# Solutions to Soft Matter exercise 2, Liquid Crystals:

## 1.     Liquid crystals
A thermotropic liquid crystal is a pure material and does not contain any solvent. It changes phase if the temperature is changed.
A lyotropic liquid crystal is composed of molecules that are dispersed in a solvent. Its phase is a function of the mesogen concentration and temperature.

## 2.     Structure
Short range order means that there is some order in the orientation or spacing of molecules (or atoms) over a short distance (there is a correlation between the distances of nearest neighbors), but there is no order over longer distances. The order of liquid crystals is higher than that in liquids, that have no long or short range order at all, but it is lower than that in crystals that have short and long range order.

## 3.     Thermodynamics
The free energy decreases because the intermolecular forces increase which results in a decrease in the enthalpy $\Delta H = H_{final} - H_{initial}$. In this case, the intermolecular forces in the liquid state are smaller than those in the nematic state such that $H_{initial} > H_{final}$ and hence $\Delta H < 0$. This decrease in the enthalpy overcompensates the reduction in entropy such that the Gibbs free energy, $\Delta G$, decreases.

## 4.     Quarter-wave plate
The definition of a quarter waveplate is that $\delta = \frac{\pi}{2} = 90°$.
Hence, we obtain
$\delta = \frac{2\pi}{\lambda}\Delta n d = \frac{\pi}{2}$ such that
$d = \frac{\lambda}{4\Delta n} = \frac{488nm}{4 \times 0.22} = 0.55\mu m$

## 5.  Birefringence
Birefringence is an optical property of a material where the refractive index depends on the polarization of the light. Only materials with refractive indices that are anisotropic can be birefringent. They are birefringent if the refractive indices in the two directions that are perpendicular to the propagation direction of the light are different. For example, if the light is propagating along the z-direction, a material is birefringent if the refractive index in the x-direction is different from that in the y-direction.
   a. homeotropically aligned nematic phase: This phase is birefringent if the light propagation direction is not perpendicular to the director.
   b. planar-aligned smectic A phase: This phase is birefringent if the light propagation direction is not perpendicular to the director.
   c. cholesteric phase: This is birefringent because it is made of chiral mesogens which, if aligned, are birefringent.
   d. isotropic phase of a discotic material: This is not birefringent because its properties are isotropic.
## 6.     Nematic liquid crystals

a. The melting transition temperature from a crystal into the nematic phase, $T_m$, increases if
- the aliphatic chain is shortened. The aliphatic chains hamper packing and thus lower $T_m$. If they are shortened, it is easier to pack the mesogens into a crystal and hence, $T_m$ increases.
- electronegative elements are added -> increased Van-der-Waals interactions.
- of a phenol ring or another unit that forms strong intermolecular forces is added.

b. The transition temperatures can be quantified using differential scanning calorimetry (DSC). The operation principle is the following: You have an empty pan that serves as a reference and a pan filled with a known amount of your sample. You heat both pans, with the goal to keep the temperature in both pans the same. You measure the amount of energy needed to increase the temperature of the sample pan relative to the energy needed to increase the temperature of the reference pan. The difference in energy allows you to determine the difference in the specific heat capacity. If there is a phase transformation, the temperature does not increase or decrease until the phase transition is completed. Hence, at this point, much more energy is required to increase the temperature of the sample relative to the energy needed to increase the temperature of the reference. This will be seen as a peak in the energy that is given to the sample at the phase transition temperature. If the phase transition is exothermic, you will heat the sample without putting in any energy. This will again display as a peak at the transition temperature (with the opposite sign).

## 7. Cholesteric liquid crystals

The pitch distance of cholesteric liquid crystals determines the wavelength of the reflected light. Thus, it determines the color of the liquid crystal. The pitch distance changes with temperature. Hence, the color of the liquid crystal changes with temperature.

Limitations: They can only be used in the nematic range. Only a limited number of molecules can be used because they must be chiral.

## 8. Twisted nematic liquid crystal

a. To determine the switching voltage, $U$, we use $U = E \times d$ where $E$ is the electric field and $d$ the distance between the plate. From the course, we know

$$E_{crit} = \frac{2\pi}{d} \sqrt{\frac{\pi}{\Delta\varepsilon} \left[ K_1 + \frac{1}{4}(K_3 - 2K_2) \right]^{\frac{1}{2}}} = \frac{2\pi}{10 \times 10^{-6} m} \sqrt{\frac{\pi}{0.7 \times 8.85 \times 10^{-12} \frac{F}{m}} \left[ 5.3 \times 10^{-12} N + \frac{1}{4} \left( 7.45 \times 10^{-12} N - 2 \times 2.2 \times 10^{-12} N \right) \right]^{\frac{1}{2}}}$$

$$E_{crit} = 1.1 \times 10^6 V$$

and

$$U = E_{crit} d = 11V$$

Note that the switching voltage is independent of the sample thickness!

b. To reduce the switching constants, the elastic constants could be reduced. This can be achieved by reducing the intermolecular forces by weakening the Van-der-Waals interaction forces or increasing the intermolecular distances.

## 9.    Liquid crystal display

Because the mesogens of nematic liquid crystals rotate around the axis perpendicular to the plane if they are oriented parallel to the plane, it must be a twisted nematic liquid crystal. Hence, to determine the critical electric field needed to switch such a crystal, we can use

$$E_{crit} = \frac{2\pi}{d}\sqrt{\frac{\pi}{\Delta\varepsilon}}\left[K_1 + \frac{1}{4}(K_3 - 2K_2)\right]^{\frac{1}{2}}$$

Using the values given in the text, we obtain

$$E_{crit} = \frac{2\pi}{d}\sqrt{\frac{\pi}{\Delta\varepsilon}}\left[K_1 + \frac{1}{4}(K_3 - 2K_2)\right]^{\frac{1}{2}}$$

a.
$$E_{crit} = \frac{2\pi}{100\times10^9\,m}\sqrt{\frac{\pi}{(5.4-4.7)\times8.85\times10^{-12}\frac{F}{m}}}\left[5.3\times10^{-12}\,N + \frac{1}{4}\left(7.45\times10^{-12}\,N - 2\times2.2\times10^{-12}\,N\right)\right]^{\frac{1}{2}}$$

$$E_{crit} = \frac{2\pi}{d}\sqrt{\frac{\pi}{\Delta\varepsilon}}\left[K_1 + \frac{1}{4}(K_3 - 2K_2)\right]^{\frac{1}{2}}$$

$$E_{crit} = \frac{2\pi}{100\times10^{-9}m}\sqrt{\frac{\pi}{(5.4-4.7)\times8.85\times10^{-12}\frac{F}{m}}}\left[5.3\times10^{-12}N\right.$$

$$\left. + \frac{1}{4}(7.45\times10^{-12}N - 2\times2.2\times10^{-12}N)\right]^{\frac{1}{2}}$$

such that

$$E_{crit} = 110\frac{MV}{m}$$

b. $E_{crit} = 11\dfrac{MV}{m}$

c. $E_{crit} = 110\dfrac{kV}{m}$

d. If the chamber becomes too thick, it is difficult to maintain the good alignment of the mesogens and prevent domain formation.