

Liquid Crystal Phase in DNA

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Abstract

Liquid crystal phase is an emergent phase in many of the condensed matter and biological systems it has properties between those of normal crystalline solid and liquid. In this paper a brief introduction to different types of liquid crystal ordering is given. Features and properties observed in liquid crystals are presented. The rest will discuss a specific system namely the liquid crystal phases due to the helix-helix interaction in DNA. Qualitatively I will argue that DNA in electrolyte solution should exhibit liquid crystal phase transition. Experimental results confirming the existence are presented. A theory based on mean field approach will also be discussed

1 Introduction

The study of DNA and its structure has been a major interest in Biology since its structure was identified by Watson and Crick. Initially each DNA molecules are thought as being free from each other but X-ray diffraction results from experiment done on DNA oligomers show significant deviations from that expected from ideal helices[1]. It was found that through helix-helix interactions, DNA molecules aggregate to form emerging liquid crystal phases. These emergent states are important since they provide understanding to many biological mechanism such as condensation and decondensation of chromosomes, protein folding, and collagen self-assembly[1]. Therefore understanding physics of DNA liquid crystals are crucial in our study of biological systems. I will first introduce different types of liquid crystal ordering,

order parameter, and their experimental signatures. Then I will describe a simple model of helix-helix interaction. I will also present some experimental evidences of an emergence of DNA liquid crystal phases.

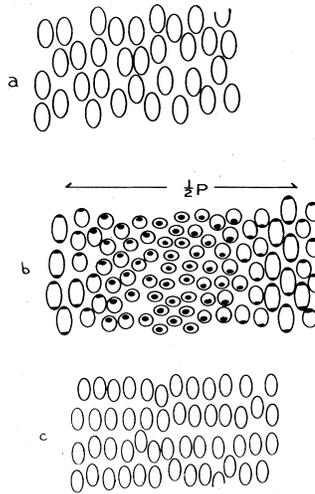


Figure 1: This figure illustrate the arrangement of molecules in different types of liquid crystals:(a) The nematic phase with same orientational arrangement but with no positional correlaton. (b) The cholesteric phase in which the director varies in a periodic manner with periodicity $p/2$ where p is called the pitch. (c) The smectic A phase has the following properties: molecules are oriented perpendicular to the planes but with no configurational order within the planes.[2]

2 Liquid crystals

Liquid crystal phase is a phase with properties borderline those of a liquid and of a crystalline solid as the name suggests. The properties are such as an ability to flow like a liquid, inability to support shear, and the formation of droplets. Its optical, electrical, and magnetic properties exhibit anisotropy which are signature of crystalline solids. An optical properties in particular birefringence is used to distinguish between different types of liquid crystals namely: nematic, cholesteric, smectics. These different phases will be discussed. The discussion on different liquid crystal phases will be paralleled to

that in ref.[1]. Liquid crystals can also be categorized into classes based on the principle parameters that are tuned in order to achieve the liquid crystal phase. The two classes we are interested in the context of this paper are thermotropic and lyotropic. Thermotropic class is obtained by controlling primarily temperature and also by controlling pressure accordingly. In lyotropic class the phase transition occurs not only as a function of temperature but also as a function of the concentration of the liquid crystal molecule in a solvent. I will present later in the paper that DNA packaging in vivo shows liquid crystal phases of this class.

2.1 Different types of liquid crystals

2.1.1 Nematic ordering

Nematic ordering is defined by a long-range orientational order and the lack of positional order. Broken rotational symmetry gives rise to anisotropy similar to solids however it lacks long-range positional order of the center of mass of the nematic molecules. The absence in translational order contribute to its fluid-like properties. Nematic molecules can be portrayed as collection of rods or ellipses with their long axis align in a preferred direction(fig.1). This preferred direction can be affected by external agents such as electric and magnetic fields. It is convenient to quantify a local preferred orientation by defining a unit vector field $\vec{n}(\vec{r})$. We call this a director[2]. Note that there is no preferential direction in the arrangement of the two ends of the molecules. This entails that the sign of the director is irrelevant. The nematic phase if observed through a cross-polarizer appears as threads. The nematic phase behaves optically as a uniaxial material with a center of symmetry([2]). This will be an important point in defining the order parameters.

2.1.2 Cholesteric ordering

The cholesteric phase is the same as the nematic phase in having orientational long-range order and the lack of long-range translational order. Therefore we can define similarly to the nematic case a director field. The only difference from the nematic order is that the director rotate around the axis perpendicular to the the long axis of the molecules. In any planes perpendicular to the axis of rotation the molecules align along a single preferred direction. This rotation is periodic with spatial period of $p/2$ where p is defined as the

pitch of the cholesteric. The twisting of the director field is illustrated as the black dots on (b) of fig.1. In the left and right clusters the director is in the y-axis while in the middle cluster it is in the z-axis. Optical investigation of the cholesteric shows the following: if the cholesteric is placed between tilted glass plates, one observes alternating patterns of dark and light stripes[2].

