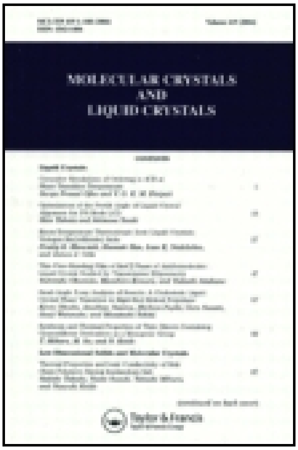

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LIGHT SCATTERING INTENSITY CORRELATION FUNCTION IN DISORDERED NEMATIC SYSTEMS

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Abstract In dynamic light scattering in nematic liquid crystal in silica aerogel matrix, the light intensity correlation function in the single scattering regime is an average over the orientations of the nematic director **n** with respect to the laboratory frame. We have calculated the expected correlation function and its dependence on the scattering angle and incident and scattered polarizations. Due to the substantial dependence of the orientational diffusivities on the relative orientation of **n** and the scattering vector, the correlation function is non-exponential. In the calculation, the effect of the refractive index anisotropy on the scattering vector is also taken into account.

INTRODUCTION

Recently several dynamic light scattering experiments in a nematic liquid crystal in silica aerogel were carried out[1,2]. The light intensity correlation function obtained in these experiments is non-exponential. This indicates a process with a broad distribution of relaxation times. There are several reasons for that. The nematic liquid crystal in the aerogel can be considered as a polydomain system with a domain size distribution given by the pore size distribution of the aerogel matrix. The decay time of the orientation fluctuation depends on the size of the domain, so each domain size contributes a single exponential relaxation with different relaxation time to the correlation function and that makes the correlation function non-exponential[2]. The orientation of each domain is arbitrary, thus the light intensity correlation function is also an average over orientations of the nematic director **n** with respect to the laboratory frame which also causes the correlation function to be non-exponential. There are other possible processes which also contribute to the long time behavior of the correlation function. The system is nonergodic[2,3], the mode structure is changed because of the restricted geometry[4] and multiple scattering can not be neglected in this system[5,2].

To analyze the effect of arbitrary orientation of the director we have calculated the expected correlation function for a disordered bulk nematic. We will show that the calculated correlation function is non-exponential due to the substantial dependence of the relaxation times on the relative orientation of **n** and the scattering vector. The results of our calculation are in agreement with measured correlation function of disordered bulk nematic.

ORIENTATIONAL FLUCTUATIONS AND LIGHT SCATTERING

The director fluctuations give rise to fluctuations of the optical dielectric tensor which cause strong scattering of light. For a given scattering vector **q**, the scattered-light amplitude depends on two independent Fourier components $n_1(\mathbf{q})$ and $n_2(\mathbf{q})$ of the director fluctuation $\delta\mathbf{n}^6$, which in k-space correspond to the components along the axes of the coordinate system defined as

$$\mathbf{e}_3 \parallel \mathbf{n},\ \mathbf{e}_2 = \frac{\mathbf{e}_3 \times \mathbf{q}}{|\mathbf{e}_3 \times \mathbf{q}|} \text{ and } \mathbf{e}_1 = \mathbf{e}_2 \times \mathbf{e}_3. \tag{1}$$

In this coordinate system the scattering vector lies in e_1-e_3 plane and can be written as $\mathbf{q} = (q_1, 0, q_3) = (q_\perp, 0, q_\parallel)$. The first component of the director fluctuation $n_1(\mathbf{q})$ describes splay-bend and the second $n_2(\mathbf{q})$ twist-bend mode with the relaxation times that depend on the scattering vector

$$\frac{1}{\tau_\beta(\mathbf{q})} = \frac{K_\beta(\mathbf{q})}{\eta_\beta(\mathbf{q})}, \tag{2}$$

where

$$\beta = 1,2\ ,$$

$$\eta_1(\mathbf{q}) = \gamma_1 - \frac{(q_\perp^2\mu_3 - q_\parallel^2\mu_2)^2}{q_\perp^4\eta_b + q_\perp^2 q_\parallel^2(\mu_1+\mu_3+\mu_4+\mu_5) + q_\parallel^4\eta_c},$$

$$\eta_2(\mathbf{q}) = \gamma_1 - \frac{\mu_2^2 q_\parallel^2}{q_\perp^2\eta_a + q_\parallel^2\eta_c},$$

$$\text{and} \quad K_\beta(\mathbf{q}) = \mathrm{K}_\beta q_\perp^2 + \mathrm{K}_3 q_\parallel^2 . \tag{3}$$

Constants μ_i are Leslie viscosity coefficients, η_a, η_b and η_c Miesowicz viscosities and K_i Frank elastic constants.

