

## Nematic order in polymer-stabilized liquid crystals

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We have studied both experimentally and theoretically how the presence of polymer fibrils can influence the ordering in liquid crystal systems. When such fibrils are formed by polymerization in a nematic solution, the polymer structure can reflect the director orientation at the time of polymerization. This anisotropic structure can be retained even when the liquid crystal is heated into its isotropic phase. We report measurements of this effect and also calculations based on a simple model of the mechanism by which the polymer fibrils can be expected to influence the nematic order of a liquid crystal matrix. A numerical solution of the theoretical model suggests that the discontinuity in order parameter that occurs at the transition temperature should gradually diminish as polymer concentration is increased and should vanish at a critical concentration. This is in agreement with our experimental observations. [S1063-651X(98)00810-1]

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### I. INTRODUCTION

We have constructed a network consisting of an intimate mixture of polymer fibrils in a nematic liquid crystal. This network mimicked the order and orientation of the liquid crystal at the time of polymerization [1–3]. At all later times the polymer network was found to have a strong effect on the alignment of the liquid crystal. This was seen in the modification of the nematic ordering, as observed by measurements of the optical birefringence as a function of temperature [4]. The order parameter appeared to be enhanced when the liquid crystal was in the isotropic phase, but diminished when it was in the nematic phase. In a study aimed at understanding the microscopic processes involved, we have modeled this system theoretically. We do this by taking the usual mean-field model of nematic ordering and generalizing it to include the effective field generated by the polymer. Our goal in this work is to develop an understanding of the effects of the various parameters associated with the presence of polymer on the ordering of the liquid crystal material.

### II. EXPERIMENT

Samples were prepared by dissolving the diacrylate monomer 4,4'-(6-acyloxyloxy-hexyloxy)-1,1'-biphenylene (BAB-6) and the photoinitiator benzoin methyl ether in a 20:1 ratio by weight in the nematic liquid crystal 4'-penty-4-cyanobiphenyl (5CB). The materials were mixed well and then filled into cells consisting of two parallel glass plates with a 10- $\mu\text{m}$  separation. The inner faces of the glass plates were coated with polyimide in order to induce a homogeneous alignment at these surfaces. After the cells had been filled they were then irradiated for 30 min with UV light at 18 mW/cm<sup>2</sup>. The resulting polymer network was studied by means of birefringence measurements and also directly by scanning electron microscopy. The microscopy study appeared to show that a polymer network con-

sisting of fibrils of submicrometer thickness had been formed with an alignment more or less in the direction of the liquid crystal (LC) director [2]. This result must be treated cautiously, however, as it is possible that the network may have compacted when the liquid crystal was extracted. This possibility is given credence by the fact that the birefringence studies indicated a much smaller fibril diameter, perhaps of the order of a few nanometers.

The nematic-isotropic transition was studied in this system by measurements of the optical birefringence. A 2-mm-wide light beam from a 5-mW He-Ne laser was directed at a cell contained between crossed polarizers, with the liquid crystal director at an angle of 45° to the polarizer transmission axis. The birefringence  $\Delta n$  was found from measurements of the intensity  $I$  of transmitted light through the relationship  $I = I_0 \sin^2(\pi d \Delta n / \lambda)$  with  $\lambda$  the wavelength of light and  $d$  the cell thickness. The temperature was varied at a rate less than 0.1 mK/min and was controlled with a precision of 5 mK.

The results are shown in Fig. 1. In the absence of polymer, the transition from the nematic to the isotropic phase was seen as an abrupt vanishing of the birefringence when the temperature was raised above 35 °C. As the polymer concentration was increased, the birefringence, which is proportional to the LC order parameter, decreased in the nematic phase and the transition was shifted to lower temperatures. At temperatures above the transition temperature some residual order remained in the liquid crystal, presumably as a result of the anisotropic environment caused by the presence of the polymer.