2.1.3 Smectic ordering

The main difference of the smectic from nematic is its stratifications. The molecules are arranged in multiple layers. In each layer, the molecules exhibit some positional order in addition to the orientational order observed in the nematic. There are many different classes of smectic phase. Class A smectic phase is illustrated in (c) of fig.1. The molecules are aligned such that the long axis is perpendicular to the layer but with no positional long-range order within the layer. An important feature is that the layers can slide freely from each other. There are many evidences from x-ray scattering showing the stratifications([2]. Nematic and smectic phases are categorized as thermotropic type with nematic phase occurring first at higher temperature. At high temperature the molecules are in the isotropic liquid phase. There is no preferred angle so the alignment is random. When the temperature cools down nematic phase emerges. As the temperature cools down further molecules separate into layers thus giving rise to class A smectic phase.

2.2 Order parameter

In this section for simplicity, we assume that the molecules can be modeled as rigid rods. First for the general case we can introduce a unit vector v^i that describes the orientation of an i th molecule. Since the rotational symmetry is broken it is tempting to define a vector order parameter equivalent to the magnetization in ferromagnet, $M = \langle S^i \rangle$. However the order parameter can not be defined in terms of this unit vector alone since we presented in section 2.2.1 that liquid crystals possess a center of symmetry. This results in the average $\langle v^i \rangle = 0$. From [2], the natural choice of the order parameter is

$$S_{\alpha\beta} = \frac{1}{N} \sum_i (v_{\alpha}^i v_{\beta}^i - \frac{1}{3} \delta_{\alpha\beta}) \quad (1)$$

where the sum is over all the N molecules in a small but macroscopic volume. This is a symmetric traceless second rank tensor therefore in general has five

independent components. For the case of nonlinear rigid molecules, the order parameter tensor is defined based on eq.1as

$$S_{\alpha\beta}(r) = \langle \cos \theta_\alpha \cos \theta_\beta - \frac{1}{3} \delta_{\alpha\beta} \rangle \quad (2)$$

Where it is averaged over the molecules in a small but macroscopic volume. This makes sense if θ is the angle between the molecular axis and the preferred direction. The order parameter defined here is needed to understand the Nuclear magnetic resonance (NMR) spectra of the nematics. Liquid crystal phases has an NMR spectra which differs from that of normal liquids. Because the molecules are oriented in a preferred direction, gives rise to dipole-dipole interaction that can shift the line-width of the spectra. To see this clearly we first look at the Hamiltonian for nuclear spins I_j in an external magnetic field H along the z direction.

$$H = - \sum_i g_i \beta_n H I_{iz} - \sum_{i>j} \left(\frac{g_i g_j \beta_n^2}{r_{ij}^3} \right) \times (3(v_{ij} \cdot I_i)(v_{ij} \cdot I_j) - I_i \cdot I_j) \quad (3)$$

where This equation is just the usual quantum mechanics spin in a magnetic field Hamiltonian plus the semiclassical dipole-dipole interaction. In liquid crystals we consider the molecules as rigid rods with two identical nuclear spins distance a apart. The first order correction is

$$H_1 = - \left(\frac{g^2 \beta_n^2}{a^3} \right) (3v_z^2 - 1) (I_{1z} I_{2z} - \frac{1}{4} (I_1^+ I_2^- + I_1^- I_2^+)) [2] \quad (4)$$

$I_+/-$ is the the usual spin raising/lowering operator. If $I=1/2$ then with some algebra

$$\hbar \delta \omega = \frac{3}{2} \left(\frac{g^2 \beta_n^2}{a^3} \right) \langle 3v_z^2 - 1 \rangle \quad (5)$$

The average is over all the configuration in phase space. Since in liquid crystals the relaxation time for the molecule to reorient itself it really short the average depends on the mean molecular orientation hence it propotional to the order parameter we calculated earlier. Finally it is important to note that in real liquid crystals the molecules are not rigid but flexible. For this case, it was suggested by de Gennes([2]) that the definition of parameter can be modified so that it depends on the thermodynamic quantity. This modification helps avoid having to define different order parameter tensor for

different parts of the molecule. The order parameter tensor can be defined as the anisotropy in diamagnetic susceptibility

$$Q_{\alpha\beta} = \chi_{\alpha\beta} - \frac{1}{3}\delta_{\alpha\beta}\chi_{\gamma\gamma} [2] \quad (6)$$

In this section we can conclude that liquid crystal ordering emerges in a system of rigid rods that strongly interact with each another.

