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Dynamic behaviour at a nematic liquid crystal–rubbed nylon interface using evanescent wave photon correlation spectroscopy†

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Photon correlation spectroscopy of light scattered by director fluctuations from an evanescent optical wave propagating in the nematic liquid crystal 5CB is used to study the interfacial dynamic behaviour of the liquid crystal. The intensity correlation function of light scattered by interfacial orientation fluctuations is measured by illuminating to give a short optical penetration depth within the nematic. These surface scattering correlation functions strongly differ from the bulk correlation function and are interpreted in terms of a nematic surface orientation mode arising from the coupling between the director field and the fluid velocity. It is shown that the analysis of the surface mode gives a method for measuring anchoring energies in liquid crystals. The anchoring energy obtained for rotation of the director away from the rubbing direction about an axis normal to the surface for 5CB at a rubbed nylon surface is $7{\cdot}14 \pm 0{\cdot}7 \times 10^{-2}\,\mathrm{erg\,cm^{-2}}$.

1. Introduction

Photon correlation spectroscopy of light scattered by director fluctuations in bulk nematic liquid crystals (NLCs) has been investigated by many authors [1–3]. The evanescent-optical-wave technique [4] has been used to study the static properties of liquid states in the near vicinity of an interface with a solid, and is well established for measuring various static properties such as density profiles [5], the director orientation found in the surface stabilized ferroelectric liquid crystal cells [6], and wall-induced orientational order in the isotropic phase [7]. Several studies of dynamic properties using evanescent wave illumination and photon correlation spectroscopy of light scattered by a liquid near the interfaces between the liquid and the solid have been reported [8–10]. In addition, it has been shown that the cross-section for the small angle scattering by fluctuations of the director orientation in a planar nematic can be found as a function of the anchoring energy [11].

Recently, we have deduced the field correlation function of light scattered from an evanescent wave at a solid–nematic interface by director orientation fluctuations, not considering the influence of the fluid velocity [12]. The result showed only a bulk mode (no surface mode) and a complex expression for the correlation function depending on scattering wavevector, elastic constants, and anchoring energy. More recently, it has been shown that if the coupling between the fluid velocity and the director is strong enough, a surface mode, slower than the bulk mode, but with the same surface

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component of the wavevector appears and can be considered as a pure rotational bend motion with a larger effective viscosity [13].

In this paper, we report on the interfacial dynamic behaviour of the nematic liquid crystal 5CB with homogeneous alignment at a rubbed nylon 6/6 coated glass interface. The interface is illuminated by an evanescent wave with short penetration range, and the light scattered from the evanescent wave at different angles is analysed with a photon correlation technique. These correlation functions are interpreted in terms of both the bulk and the surface mode mentioned above.

2. Experiment

The experimental sample cell used in this research was nematic 5CB with homogeneous alignment between a high refractive index ($n = 1{\cdot}902@632{\cdot}8$ nm) glass hemisphere and a flat glass plate, both coated with rubbed nylon 6/6, and separated by $d = 6\,\mu$m. An argon laser beam ($\lambda = 514{\cdot}5$ nm) illuminates the planar hemisphere–liquid crystal interface through the hemisphere, with an angle of incidence θ_i which can be adjusted above the critical angle θ_c to illuminate the liquid crystal only close to the interface with an evanescent optical wave. Therefore, we can observe scattering only from fluctuations near the surface. The nematic director $\hat{\mathbf{n}}$ is in the plane of incidence and parallel to the interface. The incident light polarization in the liquid crystal is in the plane of incidence (extraordinary (e) direction) and the outgoing scattered light polarized normal to the plane of incidence (ordinary (o) polarization) is collected on a PM tube. Because the scattering is expected to originate from director angular fluctuations, the scattering polarization selection rules are the same for the surface scattering as for the bulk. In this geometry we probe twist–bend fluctuations with scattering vector $\mathbf{q} = \mathbf{k}_s - \mathbf{k}_i$ in the plane of incidence. Figure 1 illustrates the set up and the scattering geometry for measuring the intensity autocorrelation function. The

