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Physics of Surfaces

Biosensors Based on Liquid Crystal Anchoring

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Abstract

Surface science appears in a huge range of areas including basics science and large scale industrial production. In small particles the surface has a big effect on their properties or the properties of the material containing them. Liquid crystals are especially interesting in this regard, since the effect of the surface extends deep into the bulk phase. In most liquid crystal applications, such as LCDs, the surface is treated so that the correct anchoring of the liquid crystal is achieved. Planar anchoring is made by rubbing the surface, whereas the homeotropic anchoring is achieved by the deposition of a surfactant to the substrate. Similarly the surfactant molecules can be absorbed to the interface between a LC and water changing the alignment from planar to homeotropic. Since the anchoring angle is very sensitive to the surfactant concentration, this sistem can be used as a sensor. The anchoring also affects the bulk liquid crystal, so the changes can be easily observed under a polarizing microscope. However small changes in the anchoring can not be detected in this way. In the seminar I present a novel way for measuring the anchoring of liquid crystal on the interface with water. The method is based on measuring peaks in the fluorescence spectrum corresponding to resonances in spherical droplets of liquid crystal floating in water. This technique could be very sensitive to the anchoring, thus allowing detection of very small concentration of surfactants or other molecules.

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1 Introduction to Liquid Crystals

In nature there are three basic states of matter: solid, liquid and gas. However there are substances, that have several pases between solid and liquid state. Their symmetry properties are in between solids and liquids. This kind of substances are therefore called *Liquid Crystals* (LC). Their molecules diffuse like molecules in liquids but maintain some degree of orientational order and sometimes also positional order. This order brings several anisotropies like: birefringence, anisotropy in the viscosity and transfer of statical torques. The properties of LCs derive from the shape of the molecules. They are elongated in one direction or in the shape of a disk. In the seminar I will focus only on LCs of rod like shape.

The elongated LC molecules orient in the same direction (nematic phase) and sometimes also in distinct layers (smectic phases). All LCs also have isotropic and crystalline phase. In the isotropic phase the LC behaves as a normal liquid. The typical succession of phases as the temperature is raised is *solid* \rightarrow *smectic* \rightarrow *nematic* \rightarrow *isotropic*. With some LCs either smectic or isotropic phase is not present. There exist many more LCs phases, but they are out of the scope of this seminar.

1.1 Nematic Liquid Crystals

Figure 1 shows the molecules in nematic liquid crystal. The molecules do not have long range positional order but they have orientational order. This means that in average all the molecules point in the same direction. This is the most important property of the LCs. This direction is characterized by a vector of unit length \vec{n} called the *director*. Directions \vec{n} and $-\vec{n}$ are always equivalent. The director of the director in bulk is arbitrary or it is defined by an external field. In confined systems the director is defined by the boundary conditions at the interface between the LC and another substance. The molecules of nematic LC are non-chiral. If they have rotational symmetry around the long axis they are called uniaxial nematic LCs.



Figure 1: a) Deviation of the LC molecule direction from the director and b) orientational disorder of LC molecules. [1]

1.2 Order Parameter

With the director we described the mean direction of the LC molecules. Now we want to characterize how good is the orientation of the molecules in that direction. For that purpose we construct a

scalar quantity called Order Parameter, defined as

$$S = \frac{1}{2} < (3\cos^2\theta - 1) > = \int f(\theta) \frac{1}{2} (3\cos^2\theta - 1) d\Omega.$$
 (1)

where θ is the angle between the director and the long axis of the molecules (Fig 1a). In the isotropic phase it is equal to zero, in the crystal phase equal to one, whereas in the nematic phase its value is usually in between 0.3 and 0.7

1.3 Elastic Properties of LCs

In the nematic phase the director is uniform in space. However usually because of confinement and external fields the director varies spatially. This deformation of LC costs energy. Elastic energy density is equal to

$$f_{elast} = \frac{1}{2} K_{11} (\nabla \cdot \vec{n})^2 + \frac{1}{2} K_{22} (\vec{n} \cdot \nabla \times \vec{n})^2 + \frac{1}{2} K_{33} (\vec{n} \times \nabla \times \vec{n})^2.$$
(2)