2.3 Landau theory

For current discussion we limit the scope to the nematic phase. By assuming that the free energy is an analytic function of the order parameter and considering the symmetries in the system, we can write down the free energy expansion similar to what we did in class.

$$F = F_i + \frac{1}{2}AS_{\alpha\beta}S_{\alpha\beta} - \frac{1}{3}S_{\alpha\beta}S_{\beta\gamma}S_{\gamma\alpha} + \frac{1}{4}CS_{\alpha\beta}S_{\alpha\beta}S_{\gamma\delta}S_{\gamma\delta} - \frac{1}{2}H_\alpha S_{\alpha\beta}H_\beta \quad (7)$$

where A, B, C are coefficients that depend on pressure and temperature. F_i is the free energy of the isotropic phase. These terms are allowed since the free energy must be invariant under the rotation of the rigid rods. The last term is due to external an magnetic field. To demonstrate that phase transition is possible, we work near the critical temperature T_c .

$$A = A'(T - T_*)$$

From ref[1] and eq.7 we show that for uniaxial liquid crystal in an absence of external fields.

$$S_{\alpha\beta} = S(n_\alpha n_\beta - \frac{1}{3}\delta_{\alpha\beta}) [2] \quad (8)$$

$$F = F_i + \frac{1}{3}AS^2 - \frac{2}{27}BS^3 + \frac{1}{9}CS^4 \quad (9)$$

Equation of motion can be solved by minimizing the free energy. We obtained two solutions:

$$S = 0 \quad (10)$$

$$S = (B/4C)(1 + (1 - 24\beta)^{1/2}) \quad (11)$$

where $\beta = (B/4C)$. The first solution is clearly an isotropic phase in which the order parameter while the second one is a nematic phase [2].

3 DNA

In the past section a brief introduction to the general properties and features of liquid crystals is given. The connection between liquid crystals and phases of aggregated DNA will be qualitatively argued. Watson and Crick discovered the double-helix structure of DNA by analyzing the x-ray diffraction pattern. They found that DNA are composed of two helical chains with sugar-phosphate chain from the backbones. Genetic information is carried in the base pairs. There are four different base pairs: adenine, cytosine, guanine, and thymine. Two strands are linked by hydrogen bonds between the base pairs. The hydrogen-bonded base pairs end up forming the core of the DNA polymer. There are several isomers. The most common ones are the right-handed A-DNA, right-handed B-DNA, and the left-handed Z-DNA([1]). The analysis is based on the Cochran-Crick-Vand (CCV) theory. This theory states that the x-ray scattering intensity is

$$I(k) = \sum_{\nu,\mu} \sum_{i,j} f_i f_j \langle F_i^\nu(k) F_j^\mu(-k) \rangle \quad (12)$$

in momentum space. k is the scattering wave vector and f_i is the scattering amplitude where i denotes different type of center for example phosphate, carbon, oxygen, etc. F is the fourier transformed of density of scattering center.

$$F_i^\nu(k) = \frac{1}{(2\pi)^{3/2}} \int n_i^\nu(r) e^{ik \cdot r} d^3r \quad (13)$$

We switch to cylindrical coordinates. The axis is chosen to coincide with the main axis of the molecule. According to the result from [1] the structural factors for ideal helical chains on DNA are given as

$$s_{p,p}^{\nu,\mu}(k_z, n, m) = \frac{N_p^2}{\pi^2} \cos n\tilde{\phi}_s \cos m\tilde{\phi}_s \sum_{i,J=-\infty}^{\infty} \delta_{k_z, G_j - g_n} \delta_{m, n + JG/g} [1] \quad (14)$$

Where N_p is the total number of phosphates on each strand. $G = 2\pi/h$, $g = 2\pi/H$. h is the axial rise per residue, H is the pitch of the helix(the derivation can be found in [1]). CCV was used to interpret the x-ray diffraction pattern(experiment by Franklin and Gosling, 1953). CCV explains the experimental results really well based on the assumption that DNA chains are independent of each other. However the atomic resolution structures of DNA oligomers were obtained by Dickerson and Drew in 1981(ref.[1]. The

structural parameters are found to be dependent on the sequence of the base pairs. This is puzzling since the high density result obtained earlier agrees well with the non-interacting assumption. This suggests that there must be interaction between segments of DNA results in non-trivial aggregation of DNA molecules.