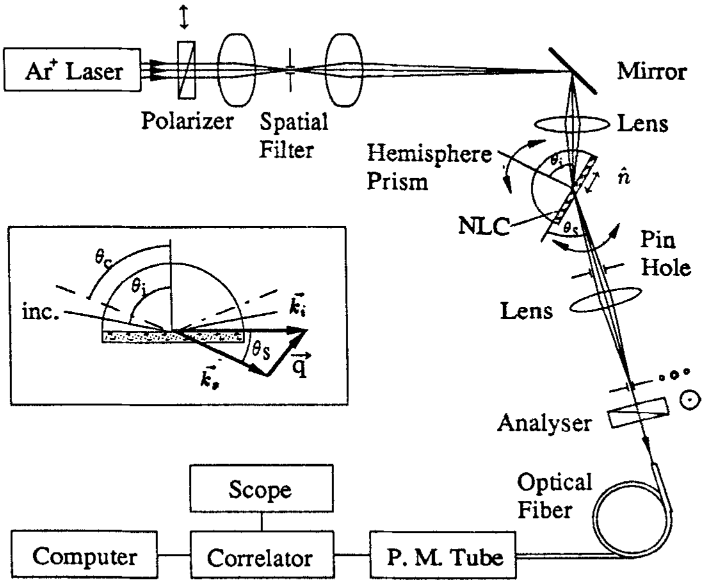

Figure 1. Experimental set up of TIR dynamic light scattering. Inset: scattering geometry; $\mathbf{k}_i$ and $\mathbf{k}_s$ are, respectively, the incident and scattered wavevectors in the medium, and θ_i, θ_c and θ_s are the above, critical total reflection angles and scattered angle.

sample holder is placed on a precision turntable, so that the angle of incidence could be easily changed and the detector arm orientation is also changeable to get the various scattering wavevectors. The critical angle of incidence for total reflection of e light is given by $\sin\theta_c = n_e/n_g$, where $n_g = 1{\cdot}912$, $n_e = 1.734$ and $n_o = 1{\cdot}537$ are the refractive indices of the glass and the liquid crystal [14]. The inverse penetration depth of the optical wave is given by

$$\kappa = k_0(\sin^2\theta - \sin^2\theta_c)^{1/2}, \qquad (1)$$

where k_0 is the magnitude of the wavevector in the glass and θ_c is the angle of incidence for total internal reflection for the particular incoming polarization.

3. Results and discussion

Strong bulk scattering is observed by setting $\theta < \theta_c$, and its intensity autocorrelation function shows a single exponential decay with an inverse relaxation time $1/\tau_b = 78$ kHz for $\theta_s = 60°$. To detect the surface scattering signal, various $\theta > \theta_c$ were chosen to illuminate only the region close to the planar hemisphere interface with evanescent surface waves of different penetration depths. The experimental surface correlation function for $\theta > \theta_c$ but at a large penetration depth, i.e. slightly larger than the critical angle of incidence for total reflection, for $\theta_s = 60°$ is shown in figure 2 which also shows the relaxation for the bulk mode. As can be seen, the correlation function for evanescent illumination and κ^{-1} large is just that of the bulk. The correlation function for short optical penetration depth, shown in figure 3, is also single exponential, but with a much slower relaxation time. This behaviour may be understood as follows.

Let us first consider director fluctuation dynamics calculated from the boundary conditions determined by the surface anchoring potential for a confined nematic