When the concentration of polymer reached a point somewhat above 10%, the first-order phase transition was no longer apparent. Instead, the birefringence decreased continually from its low-temperature value as the temperature was raised. The most striking aspect of these results was that there was an appreciable range over which the birefringence decreased linearly with temperature. The possibility of there

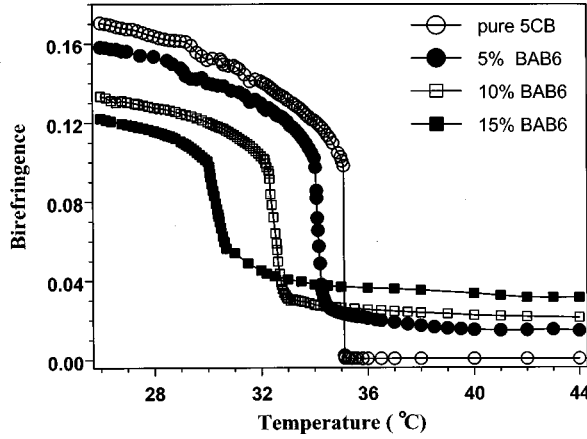


FIG. 1. Measured birefringence of the liquid crystal 5CB in a cell containing an ordered network of polymer fibrils, shown as a function of temperature for various concentrations of polymer.

being two continuous phase transitions at the boundaries of the linear region could not be excluded by our measurements.

### III. THEORY

In the absence of polymer, the liquid crystal director  $\hat{\mathbf{n}}(\mathbf{r})$  will be a unit vector  $\hat{\mathbf{n}}_0$  whose direction will be independent of position. The order parameter  $s$  will similarly be position independent. The introduction of partially oriented polymer fibrils will have the effect of modifying both  $s$  and  $\hat{\mathbf{n}}$  from their previously uniform values. We consider the effect of the polymer as being equivalent to that of some spatially varying applied field  $\mathbf{H}(\mathbf{r})$ . Here  $\mathbf{H}$  is not a magnetic field, but is a generalized force field that changes the local energy by an amount proportional to  $\mathbf{H}$  and  $s$  and dependent on the angle between  $\mathbf{H}$  and  $\hat{\mathbf{n}}(\mathbf{r})$ . The action of  $\mathbf{H}$  on the liquid crystal is then to reorient the molecules and to either reduce or amplify the local order parameter. The immediate, or zeroth-order, effect of  $\mathbf{H}$  is to tend to reorient  $\hat{\mathbf{n}}_0$  into the volume-averaged preferred direction of the polymer fibrils. The next effect observed will be a change in the volume average of  $s$  that will be of first order in  $\mathbf{H}$ . Following this there will be some local reorientation of  $\hat{\mathbf{n}}(\mathbf{r})$  as molecules tend to align themselves with the local variations in orientation of this spatially varying field. The changes in energy resulting from these shifts will be at least of order  $\mathbf{H}^2$  and thus of less importance than the changes in  $s$  when the field is weak. For this reason we shall adopt a model in which the elastic energy due to variation of  $\hat{\mathbf{n}}(\mathbf{r})$  is neglected and in which the dominant effects are due to local variations in  $s$ . This approximation is not strictly necessary, but has the effect of reducing the number of parameters in the theory to a manageable quantity. A more thorough approach would follow the approach of Palfy-Muhoray *et al.* [5], who treat spatial variations in the tensor order parameter.

Our model is then one in which the director is uniform, but in which the order parameter  $s(\mathbf{r})$  varies under the influence of the mean field  $\mathbf{h}(\mathbf{r})$  of neighboring molecules and of the applied field  $\mathbf{H}(\mathbf{r})$  due to the aligning effects of the poly-

mer fibrils. The Hamiltonian for a single molecule in these combined fields is then

$$\mathcal{H}_1 = -[h(\mathbf{r}_1) + H(\mathbf{r}_1)]P_2(\cos \theta), \quad (1)$$

where  $P_2(\cos \theta) = (3 \cos^2 \theta - 1)/2$  and  $\theta$  is the angle between the molecular axis and  $\hat{\mathbf{n}}$ . The mean field is taken to be

$$h(\mathbf{r}) = \lambda \int s(\mathbf{r}')g(\mathbf{r}' - \mathbf{r})d\mathbf{r}', \quad (2)$$

with  $\lambda$  a constant,  $s(\mathbf{r})$  the local average of  $P_2(\cos \theta)$ , and  $g(\mathbf{r}' - \mathbf{r})$  a normalized function of sufficiently short range  $l$  that we can rewrite this equation without significant error as

$$h(\mathbf{r}) = \lambda[s(\mathbf{r}) + \frac{1}{2}l^2\nabla^2s(\mathbf{r})]. \quad (3)$$

