

LES ÉTATS MÉSOMORPHES DE LA MATIÈRE

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INTRODUCTION

Je désignerai sous ce nom les états particuliers que présentent les corps signalés par Lehmann à partir de 1889 sous les noms de *cristaux liquides* ou *fluides cristallins*. Sur la foi de ces dénominations, très malheureuses mais sans cesse répétées depuis trente ans, beaucoup de gens s'imaginent que les corps si curieux sur lesquels Lehmann a eu le grand mérite d'attirer l'attention, mais qu'il a eu le tort de mal nommer, ne sont autre chose que des substances cristallisées, différant simplement de celles qui étaient antérieurement connues par leur degré plus ou moins grand de fluidité. En fait, il s'agit de tout autre chose, et de quelque chose d'infiniment plus intéressant que ne seraient de simples cristaux plus ou moins fluides.

Mettons à part l'iodure d'argent cubique, que Lehmann a joint à tort aux corps que nous proposons d'étudier ici, et qui est tout simplement cristallisé, sans rapport aucun avec les autres « cristaux liquides ». Il n'est d'ailleurs nullement liquide, mais seulement plastique, comme beaucoup d'autres corps cristallisés. Sous cette réserve, les corps de Lehmann ne sont ni des cristaux ni des substances cristallisées. En les nommant cristaux ou en leur appliquant l'épithète de cristallisé on ne donne aucune idée de leurs propriétés. *Ann. de Phys.*, 9^e série, t. XVIII (Novembre-Décembre 1922) 19

THE MESOMORPHIC STATES OF MATTER

by
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Introduction

I use the term mesomorphic to designate those states of matter observed by Lehmann in the years following 1889, and for which he invented the terms *liquid crystal* and *crystalline fluid*. Lehmann had the great merit of drawing attention to these materials, but he erred greatly in naming them. The unfortunate names have been repeated again and again over the last 30 years. As a result many people suppose that these substances are merely crystalline materials, albeit rather more fluid than those hitherto known. The exact opposite is the case. Indeed, these materials are infinitely more interesting than they would be if they were simply crystals exhibiting some unexpected degree of fluidity.

Let us put to one side the cubic silver iodide which Lehmann incorrectly regarded as one of the substances which we propose to discuss here. This is simply a crystal, without any connection with the other 'liquid crystals'. This material is, by the way, not liquid at all, but merely plastic, like many other crystalline materials. Subject to that reservation, Lehmann's materials are neither crystals, nor crystallised substances. By calling them crystals, or by applying to them the epithet crystallised, one gives no hint of their properties. These properties are entirely different from those of substances which usually carry this designation. On the other hand, the terms 'liquid' or 'fluid' must not be taken to carry their usual meaning in this context. The majority of Lehmann's materials, it is true, are quite fluid indeed, certainly as fluid as water. But there are some whose structure does not differ in any way from the others, but which are nevertheless obviously solid. It is sufficient to use as an example ordinary soap in cake form. It is known, besides, that physics is unable to fix a natural boundary, a discontinuity between the solid and the liquid state. What characterises Lehmann's materials is not their state, which is more or less fluid. It is their special structures. There are only a small number of structural types and they are always the same. Everything that

follows will, I hope, show that the Lehmann materials constitute two completely new forms of matter. These are separated, without exception, from the crystalline and amorphous forms by discontinuities, in the same way that these two forms are separated from each other by a discontinuity. These two new forms themselves possess some common properties. It will be necessary from time to time to concatenate them under a single banner, but they are distinctly different from each other, and can be present in the same body. They are separated from each other, without exception, by a discontinuity. Before Lehmann's time it was not known that the two very general crystalline and amorphous forms of matter corresponded to two types of molecular structure. Nowadays, in admittedly a relatively small number of materials of a very special chemical type, two more are known. These correspond to special types of structure, neither crystalline nor amorphous.

However distasteful one finds the coining of new terms, it should be seen that it is absolutely necessary in these circumstances to find an adjective which unambiguously describes all these forms. This will be the analogue of the adjectives crystallised (or crystalline) and amorphous, which are used to describe the forms, substances, phases and so on which were already known.