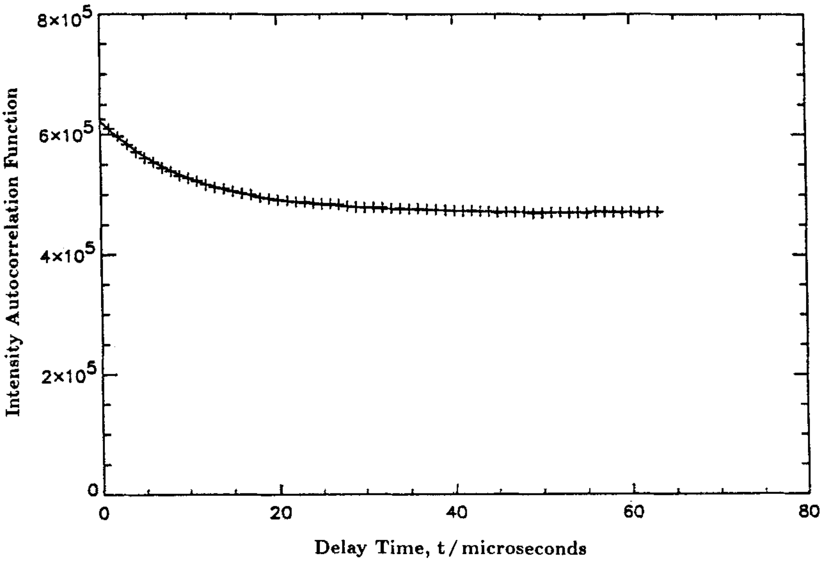

Figure 2. Experimental intensity autocorrelation function $G_I(t)$ of light scattered from an incident evanescent wave with a large penetration depth ($\kappa^{-1} \sim \infty$) for a scattering angle $\theta_s = 60°$ versus delay time t. The line shows the best single-exponential fit giving a decay time. The decay time is the same as the bulk relaxation time τ_b, obtained for $\theta \leqslant \theta_c$.

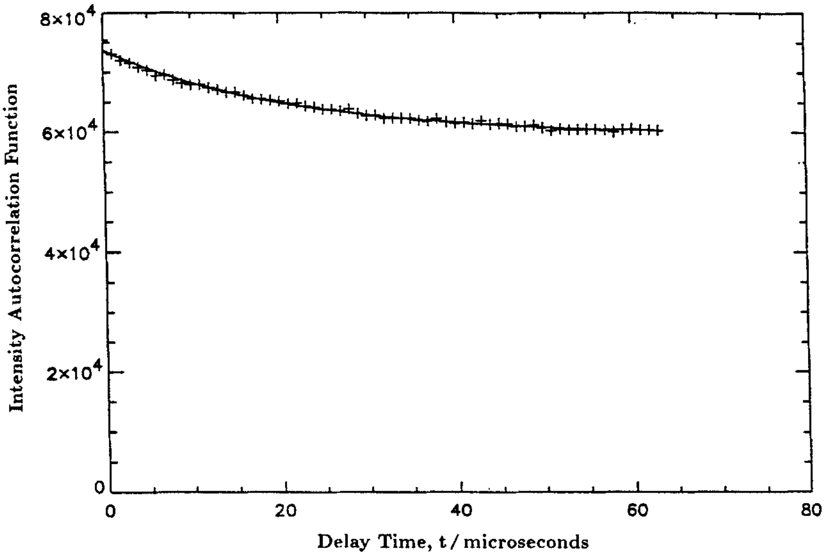

Figure 3. Experimental intensity autocorrelation function of light scattered from an incident evanescent wave with a small penetration depth ($\kappa^{-1} \sim 0{\cdot}3\,\mu\text{m}$) for a scattering angle $\theta_s = 60°$. The line shows the best single-exponential fit. The decay is much slower than for the larger κ^{-1}, which is evidence for the surface mode.

sample. If we ignore the coupling to the fluid velocity field, the complete expression for the field correlation function $G(t)$ for the twist–bend mode is given by [12]

$$G(t) = 4Vk_BT\exp\left(-\frac{K_3}{\gamma}q^2t\right)$$
$$\times\int_0^{\infty}\frac{\exp[-(K_2/\gamma)\beta^2t]\beta^2[(\kappa+\lambda)^2+k_\perp^2]}{(K_2\beta^2+K_3q^2)(\beta^2+\lambda^2)[(\kappa^2+k_\perp^2+\beta^2)^2-4\beta^2k_\perp^2]}\,d\beta, \tag{2}$$

where K_2 and K_3 are the twist and bend elastic constants, and γ is an effective viscosity for the twist–bend mode. We have introduced the inverse anchoring length $\lambda = \omega/K_2$ where ω is the anchoring energy for the rotation of the director about the surface normal. The scattered wavevector is given by $k_s = (k_\parallel, 0, k_\perp)$ in the liquid crystal and $q = k_0\sin\theta_i - k_\parallel$.