This elastic energy is called also Oseen-Frank energy, and K_{11} , K_{22} and K_{33} are referred to as the Frank elastic constants. For 5CB at room temperature the values are $K_{11} = 0.64 \times 10^{-11}$ N, $K_{22} = 0.3 \times 10^{-11}$ N and $K_{33} = 1 \times 10^{-11}$ N.

2 Surface Anchoring of Liquid Crystals

In most technological applications of LCs, the liquid crystal is in contact with another substance. The contact can be either with air, liquid or solid substrate. Because the interaction of LC on the intereface, the LC can be oriented in the preferred direction¹. We distinguish three main types of orientation: homeotropic, planar and tilted.

2.1 Anchoring on a Anisotropic Surface

If the surface is anisotropic there is a preferred direction of LC molecules at the interface, referred to as the *easy axis*. The interaction energy is minimal when the liquid crystal director is pointing in the direction of the easy axis. However the direction of the director can be different in the bulk, which can also influence the director at the interface. So the director at the interface is not always parallel to the easy axis.

We define polar angle θ_0 and the azimuthal angle ϕ_0 for the easy axis (Fig 2). If $\theta_0 = 0$, the anchoring is *homeotropic*. If $\theta_0 = 90^\circ$ and ϕ_0 is well defined the anchoring is referred to as *homogenous planar*. If $\theta_0 = 90^\circ$ and there is no preferred azimuthal angle, the anchoring is called *planar*. If $0^\circ < \theta_0 < 90^\circ$ and ϕ_0 is well defined, the anchoring is *tilted*, whereas if there is no preferred azimuthal angle the anchoring is *conical*.

The liquid crystal director \vec{n} is pointing in the direction specified by the polar angle θ and the azimuthal angle ϕ . The mismatching of \vec{n} and easy axis gives rise to the anchoring energy function

¹Instead of using a substrate the LC can be also oriented using external field or flow of LC.



Figure 2: Schematic diagram showing the easy axis of the anchoring and the liquid crystal director. [1]

of the liquid crystal: $f_s = f_s(\theta, \phi)$. When $\theta = \theta_0$ and $\phi = \phi_0$, f_s has a minimum value of 0. For small deviations the anchoring energy function can be expressed as

$$f_s = \frac{1}{2} W_p \sin^2 \beta_p + \frac{1}{2} W_a \sin^2 \beta_a,$$
(3)

where β_p and β_a are the angles between \vec{n} and the easy axis when \vec{n} deviates from the easy axis only in the polar angle direction and azimuthal angle direction, respectively. W_p and W_a are the polar and azimuthal anchoring strengths. For small $\theta - \theta_0$ and $\phi - \phi_0$, we have the approximations $\sin^2 \beta_p \approx \sin^2(\theta - \theta_0)$ and $\sin^2 \beta_a \approx \sin^2(\phi - \phi_0) \sin^2 \theta_0$. Therefore the anchoring energy function is

$$f_s = \frac{1}{2} W_p \sin^2(\theta - \theta_0) + \frac{1}{2} W_a \sin^2 \theta_0 \sin^2(\phi - \phi_0).$$
(4)



Figure 3: a) Homogeneous and b) homeotropic anchoring. [1]

The direction of the easy axis and the strengths of the anchoring depend on the chemistry and the topology of the surface in contact with the LC.