The terms 'birefringent liquids' and 'anisotropic liquids' are generally used by those people who have not accepted the identification of the Lehmann materials with crystals. They are inadequate because some of these materials are not liquids. In addition, the birefringence, and in general the anisotropy, although remarkable, are not what is most special about these materials. These properties are also associated with crystalline substances, and can also occur in amorphous substances either subject to mechanical forces, or subject to a magnetic or electric field, or even permanently when they are solid. What is required is a language which absolutely eliminates all these possibilities.

Without exception, the regions of stability of the two new types, in any given material, come between the crystalline region of stability at low temperatures and the amorphous region of stability at higher temperatures. Similarly, their molecular structures form an intermediate stage between perfectly ordered periodic crystalline structure and the completely disordered amorphous structure. For these two reasons the term *mesomorphic* seems to be appropriate. No doubt it would have been preferable to have found a term like 'crystallised', linked to a very ancient usage, completely devoid in itself of any meaning which could make it one day inappropriate in the light of new facts. Nevertheless, the term seems vague enough to avoid any embarrassment.

On the other hand, and for the same reasons, we will have to be able to describe the two mesomorphic forms separately. The distinction between them was recognised by Lehmann almost right at the beginning of his discovery. He called the first 'Fliessende Krystalle', or 'Schleimig flüssige Krystalle' (flowing crystals, or slimy liquid crystals), and the other 'Flüssige Krystalle', or 'Tropfbar flüssige Krystalle' (liquid crystals, or drop-forming liquid crystals), thus attributing an exaggerated importance to the latter's normal degree of

fluidity.¹ On the other hand, although he did notice a difference between the two types, he was sure that they were two variations of one and the same thing. This he wanted to call a 'crystal', even though he realised that it did not possess a periodic structure. He was inventor of the term 'liquid crystal', and was aware of the striking effect that this association of words could have, and indeed unfortunately did have, on many people. He did not, however, know how to escape from this awkward concept, and too often described the properties of the two types in a confused way.

Actually, as we shall see, there is a strict distinction between the two types. What constitutes the essential difference between them is not the degree of fluidity but the structures. Having recognised this, Grandjean and G. Friedel called materials of the first type 'conic section liquids', because of the role played in their structure by groups of focal conics. In a similar way, they called those of the second type 'thread-like liquids' (*liquides à fils*) or 'liquids with nuclei' (*liquides à noyaux*), so as to emphasise the crucial structural features. I am no longer going to use this terminology because, as I have said, the word liquid should not play any role. Here again, what are required are two adjectives without too exact a meaning, whose only purpose is that of unambiguous description. I am going to use the term *smectics* (σμηγμα, soap) to describe the forms, bodies, phases, etc. of the first type (this includes Lehmann's *Fliessende Kr.* and *Schleimig flüssige Kr.* and also conic section liquids). The motivation for this terminology is that soaps at ordinary temperatures belong to this group, and that ammonium and potassium oleates were in particular the first materials of this type to attract attention. I am going to use the term *nematic* (νημα, thread) to describe the forms, bodies, phases, etc. of the second type (Lehmann's *Flüssige Kr.*, *Tropfbar flüssige Kr.*, as well as thread-like liquids) because of the linear discontinuities, which are twisted like threads, and which are one of their most prominent characteristics.

It is not without hesitation that I propose new terminology. For the example of 'liquid crystals' gives us the opportunity to observe the influence of a word badly chosen. Lehmann did not understand clearly how the substances he was studying would take their places in the hierarchy of material phases. He did however perceive, albeit in a rather confused fashion, that here indeed was something entirely new. We must be grateful to him for trying to convince his contemporaries of that fact. He was misled by the inadequate definitions of crystalline materials which were current at that time, and thus erred in classifying his liquids as crystals. But much more serious were the errors of the numerous scientific opponents whom he encountered, especially in Germany. These opponents failed to see anything in the new materials other than crystal suspensions in an amorphous liquid

¹It should be added that Lehmann's 'Fliessende Kr.' include cholesteric materials, which are, as we shall see, very different from the others. In this respect the classification by degree of fluidity is misleading.

