Condensed Phases

Condensed Phases is the general description given to states of matter in which the molecules are close to each other. That is, everything except gases and supercritical fluids (dense, high-temperature gases). Condensed phases form because of attractions between the atoms, ions, or molecules that make them up. We have already looked at some classes of crystalline solids:

- Ionic Solids (salts). These form because of attractive electrostatic interactions between cations and anions. As an attraction, this lowers potential energy.
- Covalent (Network) solids. These form due to electron delocalisation into covalent bonds between atoms. Bond formation lowers the total energy.
- Metals. These form due to electron delocalisation throughout the material.

Molecular Solids

These crystalline solids overlook a huge and important class of condensed phases whose properties depend on other kinds of intermolecular attractions.

Atomic and molecular solids are made up of discrete molecules held in their positions on the crystal lattice by a variety of other attractive forces. We have seen how bonds, functional groups, and entire molecules may have dipoles. These lead to weaker interactions than those between ions, but are still electrostatic in origin.

Two other important classes of intermolecular attractions will be discussed later. These are Hydrogen Bonds and Dispersion Forces.

The structure of these solids depends on both the shape and the nature and strength of the intermolecular attractions between the molecules.
Solids, Liquids and Gases

The normal sequence of phases we expect to see on warming is

Solid ® Liquid ® Gas

The melting transition from solid to liquid is not a good way of measuring intermolecular forces, as the molecules are held together by attractive forces in both phases. In order to get an idea of the strength of the interaction, we need to separate the molecules. This requires a transition to a gas, i.e.

Liquid ® Gas (vapourisation or boiling)  
Solid ® Gas (sublimation)

Low boiling or sublimation points indicate weak intermolecular interactions, and high boiling points strong ones.

Melting points Solid ® Liquid can only be used as a rough guide, as the melting point must be below the boiling point.

Intermolecular Forces

1. Non-polar atoms and molecules
   Low boiling points E.g. Ar $T_b = 87K$; N$_2$ $T_b = 77K$

2. Polar molecules
   Broad range of boiling points depending on attractions. (More details later)
   E.g. Propane $T_b = 231K$; chloromethane $T_b = 249K$; acetonitrile $T_b = 392K$.
   Boiling point increases with increasing dipole moment of molecule.

3. Metals
   High ® very high boiling points. (Only Hg and Ga liquid near room temp.)

4. Salts
   Very high boiling points. Extremely difficult to put an ion into the gas phase.

5. Network Solids
   Very high boiling points. You have to break covalent bonds to make a vapour.

Liquids

Most molecules form liquids when they melt. That is, a disordered isotropic structure. A simple view of melting is that enough thermal energy is provided to shake the molecules off their lattice points.

This raises an important point about materials that we often overlook. The atoms and molecules are constantly moving.

In solids, atoms and molecules vibrate around their equilibrium position on the crystal lattice. Packing is determined by molecular shape.

In gases they move ballistically (translation) and tumble (rotation), as well as vibrating internally. The mean free path between collisions in a gas is long. Shape doesn’t matter much.

In liquids they collide with their neighbours, so their motion is not ballistic but diffusive. (Molecules wobble their way through the crowd.) They also vibrate and rotate as they move.

In liquids, rotations, vibrations, and flexibility smear out the effects of shape, so that most molecules “act like spheres.”
Liquids versus Liquid Crystals

Benzene melts from the crystal into a liquid. Although its aspherical shape allows it to interact with a receptor, in the liquid it adopts an isotropic structure by rotational motions.

However, more anisotropic molecules can form liquid crystals due to anisotropic interactions with their neighbours. The molecule p-azoxyanisole (PAA, below) does not melt directly into a liquid state, but instead forms a nematic phase.

Nematic Phase

The nematic phase of PAA is an example of a thermotropic liquid crystal, a liquid crystal formed by heating. (The other kind is a lyotropic liquid crystal, formed by mixing with a solvent.)

In a nematic phase, the molecules exhibit preferential orientation in a particular direction. The long axes all point in roughly the same direction. This requires the molecule to be both elongated and rigid. e.g., PAA and other nematic phase formers have highly delocalised MO's.

