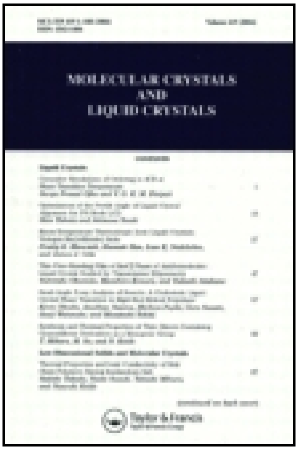

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# Magnetic Orientation of Nematic Lyomesophases

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# Magnetic Orientation of Nematic Lyomesophases

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Quantitative estimates are made for the diamagnetic mean susceptibility and anisotropy of the micellar interior and of the solvent medium of typical nematic lyomesophases. An analysis of the possible orienting mechanisms shows that both the molecular diamagnetic anisotropy of the hydrocarbon chains, which tends to align the chains perpendicular to the field, and the diamagnetic form anisotropy, which tends to align the major axis of the ellipsoids in the direction of the field, could in principle be responsible for the observed orientation if the micellar units are elastically coupled together, since the magnetic energy of a single micelle is smaller than thermal fluctuations. However, the degree of correlation among chains ensures that shape anisotropy of the micelles is negligible in front of molecular diamagnetic anisotropy, which must be responsible for the orientation of these lyomesophases.

## I. INTRODUCTION

Lyomesophases that orient in strong magnetic fields have been known for more than a decade.[1] These lyomesophases have been explored with NMR[2–4] and have been classified[3,4] as types I and II depending on whether the phase director orients parallel or perpendicular to **H**, corresponding respectively to positive and negative magnetic anisotropy. The study of these lyomesophases is receiving increasing attention;[5–11] they have been classified as nematic because of their response to magnetic fields and their textures as seen with a polarizing microscope.[6,9,10]

From small angle X-ray diffraction studies on oriented samples, the proposed structure of these nematic lyomesophases is of finite planar micelles[5,6] (platelets) for type II and finite cylindrical micelles[6,7] for type I lyomesophases. It has been argued[4–6] that the observed orientation agrees with the expected orientation of carbon chains in magnetic fields due to diamagnetic anisotropy. On the other hand, the observed orientation is the same that should be expected from the shape anisotropy of the micellar ellipsoids and it has been suggested[6] that the two processes have converging effects. However, no quantitative estimate has so far been made.

This correlation between structure and diamagnetic anisotropy seems to hold for amphiphiles with hydrocarbons, but it has been shown experimentally that the sign of the mesophase diamagnetic anisotropy can be changed without any concomitant change in micellar structure if other substances with diamagnetic characteristics opposed and larger than that of the hydrocarbons are added to the micelles[12] or if the amphiphile itself has opposed diamagnetic anisotropy.[11] However, if these results are evidence that the molecular diamagnetic anisotropy is the dominant factor, they do not prove that the effect of micellar shape anisotropy is negligible, particularly in the case of molecular anisotropy due to hydrocarbon chains. Therefore, the question of how much the contribution of shape anisotropy might be has not been answered experimentally either.

The question is relevant because since the earlier work on structures of lyomesophases[13] the hypothesis of hydrocarbon chains in a highly disordered conformational liquid state in all lyotropic mesophases has been adopted, what would make questionable the additivity of the molecular anisotropy to produce a macroscopic response. It is now accepted that the so-called disordered state retains a considerable degree of order, but the point of how much disordered the hydrocarbon chains are continues to be hotly discussed in the context of both micelles in isotropic solutions[14–16] and biological membranes.[17] No experimental results nor quantitative estimates for the effective macroscopic diamagnetic anisotropies of nematic lyotropics are available.

Magnetic orientation in thermotropic nematic phases has been widely explored;[18,19] it is due generally to diamagnetic anisotropy of aromatic rings. The diamagnetic molecular anisotropy is rather small and magnetic orientation occurs because a very large number of molecules are elastically coupled together, resulting in a magnetic energy for the bulk sample reasonably larger than thermal fluctuations.