(Quincke, Wulff), or emulsions of two liquids (Tammann, Nernst). They were not aware that these hypotheses were in no way able to explain the characteristic structural properties. They did not even try to provide a demonstration which would show, above all, that a suspension or an emulsion could exhibit such structures. Lehmann was very definitely closer to the truth than the authors we have just named. If he had not invoked any principle, but merely called his materials 'birefringent liquids', or some other description which only involved establishing the facts, no harm would have come of it. By bad luck, he made them 'liquid crystals'. This term was soon accepted more or less everywhere either by scientists who had not had the opportunity to see for themselves, or by those who had only vague ideas about crystals and crystallised matter. Now old traditions, which were justified once upon a time, have removed from the physicist the study of crystallography, by which we mean the physics of the large majority of solid bodies. It has been handed over to the mineralogist. Physicists who hear about liquid crystals have in general taken it as read that this subject belongs in the domain of crystallography, and thus of mineralogy. But the study of these materials, which are all organic and almost all artificial, has no link with the natural field of mineralogy. So in this way, with very few exceptions, perhaps more specially in our country, the study of these materials and their mesomorphic forms, which transcend the limits of crystallography, remains entrusted to naturalists, and almost unknown to physicists. I want to be able to show them that they have had in front of their noses, over the last 33 years, a field of study that is scarcely penetrated by exploration and extraordinarily rich in surprises. At each step one can find unresolved problems. The mineralogists' methods have been able to elucidate these problems in part, and these methods will still be able for a long time yet to uncover something new. However, these problems will only really be conquered for science using the tools of the physicist.

Either directly or through the good offices of Messrs Mauguin, Gaubert, Weick, Jaeger and Lehmann, I have been able to get hold of about forty substances in mesomorphic phases. I have then been able to carry out a general review of their properties using what seems to be a sufficiently large set of examples to enable general conclusions to be drawn. It is these studies on which I propose to report here. In trying to impose some order in this topic, I shall not hesitate to emphasise the numerous questions which remain, and which require further research.

History

I shall only recount the most important facts.

We are indebted to German chemists for the discovery of substances in the mesomorphic phases. Starting in 1889, Lehmann drew attention for the first time to the peculiar properties of cholesteryl benzoate. F. Reinitzer, who had prepared this material, had himself recognised in some way two melting points. When it is cold, the material is crystalline and solid. At 145.5 °C the crystals melt forming a turbid and viscous liquid (which actually is a nematic liquid of the cholesteric type).

Then, at 178.5 °C this turbid liquid suddenly switches into an ordinary liquid state, which is now completely clear and flows easily. Both of these transformations are completely reversible, and under the microscope one sees a perfectly discontinuous boundary between the two phases. When Lehmann looked at the intermediate turbid phase between crossed nicols, he recognised that it was birefringent and thus anisotropic. He was misled by poor definitions of what was meant by a crystal. And so, from that moment, believing that he could see a crystalline material in this phase, he regrettably combined its properties with the completely different properties of silver iodide. In the cubic form that it takes below 146 °C, this material is a weak plastic solid. However, all of its properties are those of a crystal and none are those of a mesomorphic substance, with which it has nothing in common.

Soon after this first example, it was Lehmann again who recognised birefringence and the main structural properties of the mesomorphic phase in para-azoxyphenetole and para-azoxyanisole, which were nematic substances prepared by Gattermann. He then found more or less analogous characteristics in potassium and ammonium oleate, which were the first smectic substances reported. It was he too who established the properties of the ethyl para-azoxybenzoate and of the ethyl para-azoxycinnamate prepared by Vorländer, which were the first non-soap smectic materials, and then of lecithin, also a smectic.¹

Since that time, many other examples of mesomorphic materials have been discovered. One should mention particularly Vorländer² for discovering a large number of substances which can exist in the new phase, and for investigating their principal chemical properties. Above all he showed that all these substances possess molecules which were remarkably long, linear, and unbifurcated, and in which the bisubstituted benzene rings only allowed a para- position, and forbidding ortho- or meta- isomers. His principal work (1908) already brought the number of 'crystalline fluid' compounds to some 200 or 250, all organic compounds with very complicated molecules. However Vorländer still included silver iodide amongst them, regarding it as 'the only inorganic compound'. This shows to what extent the true nature of these compounds continued to be poorly understood in Germany, even 20 years after the first discovery. Be that as it may, thanks to Vorländer's measurements it was possible from that time on to prepare a large quantity of new mesomorphic substances more or less at will.

Physical studies advanced more slowly. German physicists appear to have had two main concerns. One of these was to counter the idea of 'liquid crystals', and substitute it with hypotheses which were even less able to explain the facts than Lehmann's own. The other involved struggling against these hypotheses and in favour of the idea of a liquid crystal. To begin with Quincke, Tammann and Rotarski doubted the purity of the substances studied by Lehmann. Quincke and then

¹ O. Lehmann, *Flüssige Kristalle*, Leipzig, 1904; *Die Neue Welt der Flüssigen Kr.*, 1911.

