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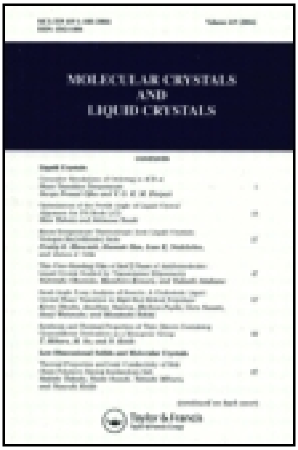

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II. Nematic and Smectic Phases of Higher Order

HANS ZOCHER

" Phases of higher order " or " superphases " are homogeneous systems in thermodynamic equilibrium as are ordinary phases. They are distinguished by the size of their structural elements and by the nature of the forces determining the equilibrium. The size is that of colloidal particles, that is of 10^{-5} up to 10^{-7} cm; the equilibrium is determined by electric forces arising from surface charges and ionic double layers. This indicates that the immersion medium is mainly water, which is able to produce high surface charges and notably thick double layers on account of its exceptionally high dielectric constant.

Usually such systems are considered to consist of two phases, water and colloid. But the concept of homogeneity, basic for the thermodynamic definition of phases, implies the structural identity of all parts of the system, maintained by the thermodynamic equilibrium, the reversibility of transformations. In the definition of a phase there is no limitation either in relation to the size of the structural elements, or to the nature of the forces governing the equilibrium. So it may be that the same system is to be considered as biphasic for dimensions smaller than 10^{-4} cm, but as one phase for macro- and microscopic dimensions larger than 10^{-4} cm.

The first examples of such phases found by the author[1] were of nematic and smectic structure. They were called " tactosols ", colloidal solutions with mutually ordered particles. In the last decade several examples of crystals were discovered which exhibit bright interference colours instead of X-ray interferences: the tipula iridescent virus,[2] lattices of high polymers,[3] colloidal tungstic acid and lepidocrocite.[4] They are all of the same nature as the nematic and smectic superphases and there is no doubt that they are to be considered as crystals.

Consequently one has to state that besides the classic series of amorphous, nematic, smectic and crystalline phases there exists another, characterized by a superimposed structure repeating the same principles of aggregation on particles larger than normal molecules and maintained in thermodynamic equilibrium by electric surface forces.

The so-called coacervates may be considered as amorphous phases of this type. They too are characterized by a medium state of charge of the colloid.

With regard to the close analogy it seems to be inevitable to include the nematic and smectic superphases into the realm of liquid crystals, though their physico-chemical nature is very different from that of the relatively low molecular organic substances exhibiting mesophases. The latter are obtained by changing temperature or concentration, the former by the variation of concentration only. Their stability in general is not very high. They are sensitive against electrolytes and changes of pH. They are distinguished by the nonspherical shape of the elementary particles which may be crystallites or virus particles. Nematic superphases are built up of needles or threads, smectic superphases of leaflets or of rodlets of equal length aggregated into layers.

Just as the number of substances occurring as common mesophases is small compared with the vast number of organic substances, the examples for nematic and smectic superphases are very rare compared with the common type of liquid crystals. Nematic superphases are known from vanadium pentoxide,[1] γ-aluminium hydroxide (γ-AlOOH or Boehmite),[5] β-FeOOH (Akaganeite), some dyestuffs such as benzopurpurine,[1] the tobacco mosaic virus (TMV) and similar viruses,[6] and the sickle cell hemoglobin. A certain difference exists relative to the shape of droplets (tactoids) surrounded by the amorphous phase. They are not spheres as in lower molecular nematic phases, but spindle-shaped. This is the consequence of the relatively lower surface tension, not high enough to subdue completely the elastic resistance against deformation of the anisotropic interior. Some authors have assumed that the surface tension here is anisotropic, but that it can never be since this " tension " is an energy, a tensor, and no vector. More complicated structures show the nematic discontinuities corresponding to nemas of the symbols ± 1 and ± 2.

Examples of smectic superphases are known for colloidal tungstic acid[7] and colloidal γ-FeOOH (lepidocrocite)[1,4] obtained by hydrolysis of a diluted solution of ferric chloride. In both cases the particles are rectangular leaflets and the smectic phase may transform into orthorhombic supercrystals. Single droplets of the smectic γ-FeOOH, surrounded by the amorphic phase, could be observed sometimes[1] in the shape of cylinders with the colour reflecting layers parallel to the basis. Mostly this phase appears as intensely iridescent sediment of the green of the second order, traversed by dark curved lines of discontinuity. This can be seen in the microscope in reflected light on the bottom of the vessel, or macroscopically with the aid of a mirror. The order of the interference colour may be determined by the variation of the angle of incidence.

A smectic superphase, built up by TMV rodlets aggregated into uniform layers in parallel position was found by Oster.[8] An aggregation of β-FeOOH needles into leaflets is regularly obtained too by heating to 60 °C a 0.2 molar solution of $FeCl_3$ with 2 equivalents of ammonium carbonate for several days. The needles themselves are of strong positive birefringency and dichroism, while the leaflets show a weaker negative anisotropy. But the surface charge is evidently too small to aggregate the leaflets into a smectic superphase. Dilution produces peptisation into the needles.

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