Homogeneous anchoring can be achieved by mechanically rubbing the substrate, such as glass with a cloth. The rubbing creates micro grooves along the rubbing direction (Fig 3a). When the liquid crystal is aligned parallel to the grooves, there is no deformation. If the liquid crystal were perpendicular to the groves, there would be deformation, which costs elastic energy. Therefore the liquid crystal is homogeneously aligned along the grooves. The problem with alignment created in this way is that the anchoring strength (10^{-5} J/m^2) is weak. A better choice for the homogeneous alignment layer is rubbed polyimide. The rubbing not only creates the micro grooves but also aligns

the polymer chains. The interaction between the liquid crystal and the aligned polymer chains also favors parallel alignment and thus increases the anchoring energy. The anchoring strength can become as high as 10^{-3} J/m². Furthermore, pretilt angles of a few degrees can be made.

Homeotropic anchoring can be achieved using a monolayer of surfactants such as lecithin and silane. The polar head of the surfactant is chemically attached to the glass substrate and the hydrocarbon tail points out and perpendicular to the surface (Fig 3b). The intermolecular interaction between the surfactant and the liquid crystal promotes the homeotropic alignment.

2.2 Anchoring on a Isotropic Surface

Consider a LC in contact with an isotropic interface such as isotropic solid (e.g. glass), isotropic liquid (e.g. water) or as a free surface. It can also be in contact with gas or isotropic phase of the LC itself. The later is especially easy to describe, since there is no interaction with the substrate involved. The only thing that changes at this kind of interface is the density and the order parameter of the LC.

On a isotropic surface there are three possible types of anchoring: planar, homeotropic and conical. Homogenous and tilted anchoring are not possible for obvious symmetrical reasons. The planar anchoring is geometrically most reasonable with elongated molecules lying parallel to the surface. An example is a free surface of nCB or nCB in contact with clean flat glass or water. However in some cases the anchoring can be also homeotropic, as with nCB in contact with the solution of PSS or the free surface of PAA. Taking into account also the electrostatic interactions between the LC molecules and the substrate, we can get conic anchoring. This is the case of the free surface of MBBA or its nematic-isotropic interface. The angle of the conic anchoring at isotropic surface is very sensitive to temperature and surface contaminants. Experimental as well as theoretical results also vary with different authors [2, 3].

3 Thermodynamics of Liquid Interfaces

3.1 Isotropic Interface

We are now going to see how the surface tension changes with the composition. Consider a flat interface between two homogenous isotropic bulk phases. The energy of the surface is equal to

$$E^S = TS^S + \gamma A + \sum \mu_i n_i^S,\tag{5}$$

where T is the temperature, S^S is the entropy, γ is the surface tension, A is the surface area, μ_i is the chemical potential of the component *i*, and n_i^S is the corresponding particle density (surface excess). The superscript S means that only surface part is taken into account. Eq. 6 can be differentiated giving

$$dE^{S} = TdS^{S} + S^{S}dT + \gamma dA + Ad\gamma + \sum \mu_{i}dn_{i}^{S} + \sum n_{i}^{S}d\mu_{i}.$$
(6)

Taking into account

$$dE^S = TdS^S + \gamma dA + \sum \mu_i dn_i^S \tag{7}$$

we get

$$0 = S^S dT + A d\gamma + \sum n_i^S d\mu_i.$$
(8)

At constant temperature and rewriting the equation pre unit area we have

$$d\gamma = -\sum \Gamma_i d\mu_i,\tag{9}$$

where $\Gamma_i = \frac{n_i^S}{A}$. And finally we get the Gibbs equation

$$\Gamma_i = -\left(\frac{\partial\gamma}{\partial\mu_i}\right)_T.$$
(10)

It describes the relation between the surface tension γ , chemical potential μ_i and surface excess Γ_i per unit area.

3.2 Anisotropic Interface Plus a Surfactant

There are substantial differences in surfactants absorbed at a solid-LC interface and a soft interface between water and LC. At equilibrium, the chemical potential of a surfactant at a water-LC interface is determined by the composition of the surfactant in the bulk aqueous phase. Changes in selfassembly of the surfactants in the bulk solution cause changes in the organization of surfactant at the interface. In contrast, surfactants deposited at solid surfaces are not in equilibrium with a bulk surfactant phase. Another difference is that the mobility of surfactants at water-LC interfaces is substantially greater than the mobility of surfactants at solid-liquid crystal interfaces. The higher mobility permits reorganization and formation of domains in adsorbed monolayer of surfactants at the interfaces. The water-LC interface can also deform under the influence of stresses developed in liquid crystals, whereas solid surface can not.