The heterodyne light-intensity autocorrelation function in the nematic liquid crystal is proportional to the sum of the time autocorrelation function of the Fourier components of the director orientation fluctuation[7]

$$G^{(1)}(\mathbf{q},t) = \mathrm{A}\sum_{\beta}\frac{S_{\beta}^{2}(\mathbf{q})}{K_{\beta}(\mathbf{q})}\mathrm{e}^{-\frac{t}{\tau_{\beta}(\mathbf{q})}}. \tag{4}$$

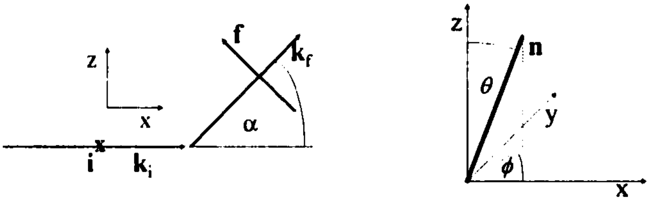
Geometrical factor S_β depends on the polarizations of incident (**i**) and scattered light (**f**)

$$S_{\beta} = (\mathbf{i}\cdot\mathbf{e}_{\beta})(\mathbf{f}\cdot\mathbf{e}_{3}) + (\mathbf{i}\cdot\mathbf{e}_{3})(\mathbf{f}\cdot\mathbf{e}_{\beta}), \tag{5}$$

where $\mathbf{e}_1, \mathbf{e}_2$ and $\mathbf{e}_3$ are coordinate axes of the nematic defined in (1). The constant A depends on the temperature and the experimental setup but is independent of director orientation and the scattering vector $\mathbf{q}$.

To obtain the correlation function of a polydomain system we first calculate the correlation function of a single domain at an arbitrary orientation of the director and then average it over all orientations of the nematic director. We assume that multiple scattering can be neglected in our system, that means the incident light beam has the same direction and polarization when entering any of domains. This approximation is valid when domains are small enough that the polarization of light does not change significantly when passing the domain, i.e., the size of domains must be much smaller than $\lambda/\Delta n$, where λ is the wavelength of light and Δn the difference between the extraordinary and ordinary index of refraction.

In order to calculate the correlation function in a single nematic domain at a given scattering angle and arbitrary incident and scattering polarizations one should take into account both ordinary and extraordinary waves. In general there are four contributions to the scattered light corresponding to four different scattering vectors, $\mathbf{k}_{fo}$-$\mathbf{k}_{io}$, $\mathbf{k}_{fe}$-$\mathbf{k}_{io}$, $\mathbf{k}_{fo}$-$\mathbf{k}_{ie}$ and $\mathbf{k}_{fe}$-$\mathbf{k}_{ie}$. Indices i, f, o and e denote incident, scattered, ordinary and extraordinary respectively. In a nematic there are only three contributions since there is no ordinary-ordinary scattering on the orientational fluctuations.



a) b)

FIGURE 1 The scattering geometry. a) The scattering plane with wave vectors and polarizations of the incident and the scattered light. b) Orientation of the director is described with angles ϕ and ϑ.

