartheta,\varphi)$ is the spherical harmonics distinct as [27].

$$Y_{l,m}(\vartheta,\varphi)=(-1)^m\sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}}e^{im\varphi}P_l^m(\cos\vartheta)$$

the $P_l^m(x)$ are the linked Legendre functions, and the symbol means the conjugate, φ and *g* are the azimuthal and polar angles of the polar spherical coordinate system. Therefore the solution of the Langevin Equation (1) for the potential from Eq. (4) can be abridged to solving an infinite hierarchy of differential-recurrence equations for the statistical moments (equilibrium correlation functions) $c_{l,m}(t)=\left\langle\cos\beta(0)Y_{l,m}[\beta(t),\alpha(t)+\pi/2]\right\rangle_0$ [so that $C_\parallel(t)\equiv c_{1,0}(t)/c_{1,0}(0)$]. By general formulae derived in Ref. 20, Eq. (7.6.1.32), one may get differential-recurrence equations for $C_{1,m}(t)$, viz.,

$$\begin{aligned}\tau_D\frac{d}{dt}c_{n,m}(t)&=v_{n,m}c_{n-2,m}(t)+x_{n,m}c_{n,m}(t)+z_{n,m}c_{n+2,m}(t)\\&+v^+_{n,m}c_{n-2,m+2}(t)+x^+_{n,m}c_{n,m+2}(t)+z^+_{n,m}c_{n+2,m+2}(t)\\&+v^-_{n,m}c_{n-2,m-2}(t)+x^-_{n,m}c_{n,m-2}(t)+z^-_{n,m}c_{n+2,m-2}(t),\end{aligned}\tag{17}$$

where $\tau_D=/2D_\perp$ is the characteristic (Debye) relaxation time for isotropic dispersion, $n\geq 1$, $-n\leq m\leq n$ and the coefficients v_{nm}, $v^{\pm}_{nm}$ etc.

Equation (17) can be changed into the three-term vector recurrence equation

$$\tau_D\frac{d}{dt}\mathbf{C}_n(t)=\mathbf{Q}^-_n\mathbf{C}_{n-1}(t)+\mathbf{Q}_n\mathbf{C}_n(t)+\mathbf{Q}^+_n\mathbf{C}_{n+1}(t),\tag{18}$$

where $C_n(t)$ are the column vectors arranged in an fitting way from $C_{n,m}(t)$, viz.

$$\mathbf{C}_n(t)=\begin{pmatrix}c_{2n,-2n}(t)\\c_{2n,-2n+1}(t)\\\vdots\\c_{2n,2n}(t)\\c_{2n-1,-2n+1}(t)\\c_{2n-1,-2n+2}(t)\\\vdots\\c_{2n-1,2n-1}(t)\end{pmatrix},\ (n\geq 1),$$

$C_0(t)$=0, and Q^-_n, Q_n, Q^+_n are super-matrices. The exact matrix continued fraction solution of Eq. (18) for the Laplace transform $\tilde{\mathbf{C}}_1(s)=\int_0^\infty\mathbf{C}_1(t)e^{-st}dt$ is [20].

$$\tilde{\mathbf{C}}_1(s)=\tau_D\mathbf{\Delta}_1(s)\left\{\mathbf{C}_1(0)+\sum_{n=2}^{\infty}\left[\prod_{k=2}^{n}\mathbf{Q}^+_{k-1}\mathbf{\Delta}_k(s)\right]\mathbf{C}_n(0)\right\},\tag{19}$$

where the infinite matrix continued fraction $\Delta_n(s)$ is defined by the recurrence equation

$$\mathbf{\Delta}_n(s)=\left[s\tau_D\mathbf{I}-\mathbf{Q}_n-\mathbf{Q}^+_n\mathbf{\Delta}_{n+1}(s)\mathbf{Q}^-_{n+1}\right]^{-1}\tag{20}$$

and **I** are the unit matrices of appropriate dimensions. The initial condition vectors $C_n(0)$ in Eq. (19) may be evaluated in terms of $\Delta_n(0)$ [20] (see Appendix B).
Consuming calculated $C_n(s)$, one may estimate the time

$$\tau_\parallel=\tilde{C}(0)=\tilde{c}_{1,0}(0)/c_{1,0}(0)\tag{21}$$

as well as the spectrum of the correlation function $\tilde{C}(\omega)=\tilde{c}_{1,0}(i\omega)/c_{1,0}(0)$ and thus the polarizability from Eq. (9). Furthermore, one can also appraise the smallest nonvanishing eigenvalue λ_1 (and consequently the greatest relaxation time) from ([20], Chapter 2)