Instead of an interface between two isotropic phases, one phase can be anisotropic (e.g. a LC). Surfactant molecules (amphiphiles) can absorb to this interface causing the LC to reorient. In the case of an anisotropic interface, the interfacial tension is equal to

$$\gamma = \gamma_{iso} + \gamma_{an} + \gamma_g + \gamma_s \tag{11}$$

where γ_{iso} is the isotropic interfacial tension used in Section 3.1, γ_{an} is the anchoring interfacial free energy density, γ_g is the gradient interfacial free energy density and γ_s is the interfacial free energy density associated with molecular order.

The gradient interfacial free energy density γ_g is given by

$$\gamma_g = \frac{1}{2} (K_{22} + K_{24}) \vec{k} \cdot \vec{g} \tag{12}$$

where \vec{g} is the surface gradient energy density vector

$$\vec{g} = (\vec{n} \cdot \nabla)\vec{n} - \vec{n}(\nabla \cdot \vec{n}). \tag{13}$$

However for our proposes we can neglect γ_g together with γ_s .

The anchoring interfacial free energy density is expressed as

$$\gamma_{an} = \gamma_2 \left(\vec{n} \cdot \vec{k} \right)^2 + \gamma_4 \left(\vec{n} \cdot \vec{k} \right)^4 = \gamma_2 \cos^2 \vartheta + \gamma_4 \cos^4 \vartheta \tag{14}$$

where \vec{n} is the LC director, \vec{k} is the normal to the interface and ϑ is the angle between \vec{n} and \vec{k} . The equilibrium, when the LC director is pointing in the direction of the easy axis (defined by ϑ^e) is given by

$$\left(\frac{\partial\gamma_{an}(T,\mu,\vartheta)}{\partial\vartheta}\right)_{T,\mu} = 0 \tag{15}$$

Using (14) and (15) we get

$$\sin(\vartheta^e)\cos(\vartheta^e)\left(\frac{\gamma_2}{2\gamma_4} + \cos^2(\vartheta^e)\right) = 0.$$
(16)

There are three stable solutions:

- 1. Planar anchoring: $\vartheta^e = \frac{\pi}{2}$ when $\gamma_2 > 0$ and $\gamma_4 < 0$,
- 2. Homeotropic anchoring: $\vartheta^e = 0$ when $\gamma_2 < 0$ and $\gamma_4 < 0$,
- 3. Conical anchoring: $\vartheta^e = \cos^{-1} \sqrt{-\frac{\gamma_2}{2\gamma_4}}$ when $\gamma_2 < 0$ and $\gamma_4 > 0$.

Ray [4, 5] showed that it is possible to express γ_2 and γ_4 as

$$\gamma_2 = \frac{\beta(T)}{\alpha(T)} (\mu - \mu^*) \tag{17}$$

and

$$\gamma_4 = -\frac{\beta(T)^2}{2\alpha(T)} \tag{18}$$

where the chemical potential μ^* corresponds to a surfactant concentration at which a transition in orientation of the liquid crystal takes place. Constants α and β are determined from the experiment and usually satisfy $\alpha > 0$ and $\beta < 0$. Taking into account this, one can see that γ_4 is always negative and that γ_2 changes with the concentration of the surfactant. If $\mu < \mu^*$ we have planar anchoring and if $\mu > \mu^*$ we have homeotropic anchoring. So with no surfactant present the anchoring is planar, but with sufficient amount of surfactant absorbed onto the interface the anchoring changes to homeotropic. We see that the conical anchoring is not possible in this simplified model. However in the experiments they observe continuous transition from planar trough conical to homeotropic anchoring when adding surfactant [6]. To describe this behavior we would need to take a more complex model and also to take into account the deformations in the bulk LC.