It has been shown that the expression can be simplified in the limit of a small penetration parameter κ, that is large optical penetration depth, as [12]

$$G(t) \approx \frac{Vk_BT}{\kappa(K_3q^2+K_2k_\perp^2)}\exp\frac{(K_3q^2+K_2k_\perp^2)}{\gamma}t, \tag{3}$$

which is essentially the same as in the ordinary bulk scattering. This result agrees with the observed surface correlation function for large penetration depth, i.e. $\tau_b^{-1} = 2[(K_3q^2+K_2k_\perp^2)/\gamma]$.

However, even for the experimental situation of short penetration shown in figure 3, the calculated difference between the evanescent wave scattered field correlation function and the single exponential bulk one is also small, i.e. the complicated form of equation (2) is not sensitive to changing the penetration depth, and in all our experimental situations it is very nearly the bulk, single exponential function. So, the surface correlation function for short penetration depth, which shows a slower relaxation time than that for the bulk, cannot be explained unless account is taken of the coupling between fluid velocity and director.

It has been shown that the coupling between the director and flow is particularly strong for the bend mode [13] and the inclusion of the fluid velocity can add a new surface orientational mode. The most interesting situation occurs when the nematic director is parallel to the surface along the x direction (planar orientation) and the director fluctuations $\delta\mathbf{n}$ are perpendicular to the plane of unperturbed director $\mathbf{n}$ and the normal to the surface which is along the z direction. This corresponds to the twist–bend branch of the bulk modes. In this case the y component, v, of the fluid velocity is coupled to $\mathbf{n}$. Let Θ be the small angle that $\mathbf{n}$ makes with the x axis. From the equations of nematodynamics we have

$$K_3\frac{\partial^2\Theta}{\partial x^2}+K_2\frac{\partial^2\Theta}{\partial z^2}-\mu^2\frac{\partial v}{\partial x}=\gamma\frac{\partial\Theta}{\partial t}, \tag{4}$$

and

$$\eta_c\frac{\partial^2 v}{\partial x^2}+\eta_a\frac{\partial^2 v}{\partial z^2}+\mu_2\frac{\partial^2\Theta}{\partial t\partial x}=0, \tag{5}$$

where K_i are the Frank elastic constants, μ_2 is the Leslie coefficient coupling orientation and flow, $\eta_{a,b,c}$ are the Miesowicz viscosities and γ is the rotational viscosity. The boundary conditions are

$$\frac{\partial\Theta}{\partial z}(x,0)=\frac{\omega}{K_2}\Theta(x,0) \tag{6}$$

and

$$v(x,0)=0. \tag{7}$$

Here ω is the anchoring strength. We seek solution to equations (4)–(6) of the form

$$\Theta=\theta(z)\exp(iqx)\exp(-t/\tau) \tag{8}$$

and

$$v=u(z)\exp(iqx)\exp(-t/\tau). \tag{9}$$

There are very many parameters in the problem and to see which combinations of them are essential we introduce dimensionless combinations

$$a=\frac{K_3}{K_2},\quad b=\frac{\eta_c}{\eta_a},\quad c=\frac{\mu_2^2}{\eta_a\gamma},\quad r=\frac{\gamma K_2}{\tau\omega^2},\quad q'=q\frac{K_2}{\omega} \tag{10}$$

and a new dimensionless independent variable $s=\omega/K_2 z$.