² D. Vorländer, *Kristallinisch-flüssige Substanzen*, Stuttgart 1908.

Wulff imagined a suspension of solid crystals in an amorphous liquid. Tammann and Nernst favoured an emulsion of two liquids. All these ideas, suggested in a very rough way by the characteristic turbidity of the mesomorphic phases (which furthermore was not uniform) did not hold up a minute once the structures were examined under a microscope. It does not matter whether one looks from far off or from close in; no impure amorphous liquid, no crystalline suspension in a liquid, and certainly no emulsion has ever shown anything at all resembling these absolutely constant and completely characteristic structures. Nevertheless, even without going into the microscopical study of the structures, it is as well to dispose of these objections. One can show conclusively that Lehmann's materials are, or at least can be in principle, completely pure. They are phases as well defined as the crystalline and amorphous phases, whose properties remain unchanged by any process of purification. A suspension or an emulsion simply would not be acceptable. This proof was provided by the researches of Schenck and his students.¹

Schenck came out in favour of the Lehmann 'liquid crystal'. But this is just language. He does not examine the hypothesis in which there is a new phase of nature. Rather he supposes, *a priori*, that there are only two possibilities. The one associates known crystalline and amorphous phases in a mixture, suspension or emulsion. The other proposes a homogeneous phase, which he calls, without examining it further, a liquid crystal. And the first group of hypotheses he is able to rule out.

From the German work we should add a certain number of measurements which were sometimes fruitful but often premature, in that the thing to be measured was not sufficiently well understood. One of the most interesting of these was the work of Stumpf² on the rotatory power of amyl cyanobenzalamino-cinnamate.

When it comes to the detailed study of the mesomorphic phases whose independence Schenck had established, the German authors seem to be little concerned. They are little concerned with their structures, little concerned with their connections with crystalline and amorphous phases, and little concerned by the need to establish order in this jungle of new facts. An exception should be made for Lehmann, whose large number of publications contain many observations with the microscope. However, these are confused, and are rendered still more unclear by the theoretical considerations which accompany them.

It has been in France above all that the main steps in understanding the principal concepts have been made, although understanding is still far from complete. We should recall particularly the study by Mauguin³ of nematic twisted films, using the experiments to provide a complete explanation of the optical properties of these liquids. These properties were so bizarre that to begin with

¹ R. Schenck, *Kristallinische Flüssigkeiten und flüssige Kristalle*, Leipzig, 1905.

² F. Stumpf, *Doctoral thesis*, Göttingen, 1911.

³ *Bull. Soc. Minéralogie*, 1911.

G. Friedel and Mauguin had described them without finding the interpretation.¹ We also recall Mauguin's work on the effect of a magnetic field on nematic liquids,² that of G. Friedel and Grandjean on focal conic structure in smectic materials,³ and Mauguin's work on the effect of Brownian motion in nematic liquids earlier seen by Friedel and Grandjean. Mauguin and subsequently Grandjean⁴ examined the orientation of mesomorphic materials on crystals. Grandjean also discovered terraced drops in smectic materials,⁵ rectilinear flow of the smectic liquid over crystals which oriented it,⁵ and the equally spaced planes which characterise nematic materials of the cholesteric variety,⁶ which remain extremely puzzling. Out of this research has come the idea that there are two new mesomorphic forms of matter. These are completely distinct from the crystalline and amorphous forms, and possess properties which absolutely cannot be found in either of the two types of matter previously known.

Crystalline materials

In this section he goes on to review what is meant by crystalline phases, going back into the history of the subject, to the ideas of Mallard and Haüy. Towards the end of this section his frustration is clearly getting the better of him . . .

. . . Lehmann understood the point, albeit in a confused way, that he could save the word 'liquid crystal' only if he discovered in his materials discontinuous properties. So he searched either for polyhedral crystal shapes with planar faces, or for twinning phenomena. He thought he had found them, but we shall see that it was only an illusion. In despair he was forced to recognise the lack of a periodic structure. All that remained was to find a definition of a crystal which neither referred to discontinuous surface properties governed by Haüy's Law, nor to the periodic structure which, depending on your point of view, is either its cause or its manifestation. Thus we obtain the bizarre definition: 'A crystal is an anisotropic body which has a "molekulare Richtkraft" and which has as a result the property of growth.' The 'Richtkraft' or 'Gestaltungskraft' is a mysterious force which is supposed to make the vertices stick out, the edges straight and the faces planar. It is supposed to counteract the surface tension which causes surfaces to be round. In fact, it is only a nebulous new Germanic Divinity, which acts against

¹ *Bull. Soc. Min.*, 1910.