And finally we can calculate the surface density (interfacial excess) of the surfactant. We use Gibss equation at equilibrium $(\vartheta = \vartheta^e)$ and at constant temperature

$$\Gamma_i = -\left(\frac{\partial\gamma}{\partial\mu_i}\right)_{T,\vartheta^e} \tag{19}$$

and simplified interfacial tension (11)

$$\gamma = \gamma_{iso} + \gamma_{an} \tag{20}$$

where according to [4, 5]

$$\gamma_{iso} = -\mu \Gamma^* - \frac{(\mu - \mu^*)^2}{2\alpha}.$$
 (21)

Combining (14), (17), (18), (19), (20) and (21) we derive the interfacial excess

$$\Gamma = \Gamma^* + \frac{\mu - \mu^*}{\alpha} - \frac{\beta}{\alpha} \cos^2 \vartheta^e.$$
(22)

The result combines surface excess of the surfactant, its chemical potential and the easy axis direction.

4 LC Biosensors Based on LC Anchoring

Liquid crystal technologies are currently being developed for use as biosensors in a variety of systems such as observation of phospholipid interactions [7, 8, 6], protein binding [9] and virus detection [10]. Optical detection of biological materials has been achieved through the observation of local changes in the orientation of the nematic director of aligned liquid crystal in contact with a desired target. The biological target induces a local perturbation in the nematic director field, which is amplified through the long range orientational order of the liquid crystal. The perturbation of the director field results in a distinct optical signature under a polarizing microscope.

4.1 Hard Surface LC Sensors

Recently it has been demonstrated [11], that it is possible to change the anchoring of LC on a hard substrate by controlled absorbtion of target molecules. In order to achieve this, chemical receptors are attached to a rubbed substrate. These receptors weakly bind the LC molecules orienting them in a well defined direction. When target molecules are introduced into the LC, they bind more strongly to the receptors replacing the LC molecules. However nontargeted molecules bind the receptors more weakly than the LC molecules, so they do not replace the LC molecules. When LC molecules are not bind any more to the receptors, the LC tend to align parallel to the rubbing.

This kind of sensors can be used for the detection of air contaminants. The molecules diffuse from the atmosphere through the LC to the receptors. R. Shah, et al. reports detection of partsper-billion vapor concentrations of targeted low molecular weight molecules, including organoamine and organophosphorus compounds.



Figure 4: The competitive interaction of a LC and targeted low molecular weight compound for a molecular receptor hosted on a surface with nanometer-scale topography. (a) Orientation of LC molecules is determined by the binding to the receptors. (b) Upon addition of the target compound the LC molecules detach from the receptors and align in the direction of surface grooves (rubbing direction). [11]

4.2 LC-Water Interface Sensors

One drawback of hard surface LC sensors is that the target molecules must be soluble in LC. However most biological molecules are soluble in water, but not in non-polar solvents like LC. The solution is to use the interface between a LC (not soluble in water) and the water environment containing target molecules. Amphiphilic molecules such as phospholipids can bind to the interface, changing the anchoring (Fig. 5). However in this way we do not have selective detection, as all the amphiphilic molecules are going to be absorbed to the interface. Alternatively a monolayer of surfactant molecules can be made on the surface. If these molecules have specific binding sites, only target molecules will attach to them, changing their order or concentration (Fig. 6). This predictably changes the anchoring of the LC. It has been also shown that is possible to measure the pH of the solution by carefully choose the molecules absorbed on LC-water interface [12].