$$\det\left(\lambda_1\mathbf{I}-\mathbf{S}\right)=0\tag{22}$$

where the matrix S is given by

$$\mathbf{S}=-\tau_D^{-1}\left[\mathbf{Q}_1+\mathbf{Q}^+_1\mathbf{\Delta}_2(0)\mathbf{Q}^-_2\right]\left[\mathbf{I}+\sum_{n=2}^{\infty}\prod_{m=1}^{n-1}\mathbf{Q}^+_m\prod_{k=1}^{n-1}\mathbf{\Delta}^2_{n-k+1}(0)\mathbf{Q}^-_{n-k+1}\right]^{-1},\tag{23}$$

i.e., λ_1 is the smallest nonvanishing eigenvalue of the matrix S.

The gain of the matrix continued fraction method is that it lets us to evaluate λ_1, $\tau_\parallel$, and $\chi_\parallel(\omega)$ for all values of the thermal and anisotropy energies. Thus, that method is an indispensable tool in approximating the accuracy of estimated analytic solutions for these parameters.

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Asymptotic formulas

Noting the preceding remarks the behavior of λ_1, $\tau_\parallel$ and $\chi_\parallel(\omega)$ can willingly be understood in the low temperature limit, where the dielectric relaxation is determined by the decay mode associated with the smallest nonvanishing eigenvalue which may be valued in the high barrier limit, using the Kramers escape rate theory [26] in the so named middle to high damping limit in which the inertia of the particle is negligible. This is entirely consistent with disregarding the inertial term in the Euler-Langevin equation or using the Smoluchowski equation (2). We comment that the Kramers escape rate theory in its original form describes the thermally activated escape of Brownian particles (with a standard separable and additive Hamiltonian consisting of the sum of the kinetic potential energies) out of a 1 dimensional potential well then must be adapted to rotational motion with two degrees of freedom as occur within the present problem with the simplification that only the very high damping case is involved. Fortunately, this escape rate problem has effectively been solved within the context of magnetic relaxation; we may summarize as follows [31]. In magnetic relaxation although canonical equations exist the Hamiltonian which is that the sum of the anisotropy and Zeeman energies is generally nonseparable and two degrees of freedom namely the polar and azimuthal angles are always involved for non-axially symmetric potentials. Furthermore, the gyromagnetic term within the underlying Langevin equation of the method will enter into the escape rate formulas through the medium of a dimensionless damping parameter an involving the gyromagnetic ratio and therefore the dissipative coupling to the warmth bath. This parameter [31] essentially plays the role of the inertia of the particle within the Kramers escape rate problem for mechanical Brownian particles during a potential. Hence in magnetism [34], the three escape rate regimes (depending on the actual value of a) first identified by Kramers, namely, very low damping (VLD, where the escape rate is decided by the energy loss per cycle of the just about periodic movement of a particle at the saddle point of the potential), intermediate to high damping (IHD, where the escape rate is dominated by friction) and a turnover region (where neither formula applies) will appear. The IHD formula for both spins and particles is just a special case of Langer's general theory of the decay of metastable states (see Eq. (1.13.5.38) of [34] and (1.18.2.20) of [20]) which extends Kramers' IHD calculations to nonseparable Hamiltonians and lots of degrees of freedom. Formulas for the escape rate for magnetic relaxation during a biaxial anisotropy potential are given for every of the three cases [34]. Now within the Debye theory of dielectric relaxation of rodlike molecules the underlying equation is that the Smoluchowski equation (2). When the rotation about the long molecular axis could also be neglected, this equation is just like Brown's Fokker-Planck equation for the density of moment of a magnet orientations of single domain particles on the unit sphere if the gyromagnetic term is omitted [20]. The IHD escape rate formula for magnetic spins (which within the present context is that the just one of interest) will yield because the magnetic damping parameter a tends to infinity the escape rate for the very highly damped inertial rotational Brownian movement in nonaxially symmetric potentials of the crystalline anisotropy. The IHD magnetic problem was first solved by Smith and de Rosario who derived from first principles the IHD escape rate for the magnetization relaxation of a fine single domain ferromagnetic particle with biaxial anisotropy which is that the exact analogue of the biaxial liquid problem posed by the potential Equation (4). Their solution for the Kramers escape rate with a tending to infinity then immediately yields 1 which governs the low frequency dielectric relaxation as [25,34]

$$\frac{\tau_{\parallel}}{\tau_D} \approx \frac{1}{\tau_D \lambda_1} \sim \frac{\pi e^{\sigma}}{2\sigma\sqrt{1+\sigma/\Delta}} \tag{24}$$