² *C. R.*, 1911, I, p. 1680.

³ *Bull. Soc. Min.*, 1910.

⁴ *Bull. Soc. Min.* 1916 and 1917.

⁵ *Bull. Soc. Min.*, 1916.

⁶ *C.R.*, 1921, I, CLXXII.

itself in an extraordinary collection of meaningless words,* and, as we shall see, lacks any basis other than that of an inexact view of the role of surface tension. As far as the growth capacity is concerned, it would force us to consider both the drop of water growing in vapour, and the vapour bubble growing in water, as crystals. The idea of growth capacity is obviously completely incapable of helping us to place a boundary between those materials which are crystalline and all those other materials which are not.

Friedel goes on to consider what is meant by an amorphous material, drawing a distinction between the concepts 'amorphous' and 'isotropic', but pointing out that if an amorphous body is not isotropic, then this is due to some external conditions extant while it was being formed. Most amorphous bodies, he avers, are fluid and all materials do exhibit a high temperature fluid amorphous phase.

Mesomorphic materials

Mesomorphic materials, like crystalline materials, are always spontaneously anisotropic, whatever the circumstances under which they have been formed. As in the case of non-cubic crystals, their anisotropy manifests itself through a birefringence which can be extremely strong. By contrast, they resemble amorphous matter in that the envelope of planes with discontinuous vector properties, which is a signature of crystalline matter and which is governed by Haüy's Law, does not exist.

All mesomorphic phases can be observed under essentially the same circumstances, and we shall shortly describe these. There are some exceptions to this rule; these are some smectic materials, such as soaps, lecithin and protagon, which are mesomorphic at room temperatures and above. It seems that the crystalline forms of these materials are not known, but they may be stable at very low temperatures. Other than that the conditions for observing mesomorphic behaviour are as follows:

At room temperature, the material is crystalline. When the temperature is increased one sees a reversible and discontinuous transformation at a well-defined characteristic temperature T_1 . The temperature T_1 depends on the type of material and is a function of pressure, and is exactly analogous to polymorphic transformations or melting. As in these latter cases, the microscope reveals a well-defined boundary between the crystalline and mesomorphic phases, lacking any transition region. Although this boundary is extremely clear, and separates two phases which look very different, it has nevertheless sometimes been able

* *Une singulière logomachie (ed.)*.

to pass unnoticed, leading one to believe that the change from the crystalline to the mesomorphic phase is continuous.

This has been the case for a number of smectic materials. In these cases the crystallisation occurs when the mesomorphic phase is frozen and the crystalline phase orients itself more or less on top of the mesomorphic phase and 'pseudomorphises' its structure. Often this is very approximate and does not hide the transformation at all. Examples include ethyl azoxybenzoate – ethyl azoxycinnamate mixtures, where the phenomenon was first noticed, and several other cases which we shall mention later. However, this pseudomorphism can sometimes be so close that the crystalline phase faithfully reproduces the conic structure characteristic of the smectic phase, right down to the most minute microscopic detail. The most notable example of this occurs in cholesteryl stearate. Almost as perfect an example is the case of cholesteryl myristate. Here the boundary between the crystalline and the smectic phases, although completely well-defined, is so difficult to observe and separates two phases which look so similar that it was missed by Lehmann, who thought he had seen an example of a continuous transformation from 'liquid crystal' to solid crystal. In fact this boundary is always present. There is always a perfect discontinuity between the mesomorphic and the crystalline phases.

The mesomorphic phase is normally either a liquid, which sometimes can be extremely fluid (particularly if it is nematic), or a viscous material (particularly if it is smectic). This is what has drawn attention to the mesomorphic phase in the first place. But the degree of fluidity varies with temperature. When the mesomorphic state continues to exist right down to room temperature, either by supercooling, e.g. ethyl anisalamincinnamate, or in equilibrium e.g. soaps or protagon, it can sometimes reach a state that one could only describe as solid. Like amorphous materials, mesomorphic materials are normally liquid or pasty, but can exceptionally be solid. The transformation T_1 thus normally looks like the melting of a crystalline solid.

