Chapter 1

INTRODUCTION TO THERMOTROPIC LIQUID CRYSTAL PHASES

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1. Introduction

The basic features that distinguish the various liquid crystalline phases from the other condensed phases will be given, and the type of chemical compounds will be discussed. The various types of thermotropic mesophases formed from rod-like molecules will be described in some detail and the order parameters that characterize them will be defined. Apart from the nematic phase, that is characterized by orientational order and translational symmetry of the molecular positions, various types of smectic phase can be distinguished. Their common feature is the existence of a one-dimensional density wave. Additional symmetry properties distinguish the different types of smectic phase. Thermotropic mesophases with disc-like molecules can also lead to a nematic phase. Reduced positional order now gives so-called columnar phases. The analogies and differences with the phases of rod-like molecules will be discussed. Both symmetry elements can be combined in lath-like molecules, leading to possible transitions between the two types of phase. In the first Chapter of this section a short overview of the various types of liquid crystals that can be observed will be given, including a discussion of the types of molecules from which they can be formed. In addition the order parameters of the most relevant phases will be defined. Emphasis will be on the smectic phases, anticipating what I suppose might be relevant to other lectures in this school. I will restrict myself to thermotropic liquid crystals (for which temperature is the important variable for the phase behaviour), and will not consider lyotropic liquid crystals (for which the variation of concentration in a solution is a dominant aspect). In spite of their increasing importance liquid crystalline polymers will also not be included. The latter subjects will be well covered in various other lectures at this school. I will rely to some extend on the treatment given in Ref.1, where also further references can be found. The two following Chapters will be referred to as Chapter 2 and 3, respectively.

2. Orientational Order: the Nematic Phase

In order to start at the very beginning I recall that a solid crystal is characterized by
long-range positional order. In the case of anisotropic molecules in addition there will be long-range orientational order: the various directions that can be assigned to a molecule will be retained throughout the lattice. Realising this distinction it is evident that not necessarily both types of order disappear at the same melting point. This leads to the following possibilities.

- **Plastic crystalline phases**, in which the positional order is still present, but the orientational order has disappeared or is strongly reduced.
- **Liquid crystalline phases**, characterized by orientational order, while the positional order has disappeared or is reduced.

I will describe first the nematic phase that occurs for substances that have (very roughly) a rod-like or a disc-like shape. It is characterized by a complete loss of positional order at the melting point, so that the centers of mass have translational symmetry as in an isotropic liquid. However, the unique axes of the molecules remain, on average, parallel to each other, leading to a preferred direction in space. This local direction of alignment can be described by a unit vector \( \mathbf{n} \), the director. The states described by \( \mathbf{n} \) and \(-\mathbf{n}\) appear to be indistinguishable. The actual orientation of the director is imposed by boundaries and/or external fields. In the simplest case this leads macroscopically to an axis of uniaxial symmetry. This orientational order disappears only when on increasing the temperature a second transition point is reached. Fig. 1 gives an 'artists view' of the nematic phases of rods and discs, respectively. These objects are far from the exact structure of nematogenic molecules, of which examples of the elongated type are given in Table 1. Note the last two examples that indicate that completely non-polar molecules can form a nematic phase.

To consider the most basic aspects of defining a nematic order parameter let us stick to the simplication of a molecule as a rigid rod. The (lack of) validity of this assumption will be discussed extensively in Chapter 2. To define the local orientation at a point \( r=(x,y,z) \) we attach to the rod a unit vector \( \mathbf{a}(r) \) along the long axis. Now consider the thermal averages of various tensors that are composed of \( \mathbf{a} \), over a small but macroscopic volume around \( r \). As the average \( \langle \mathbf{a} \cdot \mathbf{a} \rangle \) is a constant by definition, it is clear that a scalar order parameter is out of the question. The next choice is a vector order parameter \( \mathbf{a} \) analogous to the magnetization in a ferromagnet. However, a non-zero value of this quantity would violate the equivalence of \( \mathbf{n} \) and \(-\mathbf{n}\). It would describe a ferromagnetic nematic state that has not been observed.

The first relevant choice as order parameter is a second-rank tensor \( \mathbf{S} \), the elements of which are given by

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![Fig. 1. 'Artists view' of: (a) a positive uniaxial nematic phase of rods; and, (b) a negative uniaxial nematic phase of discs.](image)