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Rotational diffusion and orientation relaxation of rodlike molecules in a biaxial liquid crystal phase

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Abstract

The longitudinal relaxation time and the complex dielectric polarizability of rod-like molecules with dipole moment parallel to the long axis in a biaxial nematic liquid crystal are calculated using as model the rotational Brownian motion in a mean field potential so reducing the problem to a solution of a set of linear differential-recurrence relations for statistical moments (the appropriate equilibrium orientational correlation functions). The solution of this set is obtained by matrix continued fractions. Moreover, simple analytic equations (based on the exponential separation of the time scales of the intrawell and overbarrier (interwell) relaxation processes), allowing one to understand the qualitative behavior of the system and accurately predicting the longitudinal complex polarizability for wide range of the barrier height and anisotropy parameters, are proposed.

Keywords: Rotational diffusion; Orientational relaxation; Mean field approximation; Biaxial liquid crystal; Kramers escape rate theory

1. Introduction

Uniaxial nematic liquid crystals have the feature that [1] the long axes of the molecules tend to be aligned on average in a *particular* direction so that in this phase we have *axial symmetry* that is the optical properties etc. are cylindrically symmetric about this direction called the *director*. However, neither the mass centers nor the short axes are ordered. Thus [2] while the long axes of the molecules are aligned parallel to each other, the orientational distribution function is independent of the rotational angle of the molecules about their long axes. The well known Maier–Saupe mean field theory [3–5] 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 first-order phase transition as a function of temperature from the isotropic to the uniaxial nematic state.

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In spite of these considerations long standing theoretical analyses based on a simple generalization of the Maier–Saupe theory to particles lacking an axis of rotational symmetry [2,3,6] and recent experimental results [7–9] suggest that a second nematic phase (with a first-order phase transition from the isotropic to the uniaxial state followed at lower temperatures by a second-order phase transition to a biaxial state) exists. In this phase the molecular short axes also tend to be aligned over large distances (although the mass centers remain disordered unlike in a smectic phase, where molecules are instead [10] distributed with the mass centers being positioned on average in layers) yielding a phase with three directors about which [1] three molecular axes tend to align. This phase, commonly exhibited by organic molecules [9], which are elongated and flat is called [1,6] the *biaxial nematic* phase. Such a biaxial phase has been reported in spoon-like and bone-shaped molecules [11,12]. It is also expected to occur in boomerang-like molecules. Furthermore, [9] biaxial behavior has been reported in organic tetrapodes taking the form of quasiflat platelets. Although the existence of the biaxial nematic phase was first predicted theoretically by Freiser [2] from a generalization of the Maier–Saupe theory to include molecular asymmetry he did not introduce a subsidiary order parameter to describe the uniaxial to biaxial transition. This was first accomplished by Straley [6], who introduced no less than four-order parameters in order to describe the overall behavior of the system by a mean field theory where the molecular motion takes place in an effective molecular field potential describing the overall effect of the anisotropic solvent on a particular molecule.

The extension of the mean field theory to the orientational relaxation of molecules in uniaxial nematics was begun by Meier and Saupe [13] and given in more detail in Refs. [14–20] leading to a clear physical understanding of orientational relaxation in uniaxial nematics in the context of the Debye model of noninertial rotational Brownian motion of a particle in a mean field potential so incorporating both solid and liquid like behavior in a single model. Due to the mathematical difficulties involved, comparatively little work has appeared on the extension of the dynamical mean field theory to include the biaxial nematic behavior and few solutions exist. In this context we mention that the influence of biaxiality on various correlation functions pertaining to the reorientational motion has been discussed by Dozov et al. [21], and by Zakharov and Dong [22]. Moreover, a very detailed study of first and second rank correlation functions of a cylindrically symmetric probe in a biaxial nematic phase has been given by Berggren et al. [23] with a view towards studying the evolution of observables such as the spectral density through the uniaxial-biaxial phase transition. They represent the Fokker–Planck equation in the basis of the normalized Wigner matrices resulting in an infinite set of linear differential equations representing the differential recurrence relations for the time behavior of the statistical moments of the system. These are solved using straightforward matrix diagonalization whence the correlation functions etc. may be determined. Since the biaxial phase has a lower symmetry than the uniaxial one, they lay particular emphasis on the study of those correlation functions, which differ from zero in the biaxial and vanish in the uniaxial phase in order to determine which dynamical parameters, e.g., correlation times and spectral densities can be associated with the uniaxial–biaxial phase transition. The uniaxial–biaxial phase transition is associated according to them, with the disappearance of the cross-correlation functions of the Wigner matrix elements at that transition with change of the corresponding correlation times from nonzero to zero. Hence in order to detect the phase transition by a dynamic spectroscopic method an experiment should be performed which depends strongly on the cross-correlation functions [23]. The Wigner representation of the solution has also been used by Brognara et al. [10] in order to study rototranslational diffusion of a rigid biaxial molecule dissolved in a uniaxial smectic liquid crystal phase.

Now in relation to the present paper, a considerable body of related theory exists [20,24] for the solution of the analogous problem of the magnetic relaxation of fine single domain ferromagnetic particles with various anisotropy potentials including the biaxial one. This solution was developed by Brown [24] using the theory of the Brownian motion since the underlying dynamical evolution (gyromagnetic) equation for the magnetization inside the particle (Gilbert–Landau–Lifshitz equation augmented by a Gaussian random field term) may be interpreted as a Langevin equation which is very similar to that used to describe orientational relaxation of molecules in liquid crystals. By averaging the gyromagnetic equation of motion over its realizations or by solving the accompanying Fokker–Planck equation for the probability density function of the orientations of the magnetic moment of the surface of the unit sphere, one can obtain the differential recurrence equations for the statistical moments (relaxation functions). These can be solved exactly using matrix continued fractions [20]. Moreover, for biaxial anisotropy it is possible to obtain simple and accurate approximate analytical