The formulation of the Helmholtz free energy  $\mathcal{F}$  of this system requires some care. We cannot simply write the partition function for a single molecule in the mean field  $h(\mathbf{r})$ , as this would give an incorrect expression for  $\mathcal{F}(s)$  when  $s(\mathbf{r})$  is spatially varying. Instead, we first evaluate the free energy  $\mathcal{F}_0(s)$  for an ensemble of noninteracting molecules subject to the constraint that the order parameter be  $s$  and then add the effects of the fields and interactions. The resulting expression can then be minimized to find  $s(\mathbf{r})$ .

The maximization of the entropy of an ensemble of independent liquid crystal molecules with a constrained order parameter leads to the introduction of a Lagrange multiplier in the form of a field  $A$ . The free energy  $\mathcal{F}_1(A)$  in this field is given by the equation

$$\beta\mathcal{F}_1(A) = -\ln \int_0^1 e^{\beta A P_2(\cos \theta)} d(\cos \theta) \equiv -G(\beta A), \quad (4)$$

say, where  $\beta = 1/k_B T$ , with  $T$  the temperature and  $k_B$  Boltzmann's constant. Then

$$s = -\frac{\partial \mathcal{F}_1(A)}{\partial A} = G'(\beta A), \quad (5)$$

where  $G'(x) \equiv dG/dx$ . This relation may be inverted to give an expression of the form

$$\beta A = F(s). \quad (6)$$

Now

$$\mathcal{F}_0(s) = \mathcal{F}_1(A(s)) + A s \quad (7)$$

and so

$$\beta\mathcal{F}_0(s) = -G(F(s)) + sF(s). \quad (8)$$

To this expression, which is no more than the negative of the entropy of the constrained ensemble, we add the effects of the mean field  $h$  and the applied field  $H$  to find

$$\beta\mathcal{F}(s) = -G(F(s)) + sF(s) - \frac{1}{2}\beta\lambda[s^2 + \frac{1}{2}l^2(\nabla s)^2] - s\beta H. \quad (9)$$

Minimization with respect to  $s$  of the integral over volume of this free energy then yields the equation

$$\beta^{-1}F(s) - \lambda s - \frac{1}{2} \lambda l^2 \nabla^2(s) - H = 0. \quad (10)$$

The equilibrium state will then be the solution of this differential equation that gives the lowest value of the free energy (9).

The model that we choose for  $H(\mathbf{r})$  attempts to capture the essential features of the action of the network of polymer fibrils. The primary effect is to introduce a preferred direction of orientation and this we represent by a uniform field  $H_0$ . Because the fibrils form a cross-linked network there will also be regions in which the local fiber orientation lies at some large angle from the dominant direction and in these regions the effect will be to diminish the order parameter. We represent this effect by adding a spatially varying component to  $H$ . For this we choose the simplest possible form and superimpose on  $H_0$  a term  $H_1 \cos qz$ , with the wavelength  $2\pi/q$  characterizing the average spacing in the network.

The effect of a sinusoidal field alone acting on the liquid crystal at a temperature above the nematic-isotropic transition would be to induce a positive ordering  $s$ . The reason for this lies in the fact that the free energy  $\mathcal{F}_0(s)$  is an asymmetric function of  $s$ . It increases rapidly when  $s$  becomes negative, but does so only slowly as  $s$  becomes positive. A cosinusoidal field, which consists of equally large positive and negative regions, thus has a much larger effect in perturbing  $s$  in the positive direction than it does in the negative direction. For this reason we must apply a negative value of  $H_0$  along with the oscillatory field  $H_1 \cos qz$  if we are to mimic the effect of a dispersion of polymer fibrils of random orientation. To describe a system in which the polymer fibrils have a preferred orientation, a positive component of  $H_0$  must be added. It is not then clear whether the system studied experimentally is best described with a positive or with a negative  $H_0$ . In our numerical solution of Eq. (10) we chose a negative value of  $H_0$  equal to  $H_1/10$  simply because it appeared to give a reasonable qualitative fit to the data.