Magnetic orientation of particles in a solute can occur individually. Suspensions of various biological membrane systems such as retinal rod outer segments, chloroplasts and purple membranes have been known to show magnetic-field induced orientation.[20,21] This effect is attributed to molecular diamagnetic anisotropy which sums up when molecules are oriented within a membrane or biological unit. However, the magnetic orientation observed in biological membranes is opposed to that expected from the diamagnetism of the lipid bilayers and it has been attributed to the diamagnetism of oriented membrane proteins, which cancel the small effect of the carbon chains.

In the case of lyotropic mesophases there are finite anisotropic micelles that resemble the biological units, with planar or curved lipid bilayers, but that also may be coupled together elastically as the anisotropic molecules of thermotropic mesophases.

In this paper the effects of diamagnetic molecular and shape anisotropy in lyomesophases are compared and it is verified in which conditions the magnetic energy is larger than thermal fluctuations.

A third possibility of orientation, due to anisotropy and inhomogeneities of the applied magnetic field, has a negligible influence in the case considered here, of magnetic fields without provocated gradients in definite directions.

## II. ORIENTATIONAL EFFECTS IN MAGNETIC FIELDS

### II.1. Molecular diamagnetic anisotropy

Let us consider a micelle with N anisotropic molecules of volume $V_0$, average susceptibility $\bar{\chi} = ⅓ (\chi_\parallel + 2\chi_\perp)$ and anisotropy $\Delta\chi = \chi_\parallel - \chi_\perp$, with a degree of correlation among molecules expressed by an internal order parameter $S_{\mathrm{int}}$. The magnetic energy difference between the configurations $\mathbf{n} \parallel \mathbf{H}$ and $\mathbf{n} \perp \mathbf{H}$ due to molecular anisotropy[18,19] for one micelle is

$$\Delta U_{\mathrm{mol}} = U_\parallel - U_\perp = -\frac{H^2 N V_0}{2} S_{int}\, \Delta\chi \tag{1}$$

For diamagnetic substances the configuration of minimum energy is the one with smaller absolute value of $\chi$. Aliphatic compounds of long chains, with satured single bonds, possess small diamagnetic anisotropies[22] ($\Delta\chi/\bar{\chi}$ ~0.1 − 0.2) with the larger $\chi$ in the direction of larger refractive index, corresponding to the length of the chain, and therefore align with **H** perpendicular to the molecular length. Since the hydrocarbon chains are expected to have a preferential direction perpendicular to the lipid-water interface, the molecular diamagnetic anisotropy due to the chains should align cylindrical micelles with their axis parallel to **H** and planar micelles with the plane of polar heads containing **H**, which is the type of orientation observed.

The molar average susceptibility of molecule,$\bar{\chi}_M$, can be calculated from atomic values and constitutive constants found in the literature.[23-26] The percentual anisotropy $\Delta\chi/\bar{\chi}$ for aliphatic compounds can be calculated assuming that the anisotropy comes only from the methylene groups and using the measured anisotropy for steric acid.[22]

Table I gives calculated values of $\bar{\chi}_M$ and $\Delta\chi/\bar{\chi}$, with a precision of about 3%, for the molecules of interest in the case of two typical lyomesophases:

TABLE I

Calculated molar diamagnetic susceptibility $\bar{\chi}_M$ and estimated percentual diamagnetic anisotropy $\Delta\chi/\bar{\chi}$

| molecule | $-\bar{\chi}_M/10^{-6}$ (emu/mol) | $\Delta\chi/\bar{\chi}$ |
|---|---|---|
| Na decyl sulfate | 165 | 9% |
| K laurate | 155 | 10% |
| decanol | 124 | 12% |
| $Na_2SO_4$ | 54 | — |
| KCl | 39 | — |

Types II SDS (Na decyl sulfate 37 wt.%/water 53 wt.%/Na sulfate 5 wt.%/decanol 5 wt.%); Type I LK (K laurate 33.6 wt.%/water 64.1 wt.%/KCl 2.3 wt.%).