Further heating increases the tumbling and induces a conventional (isotropic) liquid.

Smectic or Layered Phases

Rigid rod-like molecules also form liquid crystals with positional as well as orientational order. These are called smectic phases, and form at lower temperatures than nematic phases.

In a smectic phase, the molecules are aligned but also organized in layers. This is due to packing of the rigid groups and also due to some entanglement and intercalation of the flexible alkyl chains.

In the smectic A phase, the molecules are layered and oriented on average normal to the layers.

In the smectic C phase, the molecules are layered and more highly oriented at an angle to the layer normal.

The normal sequence (if all phases are present) is

Solid → Nematic C → Smectic A → Nematic → Liquid
Properties of Liquid Crystals

The molecular alignment in liquid crystals gives rise to a number of properties intermediate between liquids and crystals that are technologically important.

1. Flow behaviour
   Liquid crystals are often quite viscous, but do flow. They can be poured into moulds and take on the shape of the container, or spread into thin films.

2. Optical Characteristics
   Liquid crystals interact differently with light of different polarisations. Because the molecules are all aligned, the electrons are not distributed isotropically as they are in the liquid state. This has two consequences
   - Polarised electronic spectroscopy. The UV absorbance spectrum depends on the orientation of the electric field (polarisation) of light with respect to the molecular axis.
   - Birefringence. The refractive index of light transmitted through a liquid crystal also depends on its polarisation. This also occurs in anisotropic crystals.

Optical Textures in Liquid Crystals

The large scale structure of liquid crystals is similar to that of a powdered solid. They consist of domains of similar orientation. However because of the less highly-developed order, the domains and molecular orientations are flexible. This can lead to a combination of effects including structural defects. In stiff, highly-ordered smectic phases these look like tears under a polarising optical microscope.

In the more fluid nematic phases the optical texture is more "gentle."

Liquid Crystal Displays

Nematic phases are quite fluid, so the molecules can re-orient and align themselves quickly in a magnetic or electric field. When there is no applied field, they align with structures on the surface of their container.

In a twisted Nematic LCD, the surfaces of each pixel are set up so that the orientation of the molecules twists in a slow helix to match the orientation of both surfaces. Polarized light shines in, and it's polarization is rotated with the molecules, allowing it to pass through a cross polarizing filter on the other side.

When a field is applied, the molecules align, and the polarization of the light is no longer affected, so it is stopped by the cross polarizing filter.
Liquid Crystal Displays

Smectic phases are in general too stiff to re-orient quickly enough for use as a display. Instead some smectic LCDs use local heating to induce phase transitions.

Such processes are sometimes much slower to switch, but allow an image to be displayed for longer on a display, without maintaining a field.

Colour displays can be achieved in both of these implementations simply by including dye molecules into either of the liquid crystals in various pixel elements, or adding a colour filter before the sample.

Some colour displays are constructed using optical interference effects, but these are outside the scope of this course.

Lyotropic Liquid Crystals

Lyotropic liquid crystals are formed from aggregates of smaller molecules in a solvent, usually water. They are also a direct consequence of molecular shape and intermolecular forces, but in this case molecular shape determines the aggregates formed, and the aggregate shape defines the liquid crystal.

Lyotropic liquid crystals are formed by amphiphilic molecules. These are molecules that contain water-soluble (hydrophilic) and water-insoluble (hydrophobic) groups. This class of molecules includes soaps, detergents, and biological lipids.

The oleate anion (a soap)

The dodecylsulfate anion (a detergent)

Amphiphilic molecules aggregate into spherical, cylindrical, or planar (bilayer) structures according to the shape of the molecule. Molecules with large hydrophilic (‘head’) groups form spheres, and those with small heads form bilayers.

These aggregates then organise themselves into structures known as cubic phases (spheres) and hexagonal phases (cylinders).
Summary

- You should now be able to
describe nematic and smectic A & C
thermotropic liquid crystals
describe cubic, hexagonal and lamellar lyotropic
liquid crystals
explain the general features of the liquid crystal
state, and distinguish between lyotropic and
thermotropic lc’s, and a simple liquid.
describe how lc’s can be used to generate
displays
relate intermolecular forces to boiling points