Impartial as uniaxial, Equation (24) suggests an analytic equation for the delay factor of the response in the high barrier limit. According to Equation (24), defined as the ratio of the relaxation times in the biaxial and isotropic liquid is assumed by

$$g_{\parallel}^{biax} \sim \frac{\pi e^{\sigma}}{2\sigma\sqrt{1+\sigma/\Delta}} \tag{25}$$

We memory that for uniax nematics, the consistent equation for $g_{\parallel}^{biax}$ is [18,19].

$$g_{\parallel}^{uniax} = \frac{\tau_{\parallel}}{\tau_D} \sim \frac{\sqrt{\pi}e^{\sigma}}{2\sigma^{3/2}} \tag{26}$$

Noting that 1/σ is the dimensionless temperature and σ/Δ is the temperature independent ratio, Eq. (25) allows one to easily estimate the dependence of $g_{\parallel}^{biax}$ on temperature, which follows an Arrhenius-like law. The temperature need of the prefactors in Equations (24) and (26) is different, viz., $\sim T$ and $\sim T^{3/2}$, respectively. This calculation can be verified by wary clarification of dielectric relaxation data in the uniaxial and biaxial stages.

In order to escalate in qualitative style the general behavior of $\chi_{\parallel}(\omega)$, one may use the simple analytical method given in Ref. 20, Chapters 7-9. According to Ref. 20, the association function $C_{\parallel}(t)$ [in general comprising an infinite number of decaying exponentials, see Equation (7)] may be approached due to the exponential separation of the time scales of the overbarrier and intrawell procedures by two exponential modes. This include the overbarrier λ_1^{-1} and intrawell relaxation times only, viz.,

$$C_{\parallel}(t) \approx \Delta_1 e^{-\lambda_1 t} + (1-\Delta_1)e^{-t/\tau_W} \tag{27}$$

where Δ_1 and the intrawell time τ_W are expressed in terms of $\tau_{\parallel}$, $\tau_{\parallel}^{ef}$, and λ_1 as

$$\Delta_1 = \frac{\tau_{\parallel}/\tau_{\parallel}^{ef} - 1}{\lambda_1\tau_{\parallel} - 2 + 1/(\lambda_1\tau_{\parallel}^{ef})}, \quad \tau_W = \frac{\lambda_1\tau_{\parallel} - 1}{\lambda_1 - 1/\tau_{\parallel}^{ef}} \tag{28}$$

Thus the dynamic polarizability $\chi_{\parallel}(\omega)$ rendered exactly from the continued fraction as an *infinite series* of Lorentzians may be approximated by a *sum* of two Lorentzians only

$$\frac{\chi_{\parallel}(\omega)}{\chi_{\parallel}} \approx \frac{\Delta_1}{1+i\omega/\lambda_1} + \frac{1-\Delta_1}{1+i\omega\tau_W} \tag{29}$$

The parameters Δ_1 and τ_W in Eq. (29) are resolute so as to ensure the correct asymptotic behavior of $\chi_{\parallel}(\omega)$ in the cases of very low and very high frequencies, Equation (12). Equation (29) can also be used with minor changes (μ^2 in the static polarizability $\chi_{\parallel}$ must be substituted by $\mu^2 \cos^2\Theta$) in order to estimate the low frequency part ($\omega/\lambda_1 \leq 1$) of $\chi_{\parallel}(\omega)$ when the dipole moment of molecules focused at an arbitrary angle Θ with respect to the long axis of the molecule because the fast rotation about the long molecular axis does not move the low frequency response.

In applied calculations, Equation (29) requires a knowledge of the integral relaxation time $\tau_{\parallel}$, the effective relaxation time $\tau_{\parallel}^{ef}$ and the smallest non vanishing eigenvalue λ_1, which in the high barrier limit may readily be evaluated from Equation (24). Moreover, just as for uniaxial nematics [19,20], the effective relaxation time $\tau_{\parallel}^{ef} = -c_{1,0}(0) / c_{1,0}(0)$ can be estimated from Equation (17) for $n = 1$ and $m = 0$ and is given by an *exact* analytic equation in terms of the order parameter $S = \langle D_{0,0}^2 \rangle_0$[22].

