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A Review of: "The Physics of Lyotropic Liquid Crystals"

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Book Review

The Physics of Lyotropic Liquid Crystals, by Antônio M. Figueredo Neto and Silvio R. A. Salinas, Oxford University Press, 2005; xii + 304 pp., £65.

This book sets out to fill a gap in the market. It aims to do for lyotropic liquid-crystalline phases what de Gennes, Chandraskhar, and others did for thermotropics: to give a mathematically respectable, comprehensive account of the physical properties of these systems. At first sight it looks imposing: an expensive hardback with dark blue cloth binding and gold lettering on the front and spine.

The preface lays out the plan: there are eight chapters in more or less logical progression. The opening chapter is an introduction and overview of classical lyotropic systems, including, of course, the basic definitions and terminology of the topic and an outline of the major families of lyotropic mesogens and the principal experimental techniques used in their characterization. The second chapter gets down to business, with a basic, theoretical discussion of phase transitions and critical phenomena, mean field calculations, and Landau expansions. This is followed by a chapter on phase diagrams, the phase rule, and examples of binary, ternary, and multicomponent systems. Chapter 4 extends this discussion and deals with phase transitions in terms of symmetry transformations. This is followed by detailed discussion of isotropic, micellar, bicontinuous, and sponge phases. We are beginning to reach more exotic parts now, and Chapter 6 covers lyotropic nematics and cholesterics. Chapter 7 surveys one-, two-, and three-dimensionally ordered systems. The final chapter is of the "before I finish, I ought to mention..." type. There are mentions of ferrofluids, microemulsions, diblock coploymers, and Langmuir Blodgett films and a passing acknowledgment of the existence of chromonic systems. So far so good.

There are plenty of serious-looking equations and plenty of clear simple graphics, familiar phase diagrams, and drawings of phase structures involving lots of tadpoles. There is an old-fashioned feel. At first glance, it could be the Gray and Windsor two-volume survey of liquid crystals of nearly half a century ago. There is nothing in color and no particularly novel graphics. I thought there might be some interesting new illustrations—of the bicontinuous cubics perhaps,

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because, they are challenging for artists as well as plumbers—or maybe a three-dimensional ternary phase diagram. However, there is nothing so ambitious.

Among the illustrations there are one or two old friends that we have seen before. Some of the halftone figures, particularly of mesh-phase structures, are smudgy but acceptable. The usual X-ray diffraction patterns are given (and, as usual, they are completely devoid of the annotation and indexing that would make them comprehensible to a reader not already in the know). The one or two optical micrographs are in unspectacular grey tones. There is a truly awful photograph of a model of gyroid, which any competent artist could have improved in a couple of hours. Some of the figures sound alarm bells: Does anyone still believe in sharp-edged micelles anymore, or the Eckwall C phase, or, for that matter, the complex hexagonal structure?

Some illustrations are difficult to interpret. Perhaps the politest thing to say about the drawing of the cholesteric arrangement of prolate micelles (in Chapter 2) is that it is baffling. The more you study it, the worse it gets. Why complicate matters by showing the micelles as being hollow? And why does the scale change in the middle of the picture?

The two-component phase diagram shown in Fig. 3.4, which is described merely as "typical," refers to the specific situation where there is complete miscibility of the two components in the isotropic liquid phase and partial miscibility in the solids. Why not say so?

There is a page full of formulae in the first chapter (Fig. 1.2). Some look decidedly odd. A + sign is misplaced, some nitrogen atoms have strange valencies, and the O-O-O sequences are baffling. With chemical structure drawing programs so readily accessible, there is no excuse for figures like this.

It quickly becomes obvious that English is not the first language of the authors. I have the very greatest respect for anyone with a command of a second language. I can only about ask the way to the railway station in France (but, unless there is a lot of pointing, I can't understand the answer when it comes back), so I certainly have no justification for adopting any sort of superior pose and could never attempt to produce a book like this in a foreign language. However, here the language problem has led to serious shortcomings that should have been eliminated at the editing and proofreading stage. It is not just that the clumsy English is grating—inappropriate words point the reader in the wrong direction. It takes some time to realize that the authors repeatedly use the word "surface" to mean "section" and "locus" as if it were synonymous with "position." No one talks of "carbonic" chains. The introduction to the phase rule is particularly

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unfortunate. The word "isotropic" is used to describe a single-phase region when the word "homogeneous" (in the sense of composition) is clearly required. It is not just wrong; it is very wrong. To complicate matters, a sentence later, the word "homogeneous" is used in a purely mathematical sense: "entropy is a homogeneous function of the first degree of these . . . variables." "Linear function" would have been better.

Equally disturbingly, the authors do not merely use a wrong word here and there; often they make matters worse by stressing it. What do they mean when they say that hydrophobicity does not involve "interactions" (p. 2, their italics), especially when the next sentence points out that these non-existent interactions are electrostatic? (I suspect the specter of entropy is lurking somewhere off-stage in the shadows.) Surely this would have been the place to explain that hydrophillicity is a general property of both ionic and hydrogen-bonding groups, especially because we have all heard of "nonionic" detergents.

I was intrigued to read "the liquid crystalline region at high temperatures" is "limited by a domain with an isotropic solution of isolated molecules or even micelles." (page 9). The words "or even" send out the wrong message, and in what way is the mesophase limited? Is this leading to a subtle discussion of some interphase conflict in terms of the partial molar free energies? Then the light dawns. All the authors are trying to say is that the phase is "limited" in the same sense that America is "limited" in the north by Canada. "Bounded" is clearly the word. By coincidence, an earlier chapter has parts of a molecule being "bounded" together. "Bonded" or "bound" would do, but not "bounded." And so it goes on. It eventually becomes clear what the authors are trying to say, but I would not have put it in those words. It is like those infuriating instructions that come with assemble-it-yourself furniture. It is only when the job is completed that you realize what they were trying to say in the first place.

It is often a multilevel problem. It is always unfair to pick out a single sentence for criticism, but I cannot explain this point in any other way. Consider this example: "In a micellar solution there appears anistropic liquid crystalline phases if we increase the concentration of amphiphile molecules to values much larger than CMC" (page 9). First, it would read better with "the" before CMC and because the word "phases" is plural, it should be "appear" not "appears." Some modification of word order would improve matters. What is the significance of the word "molecules"? Do the authors specifically mean individual, unaggregated molecules? Probably not. Why not just say amphiphile concentration? Then there is something jarring about the wording—a liquid-crystalline phase appearing in a micellar solution. How can a phase appear in a solution? It does not, of course.

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Droplets of the phase appear. More important, there is the word "anisotropy." Wait a minute—isn't the first mesophase to be formed sometimes a cubic array of micelles, which is, of course, optically isotropic? It would have been better to leave out the word anisotropic unless the authors specifically wanted to comment on the concentration where the first noncubic phase appears (which does not seem likely). I think that all the authors are trying to say is that you have to raise the amphiphile concentration a very long way above the CMC before any mesophases appear.

I regret having to make these carping comments. The authors have been badly served by the publishers. Figueredo Neto and Salinas have gathered together and organized an impressive range of material, and this book will be a useful reference source for research students for years to come. Unfortunately, however, it is not the definitive, critical text that it could and should have been.

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