3.1 Interactions

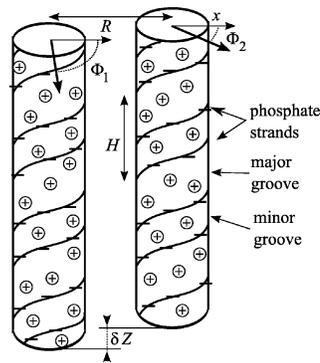


Figure 2: DNA strands are represented as ideal negatively charged phosphate backbone and positively charged surface[1]

In last section experimental results suggest that there must be some form of interactions between neighboring DNA segments. This makes sense since we know that DNA chains are composed of highly charged atoms. The main interaction concerned here is a coulombic interaction between the two strands. There are other factors involved such as elasticity of the rods but in this paper we neglect all such effects. Elasticity of DNA strands are discussed in ref[1]. We take the simplest model of DNA segments as rigid charged rods. This is illustrated in fig. 2. However even for this simple case solving exactly electrostatics problems of charged molecule in electrolyte solution(in this case it is water) is an extremely difficult task. Therefore we employ Poisson-Boltzman (PB) theory. PB equation goes as follow.

$$\nabla^2 \phi(r) = -4\pi \frac{\rho_{ext}(r)}{\epsilon} - 4\pi \frac{e}{\epsilon} \sum_i n_i q_i e^{\frac{-e q_i \phi(r)}{k_B T}} \quad (15)$$

This is a statistical modification of Poisson equation. The extra term suggests that number of electrolyte ions is coupled to the averaged field (mean-field)

potential $\phi(r)$. This holds when fluctuation of ion density and ion-ion correlation are negligible. This is a sensible condition for mean-field approximation to hold. This model is used to compute the counterions distribution near the DNA. It agrees well with the experiment in the regime of small electrolyte concentrations([2]).

3.2 Experimental evidence of DNA liquid crystal phases

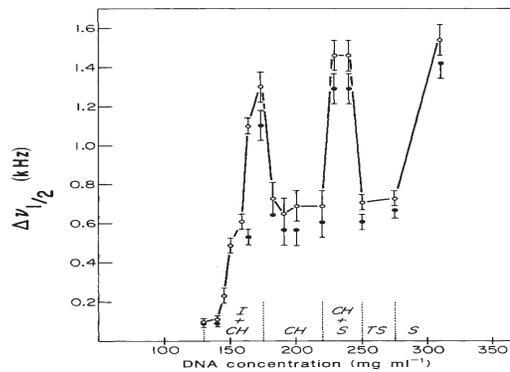


Figure 3: The graph shows NMR linewidth with respect to different DNA concentrations. The graph suggests many phase transitions into liquid crystals[3]

From the phenomenology arguments presented earlier, it is possible for DNA macromolecules to have a liquid crystal phase. An experiment is done by T. E. Strezelecka, M. W. Davidson and R. L. Rill to show this. The experiment is done in high concentration DNA in vivo. The volume concentration nearly 70 percents w/v in sperm heads, virus capsids, and bacterial nucleotides([3]). Their results show that DNA forms at least three liquid crystal phases. The optical texture of these phases are shown in fig.4. These optical textures taken using polarized light microscopy shows that there are anisotropy in the aggregation of DNA molecules. Sample of 100 mg/ml DNA is placed in the 0.25 M amonium acetate was placed on a partially sealed coverslip to create continuous concentration gradient[3]. This agrees with what we discussed earlier in section 2 on the properties of liquid crystals. The NMR spectra perform in high concentration DNA vivo shown in fig.3. The graph shows the shift in line-width vs the change in DNA concentration.

From the discussion on NMR in section 2 we know that at three different concentrations there are frequency shifts. These shifts are proportional to nonzero anisotropic order parameters. Hence there are three different lyotropic liquid crystal phase transitions.

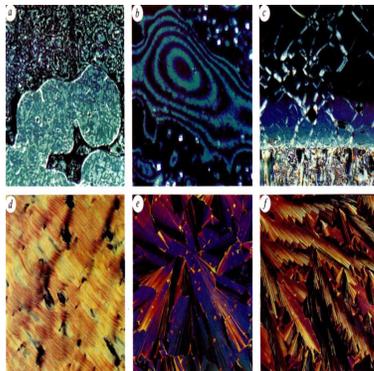


Figure 4: Optical textures of liquid crystalline phases acquired using polarized light microscopy. There are cholesteric and smectic-like domains, pre-cholesteric phase, and cholesteric phase.[3]

4 Summary

We start by introducing different types of the liquid crystal phase, their properties and experimental signatures. In order to argue that DNA in electrolyte solution can exhibit liquid crystal phase transition, phenomenological inputs are drawn from experimental results and simple models of DNA molecules. Watson and Crick shows that DNA molecules are rods of double-stranded helical molecules. Diffraction experiment on oligomers points out that DNA molecules are far from ideal non-interacting molecules. They are interacting and aggregate in a non trivial manner. The experiment done by T. E. Strezlecka, M. W. Davidson and R. L. Rill gives many evidences: optical texture and frequency shifts in NMR spectra. By comparing this to the features and experimental signatures of liquid crystals we can conclude that DNA in a high concentration solution exhibits liquid crystalline phases.

References

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