Putting equations (8), (9) and (10) into equations (4) and (5) and eliminating u we get the following equation for θ:

$$\frac{d^4\theta}{ds^4}-\left(a+b-\frac{r}{q'^2}\right)\frac{d^2\theta}{ds^2}+\left[ab-(b-c)\frac{r}{q'^2}\right]\theta=0. \tag{11}$$

The boundary conditions become

$$\frac{d\theta}{ds}(0)-\theta(0)=0, \tag{12}$$

and

$$\frac{d^2\theta}{ds^2}(0)-\left(a-\frac{r}{q'^2}\right)\theta(0)=0. \tag{13}$$

θ must also be finite at infinity. The differential equation of θ obtained with continuum equations of nematodynamics is given by

$$\frac{d^4\theta}{ds^4}-\left(a+b-\frac{r}{q'^2}\right)\frac{d^2\theta}{ds^2}+\left[ab-(b-c)\frac{r}{q'^2}\right]\theta=0. \tag{14}$$

The roots of the characteristic polynomial of equation (14) can be considered to be functions of the relaxation parameter r. For $r<r_-=(a-b+2c-2\sqrt{[c(a-b+c)]})q'^2$ all roots are real, with two being positive and two negative. At $r_-<r<r_+$, where $r_+=(a-b+2c+2\sqrt{[c(a-b+c)]})q'^2$ all four roots are complex, with two of them having a negative real part. In these two regions a surface mode may exist as shown in [13]. When $r>r_+$, there are either four imaginary roots or two imaginary and one real positive and one real negative root. In this region we get the bulk mode, which is slightly modified at the surface. An implicit dispersion relation [13] connecting relaxation time and scattering wavevector for the surface mode calculated with continuum equations of nematodynamics and proper boundary conditions is given by

$$q'=\frac{\sqrt{[a+b-(r/q'^2)+2\sqrt{(ab-(b-c))}]}}{(r/q'^2)-a-\sqrt{[ab-(b-c)(r/q'^2)]}}, \tag{15}$$

q' must be real to have a physical meaning. The relationship depends on the magnitude of the coupling parameter c. In the case that $c>(b^2/a+b)$, valid for the nematic 5CB used in our experiment, i.e. $a=2{\cdot}6$, $b=3{\cdot}1$, $c=2{\cdot}5$ [14], and q' is real and positive for $p_1<r/q'^2<r_+/q'^2$. At $r=r_+$, $q'=0$ so that the surface mode for any value of q'. Physically, the fluid velocity adds another degree of freedom to the problem and another independent boundary condition for the velocity. The result is that close to the surface, the fluid can no longer follow the motion of the director which effectively increases the viscous drag on the director close to the surface. This both modifies the bulk waves at the surface and introduces an additional slower surface orientational mode with the relaxation rate depending on the component of the wavevector parallel to the surface.

With this model, the experimentally measured surface correlation function can provide information on the surface orientational mode. The data of figure 3 for κ^{-1} small are well fitted by a single exponential with $1/\tau=48\pm1{\cdot}6\,\mathrm{kHz}$, ~ 1·66 times slower than the bulk τ_b obtained at θ_c. The fact that the bulk mode is not observed at smaller penetration depths is due to its small amplitude, a result of faster relaxation rate and quenching of the bulk mode amplitude close to the surface. This experimental result agrees with the theoretically expected one that the surface mode is always slower than the bulk one [13].

Finally, to get the surface anchoring energy from $q'=q(K_2/\omega)$ of equation (10), where we know that $K_2=0{\cdot}3\times10^{-6}\,\mathrm{erg\,cm^{-2}}$ in [14] and q is the scattering wavevector in the xy plane of interface ($q=k_0\sin\theta_i-k_{\parallel}$) we have to find the dimensionless parameter q'. Equation (15) shows that the implicit dispersion relation connecting relaxation time and scattering wavevector for the surface mode and the dispersion relation for the bulk nematic twist-bend mode is given by [13]