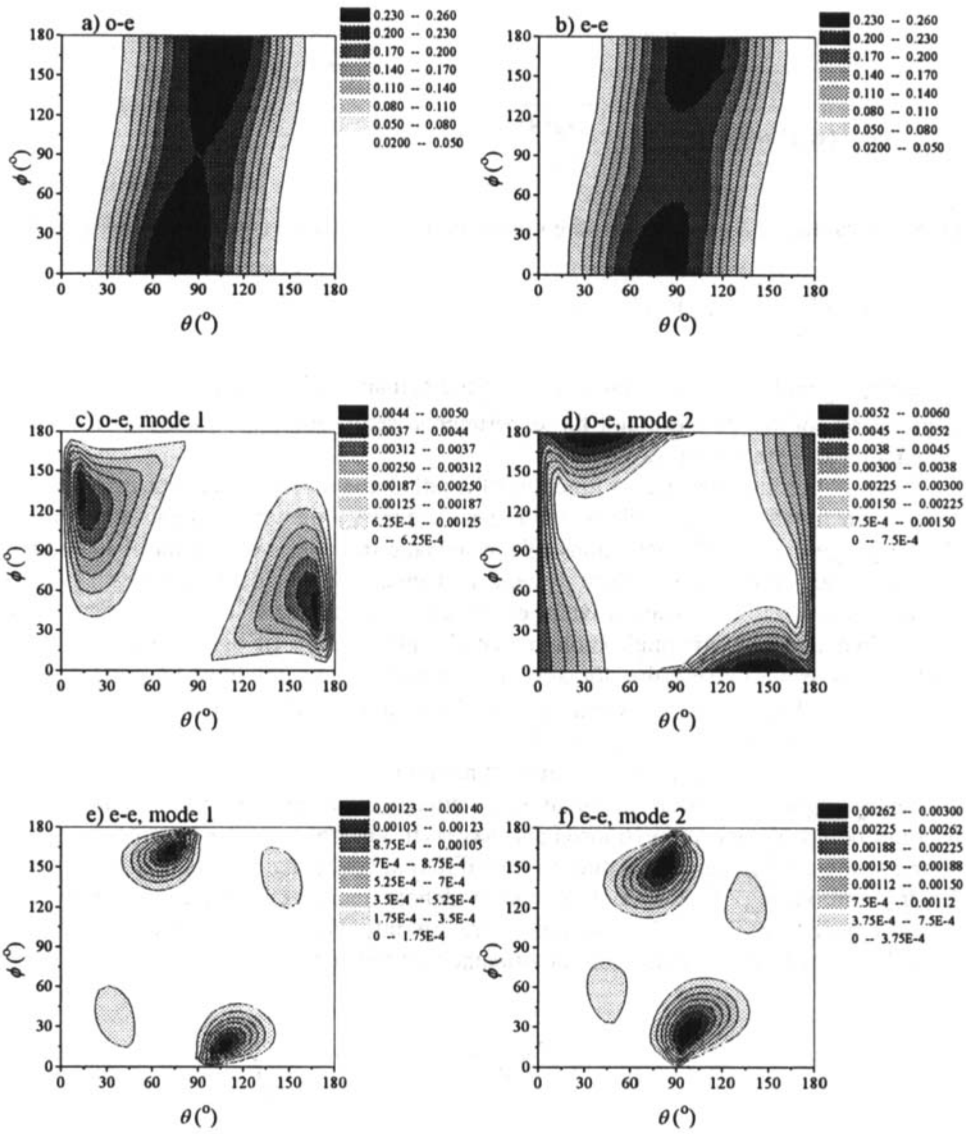


FIGURE 2 Dependencies of the relaxation times and weight factors S_β^2/K_β on the orientation of the director. a) and b) The relaxation time (in ms) of the second mode versus angles ϕ and ϑ for the o-e and e-e scattering vector respectively. The dependence of the relaxation time of the first mode is similar. c), d), e) and f) The weight factors (in m^2/N) of both modes and the o-e and e-e scattering vectors. The scattering angle and temperature are 29° and 35.1°C respectively.

The scattering geometry used in our calculations is shown in Fig. 1. The scattering plane is xz-plane of the laboratory frame with x axis parallel to the wave vector of the incident light $\mathbf{k}_i$. The angle α is inner scattering angle, angles ϑ and φ describe the orientation of the director with respect to the laboratory frame, i.e. $\mathbf{n} = (\cos(\varphi)\sin(\vartheta), \sin(\varphi)\sin(\vartheta), \cos(\vartheta))$. We choose a geometry with orthogonal incident and scattered polarizations, i.e. **i** =(0, 1, 0) and **f** = (-sinα, 0, cosα), as it is common in the dynamic light scattering experiments in nematic systems.

As said before there are three different scattering vectors **q** corresponding to ordinary-extraordinary, extraordinary-ordinary and extraordinary-extraordinary combinations of the incident and scattered wave vectors which contribute to the correlation function at a given scattering angle, a given orientation of the director and the polarizations **i** and **f**. In calculation of the weight factors for a given **q** only adequate, i.e. ordinary or extraordinary, part of polarizations must be considered.

The correlation function of a polydomain system consisting of domains that are larger than the wavelength of the light is an average of a single domain correlation function over the orientations of the director. In our case that corresponds to the average over the angles ϑ and φ,

$$\mathrm{G}^{(1)}(\alpha,t) = \mathrm{A}\sum_{\beta,\mathbf{q}}\iint \frac{S_\beta^2(\mathbf{q},\vartheta,\varphi)}{K_\beta(\mathbf{q}(\vartheta,\varphi))} \mathrm{e}^{-\frac{t}{\tau_\beta(\mathbf{q}(\vartheta,\varphi))}} \sin\vartheta \mathrm{d}\vartheta \mathrm{d}\varphi. \tag{6}$$

The ratio $q_{||}/q_{\perp}$ and projections of polarizations **i** and **f** on the axis e_1 and e_2 change with changing the angles ϑ and φ, so both the weight factors S_β^2/K_β and relaxation times depend on these angles. As can be seen from Fig. 2, in all possible choices of polarizations, different values of the relaxation time are sampled. Still, the largest contributions come from ordinary-extraordinary scattering, where well pronounced peaks for the two modes occur in the ϑ - φ plane. As one changes the scattering angle α the positions of the peaks move so that with a good signal, it should be possible to determine at least some elastic constants and viscosities even in polydomain, disordered samples.