$$\frac{\tau_{\parallel}^{ef}}{\tau_D} = \frac{1+2S}{1-S} \tag{30}$$

where S can be calculated from Equation (8). We remark that sometimes [22] Equation (30) is used for the approximation of the correlation time . However, just as for uniaxial nematics [19], Eq. (30) may be used for evaluation of $\tau_{\parallel}$ only for small barriers, σ≤1 (the retardation factor (1+2S) / (1-S) given by Equation (30) diverges exponentially from the correct asymptotic behavior Equation (25) for σ>>1). As far as the correlation time $\tau_\parallel$ is concerned, since its behavior is governed by a Fokker-Planck equation in the two variables α and β no simple exact integral form exists unlike in the uniaxial case ([20], Chapter 8). Here the approximate representation of $\tau_\parallel$ as λ_1^{-1} Equation (16) is unsuitable for the purpose of calculating τ_W using Equation (28) as that predicts $\tau_W=0$ indicating that τ_W has its origin in the *difference* in the third and higher order terms in the asymptotic expansions of $\tau_\parallel$ and λ_1^{-1}, see, for example, Equations. (7.4.3.14) and (7.4.3.15) of [20].

Results and discussion

The extreme relaxation time anticipated by the inverse Kramers rate, Equation (24), and the correlation time $\tau_\parallel$ designed numerically by the numerical method for biaxial anisotropy are exposed in Figure 2 (as a function of the barrier height parameter σ). Apparently, for high barriers, $\sigma \geq 5$, the asymptotic Equation (24) provides a good approximation to $\tau_\parallel$ for Δ≥1. We highlight that Equation (24) is not valid for Δ/σ→1 consistent to uniaxial anisotropy governed by the single coordinate β. The uniaxial asymptote Equation (26) is exposed in Figure 2 for contrast. Obviously noticeable changes in $\tau_\parallel$ for uniaxial and biaxial anisotropy be for small values of the biaxiality parameter Δ (see curve 2). If investigative expressions for all Δ are wanted it would be essential to originate bridging formulas (analogous to those used at a classical turning point in the WKBJ method in quantum mechanics) smoothly joining axially symmetric and non-axially symmetric escape rate formulas. This procedure has been described by Coffey *et al.* [31] for magnetic relaxation in the simple uniaxial potential of Equation (1) in the presence of a strong field applied at an arbitrary angle to the easy axis of magnetization which breaks the axial symmetry. The results of the calculation from Equation (29), (30)-(32) and those from matrix continued fractions are related in Figures 3 and 4. Here the imaginary of polarizability $\chi''_\parallel(\omega)$ $(\mu^2/kT=1)$ is designed for numerous values of the model parameters σ and Δ. The results indicate that a marked dependence of $\chi_\parallel(\omega)$ on σ and Δ happens. Furthermore, two different dispersal bands appear in the spectrum. The characteristic frequency and half-width of the low-frequency band are completely determined by λ_1. Thus the low frequency behavior of $\chi''_\parallel(\omega)$ is subjugated by the barrier journey mode. In totaling, a far feebler second relaxation peak seems at high frequencies. This high frequency relaxation band represents the combined effect of the infinite number of *near degenerate* intrawell modes. The characteristic frequency of this band is $\omega_{well} \sim 2\tau_D^{-1}\sqrt{\sigma(\sigma+\Delta)}$. Apparently, in Figures. 3 and 4 the agreement between the exact matrix continued fraction calculations and the approximate Equation (29) is very good in the low-frequency region, $\omega\tau_D \leq 1$, because the low-frequency response is completely determined by the overbarrier relaxation mode. The approximate Equation (29) also yields a reasonable description of the high frequency relaxation band.

In conclusion, we have preserved the longitudinal relaxation of a uniaxial investigation in a biaxial nematic liquid crystal, here restricted for mathematical simplicity to a dipole moment parallel to the long axis of the molecule, using numerical methods and asymptotic escape rate formulas borrowed from fine particle magnetism. These methods permit us to present simple analytic formulas for the electric polarizability. These formulas are relatively easy to compare with experiment due to their simple analytic form.

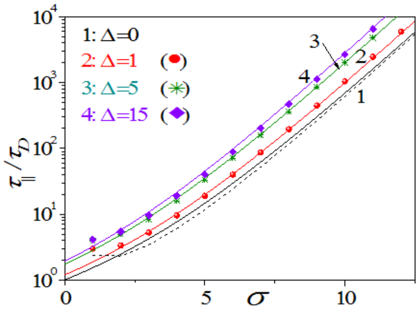

Figure 2: $\tau_\parallel/\tau_D$ vs. σ for various values of Δ. Solid lines: Numerical solution; symbols: Equation (24); dashed line: Equation (26).