On the other hand, to the naked eye the mesomorphic phase is usually turbid. Looked at between nicols, under the microscope, it is birefringent. The turbidity disappears and gives way to complete transparency. This sometimes occurs spontaneously and sometimes only when certain precautions are taken. Under the microscope the material appears either optically homogeneous or made up of a small number of optically homogeneous regions. The cloudiness, which gave rise to all the different objections by Lehmann's opponents, and led some to believe in an emulsion or a suspension, is completely explained by the birefringence. Added to this are the rapid changes in optic axis from one point to the next, which most often occur when no precautions are taken and the structure is complex. As Lehmann clearly realised, the mesomorphic phase is turbid for roughly the same reason as a closely packed collection of small birefringent crystals is turbid. The crystallites are individually clear but oriented in all directions, in such a way that a light ray cannot go through it without undergoing reflections and refractions as it passes from one crystallite to another. In fact this analogy,

although true in principle, holds only approximately. In mesomorphic materials, it is true that optical discontinuities exist and that indeed they govern the turbidity by causing light rays to scatter. But these discontinuities do not occur on separating surfaces, as they would in the crystal case. Rather they are linear, both in smectic and in nematic materials. The scattering of the light rays which causes the turbidity occurs when the light rays pass close to these discontinuity lines.

A single substance may exhibit two mesomorphic phases, one smectic and one nematic. In this case, and there are no exceptions, the smectic phase occurs at lower temperatures and the nematic at higher temperatures. At T_1 , the smectic phase replaces the crystalline. At another higher temperature T_2 a discontinuous reversible transition occurs and the nematic phase appears. This is always separated from the smectic phase by a perfectly well-defined surface with no transition region. Finally at an even higher temperature T_3 (or T_2 if there is only one mesomorphic phase) the birefringent mesomorphic phase gives way to an isotropic and amorphous liquid. The transition is always reversible, sudden and discontinuous, with a well-defined boundary between the phases and no transition region.

Lehmann and other scientists who accepted his viewpoint were influenced by the notion of 'liquid crystals'. They thought they had seen cases of three and four mesomorphic phases. In their view mesomorphic and crystalline phases were identical in nature. By taking this point of view they necessarily had to consider the transformations T_1 and T_2 as polymorphic transformations which were completely analogous to similar transitions frequently seen in these materials below T_1 . Thus, by analogy, one might sometimes expect to observe a number of such transformations above T_1 and be tempted to discover them. In fact even if one accepts that the mesomorphic form is completely distinct from the crystalline, at first sight it does not seem impossible for a single material to exhibit several smectic or nematic phases. And it could be that it will be like that. But my observation of the facts leads me to believe that it is not. In the reported cases of triple mesomorphic phases which I have been able to observe myself – see below for ethyl anisalaminocinnamate (Vorländer and Wilke), cholesteryl laureate (Jaeger), cholesteryl myristate (Jaeger) – I have always been able to establish that a structural change within a single phase had been confused with a distinct phase. The same error has led to a belief in mesomorphic phases in several cases when only one exists (see below Stumpf's amyl cyanobenzalaminocinnamate and Gaubert's anisalamidoazotoluene). As I have not been able to obtain samples of any of the other substances reported as exhibiting two 'crystalline liquid' phases, I cannot be completely sure. However, in my opinion it is very likely that there is only one nematic and one smectic phase in each material. In this the mesomorphic phases resemble the amorphous phase rather than crystals, which can often exhibit many different forms. The least that one can say is that statements about multiple mesomorphic phases should be accepted only with great hesitation. The existence of more than two of these phases, one smectic and the other nematic, should only

be accepted if an absolute proof can be provided, and at the moment there is no such proof.

In summary, and subject to this last reservation, the series of forms which a single substance goes through as temperature is increased is as follows:

		Crystalline (one or several forms)
		T_1
Mesomorphic	{	Smectic
		T_2
		Nematic
		T_3
		Amorphous

However, one or other of these forms may be absent, and the mesomorphic forms in particular only exist in a certain number of chemically special organic substances.