Our goal is to calculate the spatial average  $\bar{s}$  of the order parameter  $s$  as a function of temperature and concentration of polymer and hence to be able to predict the birefringence of the sample. The solution of Eq. (10) will give  $\bar{s}$  in terms of the dimensionless quantities  $\beta\lambda$ ,  $\beta H_0$ ,  $\beta H_1$ , and  $ql$ . At high and low temperatures some reasonable approximations can be made that lead to analytical solutions. At intermediate temperatures the problem is more difficult and requires numerical solution since there is then the possibility of the system splitting into domains of strongly and weakly ordered material. When this happens the first-order phase transition is either lost or greatly diminished. The single first-order transition disappears when  $ql$  or the ratio  $\lambda/H_1$  becomes sufficiently small.

The results of a numerical solution of Eq. (10) are shown in Fig. 2 for a range of  $H_1$  for the case where  $H_0 = -H_1/10$  and where  $ql=0.5$ . The coefficients of a three-term Fourier series for  $s(z)$  were varied to minimize the free energy. From the figure we see that the discontinuity in  $\bar{s}$  that occurs at the transition temperature is gradually diminished as  $H_1$  is increased and vanishes when  $H_1=0.022$  in units of  $\lambda$ . Because the order parameter is generally linearly related

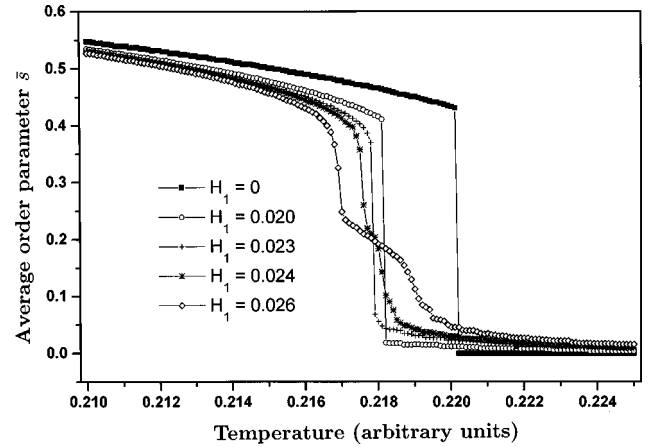


FIG. 2. Numerical solutions of the theoretical equation for the average order parameter of the liquid crystal, shown as a function of temperature. The concentration of polymer is represented by the strength of the effective field  $H_1 \cos qz + H_0$ . Here  $H_1$  is given in units of the mean-field parameter  $\lambda$  and  $H_0 = -0.1H_1$ .

to the birefringence, we would predict that the birefringence should show a similar pattern.

These theoretical results appear to capture the qualitative features of the experimental results shown in Fig. 1 and give us some confidence that we have captured the essential physics of the processes involved. As one might expect, the effect of increasing the spatially varying field is initially to reduce the discontinuity in  $\bar{s}$  at the phase transition and then to eliminate it. The theoretical results resemble the experimental ones in exhibiting a range over which  $\bar{s}$  varies linearly with temperature, although the theoretical curves show an increase in slope at the boundary of the linear region that is absent in the experimental curves.

#### IV. CONCLUSIONS

The experimentally observed effect of forming a dilute oriented web of polymer fibrils in a nematic solution is to reduce or remove the discontinuity in order parameter that occurs as the temperature is raised. At high temperatures, some nematic ordering persists as a consequence of the presence of oriented polymer. At low temperatures the effective nematic order parameter is reduced below that of the pure material. This is presumably because there are some components of the polymer network that are not favorable to ordering in the predominant direction and these prevent a uniformly ordered system from forming.

A characteristic found in both the experiments and the theoretical prediction is the existence of a range of temperatures over which the order parameter varies linearly with temperature. We interpret this phenomenon as arising from the existence of separate domains of material in the nematic and isotropic phases, respectively. The effect of raising the temperature while in this regime is to reduce the size of the nematic domains and consequently to increase the size of the isotropic domains. While the system is in this regime there will be domain walls between the two phases. Outside the range of this phenomenon there will be a single phase in which there is a smaller spatial variation in order parameter.

At present it is not clear whether there might be continuous phase transitions at the boundaries of the linear regime and this will be the subject of further experimental and theoretical study.

#### ACKNOWLEDGMENT

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