Figure 5: (a) Experimental geometry used to create stable interfaces between aqueous phases and LCs. (b) and (c) Optical images (crossed polarizers) of 5CB confined to a copper grid immersed in pure water (b) or an aqueous solution of 2.2 mM SDS (c). (d) and (e) Schematic illustrations of the director profiles of the LC corresponding to planar anchoring of the liquid crystal at the interface with the aqueous phase (d) and homeotropic anchoring (e). [6]



Figure 6: Instead of detecting the amount of absorbed surfactant molecules, they can be already present on the surface. Having specific binding groups, other molecules can attach to them, thus changing their order or concentration. This enables detecting specific non-amphiphilic molecules. [13]

4.3 Whispering Gallery Mode LC Sensors

The above described method of measuring the anchoring angle on a LC-water interface by just using cross polarizers is very simple, but inaccurate. The error in determining the tilt angle is as high as $\pm 10\%$ [14]. There are other very sensitive surface methods such as ellipsometry, but they require big and expensive equipment.

Tjipto et al. reported that it is possible to use the LC-water interface of LC droplets dispersed in water as sensors [10]. Dispersions of LCs in various materials, especially in polymers [15] are long known for their possible applications in LC display devices. Defined by the anchoring, the LC droplets can exist in different director configurations inside the droplet, which can be clearly distinguished under a polarizing microscope. But once more, one can not measure the anchoring angle, but only tell if it is planar or homeotropic.

Recently Humar et al. [16] showed that optical resonances called *Whispering Gallery Modes* (WGMs) [17] are possible inside LC droplets dispersed in water. WGMs are circulating wave modes formed as a consequence of total internal reflection on the LC-water interface². A fluorescent dye is dissolved inside the LC and the droplets are than illuminated by a laser or UV light. Peaks corresponding to WGMs can be easily observed in the fluorescence spectrum. Usually the WGMs have very high quality factors corresponding to very sharp resonance peaks. This is the reason why the position of the resonances can be determined very accurately. However the quality factor can be greatly reduced by the interface roughes, if large molecules or other particles attach to the interface, disturbing it. The quality factor is further decreased by index of refraction fluctuations caused by thermal fluctuations of LC director.

The position of resonant peaks is directly connected to the refractive index and the size of the droplet as

$$\lambda_{res} = \frac{2\pi rn}{l} \tag{23}$$

where λ_{res} is the resonant wavelength, n is the refractive index of the sphere, r is the radius of the spherical resonator and l is the mode number. Because WGMs are located very near to the surface of the resonator they are very sensitive to the local change in the index of refraction on both sides of the interface. Andrea M. Armani, et al. [18] demonstrated selective single molecule detection using WGM resonator. However extremely high quality factors and complex experimental setup is necessary for such detection.

In this seminar I present an alternative approach, using liquid crystal droplet as a resonator (Fig. 7). In this case, an molecule attaching to the resonator does not change the index of refraction only because its dielectric properties, but has an long range effect on other LC molecules. It reorients the LC molecules thus causing a change in the index of refraction of a large area on the resonator surface. A single molecule could in this way shift the resonance peak much more that with the existing WGM sensors. This means that a extremely high quality factor an big expensive equipment could not be necessary anymore. However, this principle has yet to be proven.

 $^{^{2}}$ LC has usually a higher refractive index than water, causing total internal reflection inside LC droplet.



Figure 7: Artist's conception of a whispering gallery mode biosensor inside a liquid crystal droplet. A green laser beam comming from above excites WGMs inside the nematic LC droplet which is floating in a water environment. Amphiphilic molecules attach to the surface of the droplet changing the director field of the LC. In this way also the detected WGM spectrum is changed enabling us to determine the number of attached molecules and indirectly their concentration in water.

5 Conclusion

Chemical sensors are very important in industry and science as also in everyday life. In recent times biosensors are gaining most attention and there are many research groups trying to make small, cheap and easy to use biosensors for various substances. Recently it has been shown that also sensors based on liquid crystals can be made. However, in my knowledge, there are no liquid crystal based commercial sensors, yet. What is more, there are just few articles in this field, mostly by Abbot et al. Nevertheless, this area seems to be quite promising, but a lot of research work has still to be done.

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