ABSTRACT

Introduction

Liquid crystals are fluids characterised by long – range orientational order without long-range three dimensional translational molecular order. Studies of Liquid crystals (LC) in confined geometries are particularly very important both from the fundamental and technological point of view. It is found that the order parameter at the surface of the substrate as well as the interior of the sample increases with decreasing cell thickness.

In chapter 1 (Introduction), the importance of studying the Liquid crystals and its application, the classification of liquid crystals and phenomenological theory of various phases is described.

In chapter 2 we review the earlier work. There are several theoretical and experimental studies to show that the nematic order parameter is enhanced for liquid crystals in thin cells and the enhancement is larger as the thickness is reduced. The enhancement of the order parameter due to reduction of cell thickness has two aspects. Firstly, with a strong surface ordering potential, the thickness averaged of the order parameter $\overline{S}$, in turn leads to an increase in the effective curvature elastic constant. Secondly the reduction in the number of fluctuation modes which enhances the order parameter by $\sim 0.1\%$, when the thickness is reduced from 10µm to 1µm. The combined effect of the surface potential and the stiffening of the elastic
constant has amplified the $S_{\text{meas}}$ in thin cells which is very large close to $T_{NI}$ and decreases sharply as the temperature is lowered. On the other hand, the experimental values do not decrease so drastically.

In this thesis we theoretically investigate this significant enhancement of the nematic orientation order parameter $S$, in thin cells by proposing suitable variations of surface potential w.r.t the distance from the cell wall of the thin cell. Different theories are modified by including this potential to account for the enhancement. In chapter-3 we review Maier–Saupe (MS) theory. A simple extension of MS theory is used to explain the enhancement of the nematic order for thin cells. We have tried different empirical variations of surface induced potential with respect to the distance from the cell wall.

We propose a model in which a molecule at $z$ the surface is assumed to feel the mean field potential (MS-type) and also the surface induced potential. The exact nature of the variation of surface potential with respect to $z$ is not known experimentally. The potential has to be maximum at $z=0$ and zero at large distances from the surface. Thus, the surface induced potential is taken empirically to decay exponentially as $U_{IS} = -U_S e^{-\frac{z}{r_0}}$, where $U_S$ is the surface potential at $z=0$ and $r_0$ is the characteristic length. The Average internal energy per molecule and the Free energy are calculated. The value of $\bar{S}$ is also found for different $T$, for thickness 1µm and 10µm respectively. In each case the percentage change in nematic order parameter are calculated and compared with the experimental values. Similar tabulations are made by with surface induced potential of the type $U_{IS} = U_S \times 1/[1+((z/r_0)^2)]$ Experimentally it is found that the enhancement is not significantly reduced at lower temperatures. Considering the first potential (exponential decay) the percentage enhancement of the order parameter between thick and thin cells reduces by 1.5 times with the decrease in temperature, while for
the second potential (inverse square law) the reduction is 1.7 times. However, the reduction as per the calculations due to earlier theories is 50 times. Thus, the simple empirical equations used for the decay of surface potential give results which are in better agreement with experimental data compared to earlier theories.

In Chapter 4 we consider the smectic layers near the surface. Experiments of Ocko et al. show that liquid crystal systems in the isotropic phase can often show smectic order close to the free surfaces. We consider a similar induced smectic phase near the surface of a cell due to the surface potential. This in turn enhances the nematic order parameter near the surface and hence the thickness averaged order parameter.

In our model, as earlier a molecule near the surface is assumed to feel the mean field potential (M-S type) and also the surface induced potential. In this chapter we propose a simple extension of McMillan theory, to include the surface potential. The thickness averaged order parameter $S$ is calculated as in the earlier chapter and compared with nematic phase only. We find that the enhancement is larger with smectic phase. This is due to the fact that the nematic order in the smectic phase has increased $S$. The trends agree only qualitatively and the actual $dS\%$ values are much less than the experimental values. This may be due to the presence of polar short range order since the experimental molecules are polar. The effect of including polar short range order is discussed in the next chapter.

In Chapter 5 we develop a molecular mean field model assuming the medium with polar molecules to consist of inter-converting anti-parallel and parallel pairs to explain the molecular origin of “two-lengths”. We have extended Maier-Saupe theory, using an empirical variation of surface potential, to account for the enhancement. The repulsive dipolar interaction is $\propto 1/r^3$ where $r$ is the intermolecular separation, while both the dipole-induced dipole and the dispersion interactions are $\propto 1/r^6$ and are attractive in nature. Hence there can
be a change from the antiparallel to the parallel configuration as the intermolecular separation is decreased below some value as the density is increased due to lowering of temperature or increase of pressure.

As explained above, the medium is assumed to consist of \textit{pairs} of molecules having either antiparallel (A) or parallel (P) configurations. The difference between the pairing energy of the A-type ($E_A$) and the P-type ($E_P$) configuration expressed in terms of temperature. $R_2$ is the reduced temperature at which the density of the medium is such that $\Delta E$ becomes zero.

As we have mentioned, the surface potential enhances the order parameter of the medium. This results in an increase in the density which in turn decreases intermolecular separation. This increases the fraction of parallel pairs and hence increases $R_2$. Thus, $R_2$ at some distance $z$ from the cell wall ($R_2(z)$) is greater than $R_2$ of the bulk ($R_{2B}$). Maier–Saupe theory is extended for mixtures. The calculated values of percentage change in nematic order including polar short range order show slight improvement to our earlier calculation in which polar nature of molecules is not considered.