First mesomorphic type: smectic materials

As a typical smectic material one can take the mesomorphic phase of ethyl para-azoxybenzoate, or ethyl para-azoxycinnamate, or better still octyl para-azoxycinnamate, or even ethyl anisalamincinnamate. They are all very stable and easy to study. The structures are identical for all smectic materials, whether pure or not. The study of mixtures is very instructive in this respect. Let us consider, for example, a mixture of a smectic material such as ethyl para-azoxybenzoate and a nematic material such as para-azoxyphenetole. These substances mix completely in the amorphous state; in variable proportions, depending on the temperature, in the mesomorphic state; and only finally separate in the crystalline state. Depending on the temperature and the relative concentrations, the mixture can be: (a) a completely homogeneous smectic phase, *containing all the material*, and completely indistinguishable from a pure smectic material; or (b) a completely homogeneous nematic phase, *containing all the material*, and completely indistinguishable from a pure nematic material; or (c) two coexisting phases, one smectic and the other nematic, which are completely distinct and which are separated by a surface of discontinuity. We recall that when we mix ordinary crystals and amorphous liquids, the result is either crystalline or amorphous matter, and not something in between. The two types are separated by an absolute discontinuity. In the same way, when we mix mesomorphic materials, the result is crystalline, or smectic, or nematic, or amorphous, but with no transition region, and nothing in-between. And furthermore we recall that it is impossible to distinguish one amorphous liquid from another qualitatively or structurally, regardless of whether it is pure or a mixture. In the same way a smectic material (or a

nematic material) exhibits exactly the same structures and properties in all cases, regardless of degree of purity. We shall return to this very important point later in this article.

The smectic state is thus one of the general classes of matter, on the same level as the crystalline and amorphous states. What then are its characteristics?

It can, depending on the circumstance, present several structures:¹

1. *Homogeneous structure* – Let us crystallise ethyl azoxybenzoate by melting it and then cooling it again between two glass plates. It is then easy to arrange things so as to obtain large uniform crystalline regions. First one must first melt the sample on a microscope hot stage. Then one must retrace one's steps slowly towards lower temperatures. It is important to initiate the crystallisation process in a corner by putting the sample in contact with a trace of crystal. This avoids supercooling. The crystallisation can thus take place as slowly as is desired, and beautiful elongated homogeneous crystalline regions are obtained.

One then increases the temperature slowly just past the temperature T_1 . At this temperature the crystals transform suddenly into a perfectly clear smectic material. Under the microscope the large homogeneous birefringent regions can still be seen. The boundaries of these regions are the same as for the previous crystalline regions. In the case of ethyl azoxybenzoate the birefringence is very strong, and about twice that of Iceland spar. It can be examined either in a parallel light beam, or in converging light. However it is done, the regions exhibit all the

¹ It will be useful here to specify the meaning of the words structure and phase, which can lead to ambiguity, and which some authors use without defining them sufficiently. When we talk of *structures*, we mean different ways of organising a particular homogeneous element, which is small but still made up of a large number of molecules, and whose *molecular structure* is constant. As long as this molecular structure does not change discontinuously, the properties of this small homogeneous element also do not change discontinuously, and the transformation points remain the same whatever the *structure*. There can be a structural change without a phase change. The thing that remains the same if there are no *structural* modifications, but alters when the *molecular structure* changes or when there is a phase transformation, is this small homogeneous element. In the crystalline phase, we call this the crystal, and in the mesomorphic phases it should be given a name. Lehmann wrongly described it as a 'molecule' when he described the organisation of elements in the complex structures exhibited by mesomorphic materials. This was also what Stumpf described as an 'elementary crystal' while describing amyl cyanobenzalaminocinnamate. Stumpf had already expressed his belief in the existence of these 'elementary crystals' in the first phase. He then asked himself whether in the second phase they were the same, or whether rather they constituted a different 'modification'. If we translate this question into the language used here, this amounts firstly to affirming the existence of two phases, and then to asking: Is one of these phases a simple structural modification of the other, or is it rather really a distinct phase. It was a question that Stumpf, despite his belief in the existence of two phases, never really answers. We shall resolve it further on in this article in favour of a structural modification, but the answer is not *a priori* given by stating that there are two phases.

It seems that in most cases it is the misuse of the term 'phase change' which has led to a belief in the existence of multiple mesomorphic phases. A phase change has been confused with a mere structural change, not involving modification of the molecular structure nor consequently of the physical properties of the small homogeneous element.