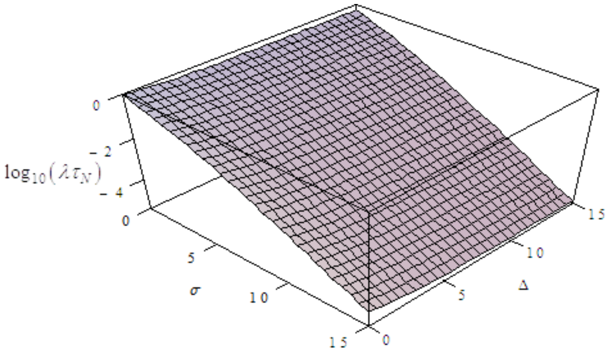

Figure 3: Plot3D $\lambda_\parallel\ \tau_D$ vs. σ and Δ:

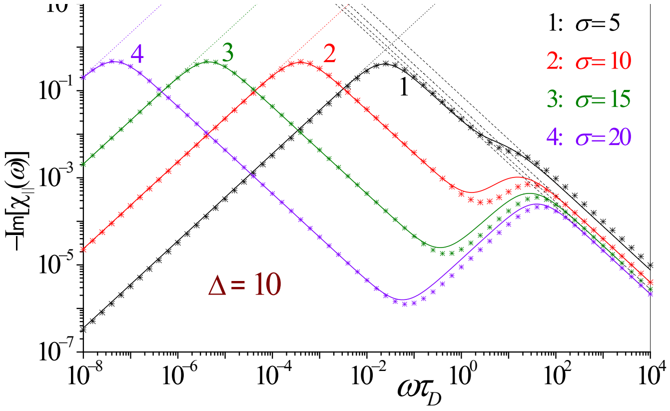

Figure 4: -Im $[\chi_\parallel(\omega)]$ vs $\omega\tau_D$ for Δ =10 and various values of σ. Solid lines 1-3: Numerical solution. Filled circles: Equations. (29), (30)-(32); dotted and dashed lines: asymptotes given by Equation (12).

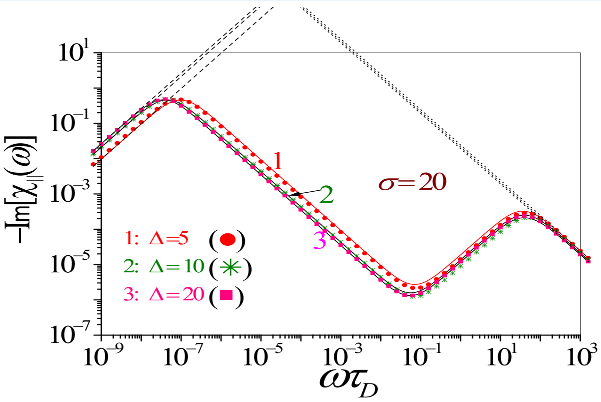

Figure 5: -Im [$\chi_{\parallel}(\omega)$] vs $\omega\tau_D$ for σ =20 and various values of Δ. Solid lines 1-3: Numerical solution. Symbols: Equations. (29), (30)-(32); dotted and dashed lines: asymptotes given by Equation (12).

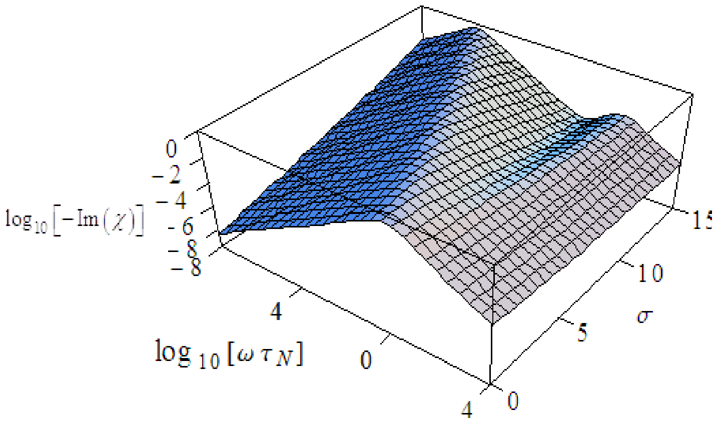

Figure 6: Plot3D Im [$\chi_{\parallel}(\omega)$] vs. $\omega\tau_N$ and σ.

Acknowledgments

We thank Professor Layadi for helpful conversations.

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