$$r=q'^2\frac{(\beta^2+a)(\beta^2+b)}{\beta^2+(b-c)}. \tag{16}$$

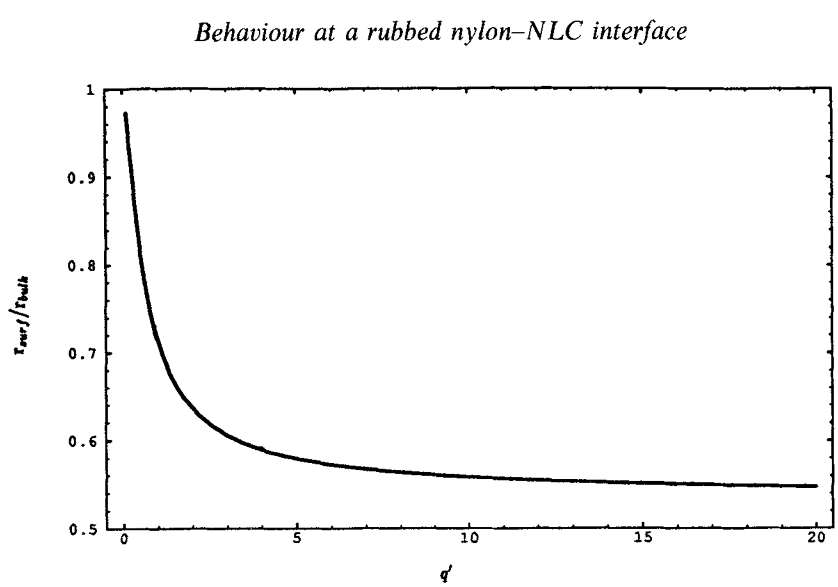

Figure 4. r_{surf}/r_{bulk} versus q' for $\beta/q' = 1{\cdot}1$ calculated equation (15) and (16), where $\beta/q' = 1{\cdot}1$ is determined from our experimental situation.

So, using equation (15) and (16), we obtain figure 4 for r_{surf}/r_{bulk} versus q' for $\beta/q' = 1{\cdot}1$ where $\beta/q' = 1{\cdot}1$ is determined from our experimental situation. A fit of the experimental value of $r_{surf}/r_{bulk} = 0{\cdot}6$ and theoretical curve gives a value of $q' = 3$. This results in $\omega = 7{\cdot}14 \pm 0{\cdot}7 \times 10^{-2}\,\mathrm{erg\,cm^{-2}}$ which can be compared to $\omega = 7 \times 10^{-2}\,\mathrm{erg\,cm^{-2}}$ measured from the optical birefringence change at high electric fields on a polyimide surface [16] and $\omega = 1{\cdot}1 \times 10^{-1}\,\mathrm{erg\,cm^{-2}}$ obtained using surface–plasmon polariton technique on a Au and SiO_2 surface [17].

It has been shown that there exists a surface mode slower than the bulk one and the measured surface correlation function provides information on the surface anchoring energy. It seems to us that this method is very promising, because it utilizes fluctuations, always present in nematic liquid crystals, and the role of light to detect the surface mode of these fluctuations near the interface. The limitations of the proposed method are the fact that it is difficult to know all the elastic and viscous constants for the liquid crystal, and to get a reasonable correlation function because the surface scattering signal is very weak. A full account of this analysis, with the wavevector dependence of the slow relaxation time for surface mode and various scattering geometries, will be published in a forthcoming paper.

4. Conclusions

We have observed that the autocorrelation function of light scattered by director fluctuations close to the interface between a nematic LC and a rubbed nylon surface has a slower relaxation time than the bulk fluctuations. Application of recent theoretical analysis of evanescent scattering by nematic director fluctuations shows them to be due to a surface orientational fluctuations mode, a result of the strong coupling between the director and flow for bend deformation. The relaxation time of the surface mode for the twist–bend deformation is about 1·66 times slower that that of corresponding bulk mode, yielding a value of anchoring energy of $7{\cdot}14 \times 10^{-2}\,\mathrm{erg\,cm^{-2}}$. In principle, this technique enables measurement of the anchoring of nematic liquid crystals at solid interfaces.

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