Numerical integration in the equation (6) was carried out for values of elastic constants and viscosities in bulk 5CB[8]. The obtained normalized correlation function can be reasonably well fitted with stretched exponential function $\exp[-(t/\tau_{\mathrm{eff}})^s]$ with value of $s \approx 0.8$ (Fig. 3a). The stretching exponent s does not depend on the temperature or scattering angle, but slightly depends on the choice of the fitting interval, anyway these changes are within few percents. In order to see whether our calculated function describes the realistic case well, we have measured the correlation function in disordered bulk nematic 5CB at room temperature. The experiment was carried out in the homodyne regime. In this case the second order correlation function $g^{(2)} = |g^{(1)}|^2 + 1$ is measured. The shape of this experimentally obtained correlation function is in agreement with the calculated one (Fig. 3b).

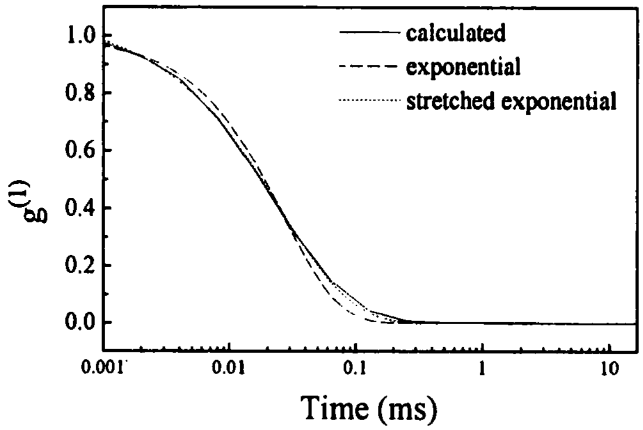


FIGURE 3a The calculated normalized correlation function (—) and its exponential (---) and stretched exponential (···) fits. The scattering angle and temperature are 57° and 35.1°C respectively.

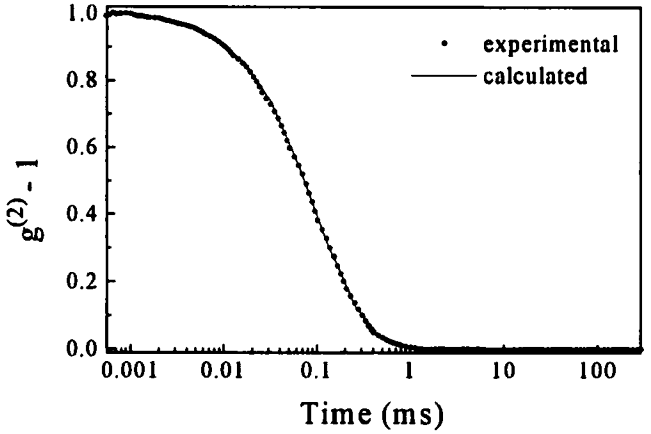


FIGURE 3b The measured (•) and calculated (—) normalized second order correlation functions $g^{(2)}(t)$. The measurements were perfomed in a homodyne regime at room temperature and scattering angle 23°.

By taking an average value for the scattering vector $q=4\pi\bar{n}\sin(\alpha/2)/\lambda$ a quadratic dependence on q of the effective inverse relaxation time τ_{eff}^{-1} is obtained. The corresponding effective diffusivity is almost temperature independent within 3K below the isotropic-nematic phase transition temperature. Its values lie between the values of bend diffusivity and splay, twist diffusivities (Fig. 4).

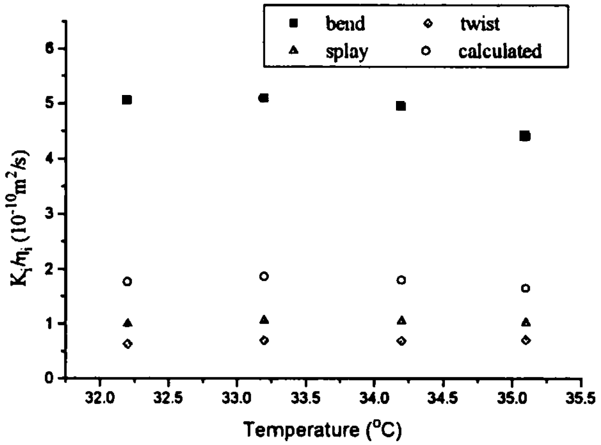


FIGURE 4 Temperature dependencies of calculated effective diffusivity and diffusivities of pure modes[8].

CONCLUSIONS

Averaging over the orientations of the nematic director with respect to the laboratory frame results in a non-exponential light intensity correlation function. The non-exponentiallity is weak and can be described with a stretched exponential function with a value of the exponent s close to 0.8. From angular dependence of the correlation function effective diffusivity can be obtained with the same temperature behavior as that of the pure splay, twist and bend modes and with its values intermediate between pure splay and pure bend modes. The results of our calculation show that at least some of the elastic constants or viscosities in polydomain, disordered systems could be determined in the dynamic light scattering experiment.

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