From these molar values the calculated average volumetric susceptibilities $\bar{\chi}$ for the micellar interior and $\chi_0$ for the solvent medium, admitting that the alcohol is inside the micelle, and the salt is in the solvent, do not differ sensibly for the two lyomesophases; typical values are $\bar{\chi} = -6.10^{-7}$ emu/cm$^3$ with $\Delta\chi/\bar{\chi} = 0.1$ and $\chi_0 = -7.10^{-7}$ emu/cm$^3$.

Therefore, as is the case with thermotropics, the magnetic interaction energy for one amphiphile molecule is exceedingly small when compared to the thermal energy. There are some discrepancies in the estimate of the micellar size, but one can say that the number of molecules per micelle is expected to be $\sim 10^2$ for the smaller estimate[6] and of $\sim 10^3 - 10^4$ for the larger estimate.[5,7] In any case it is clear that a single micelle would not be able to align in a magnetic field of 2 KG due to thermal fluctuations.

For orientation due to molecular diamagnetic anisotropy to occur the micelles must be elastically coupled together in a way analogous to thermotropic liquid crystals. This is a well accepted fact in view of the observed textures and is in agreement with X-ray results that indicate collective reorientation of the micelles.[7]

Admitting $M$ micellar units elastically coupled, with a degree of correlation among micelles expressed by an external order parameter $S_{ext}$, the magnetic energy difference is

$$\Delta U_{mol} = -\frac{1}{2} H^2 M N V_0 S_{int} \cdot S_{ext} \Delta\chi \tag{2}$$

The effective diamagnetic anisotropy is $\Delta\chi_{eff} = S_{mol}\Delta\chi$, where $S_{mol} = S_{int} \cdot S_{ext}$ is the bulk order parameter of the molecule. For orientation to occur it would be necessary $S_{mol} N M \cong 10^{10}$ molecules, a condition that can be satisfied by the bulk sample.

The separation of $S_{mol}$ in two defined order parameters $S_{int}$ and $S_{ext}$ has not been explicitly considered before, but a separation of $S_{mol}$ in the several components of the molecular movements has been already used in the interpretation of NMR results[8] in nematic lyotropics. The advantage of making this separation is that $S_{ext}$, which is the order parameter defining the nematic order of the micelles, may be experimentally obtained from X-ray diffraction results in oriented samples, since this technique gives information about the orientational order of the diffracting unit; the X-ray method does not give a very accurate result[27,28] but can give approximate values for $S_{ext}$. Other properties, that depend on interactions at the individual molecular level, will be sensitive to $S_{mol}$. The order parameter $S_{int}$ is not directly measurable, but can be compared with results for $S_{mol}$ in conditions where $S_{ext} \cong 1$, as classical lamellar and hexagonal lyomesophases. Information about $S_{int}$ may also be obtained from ratios of NMR splittings[8] that cancel $S_{ext}$.

## II.2. Form anisotropy

The problem of orientation of an ellipsoid of magnetic susceptibility $\chi$ in a medium of magnetic susceptibility $\chi_0$ in presence of a constant magnetic field **H** has been treated rather completely.[23,24,29–31] The three directions of the principal axes of the ellipsoid are directions of equilibrium but only the situation **a** $\parallel$ **H** ($a$ being the major axis) is of stable equilibrium, and this does not depend on the sign of $(\chi - \chi_0)$; the components of the torque on the ellipsoid are such that they turn the major axis in the direction of the field by the shortest way.[23,24,29] Therefore, micellar shape anisotropy would also give the observed orientations of cylinders with their axis parallel to **H** and disc-like platelets with **H** in the plane.

The energy difference between the two configurations with the major axis $\parallel$ and $\perp$ to **H** can be approximated to

$$\Delta U_{form} = U_{\parallel} - U_{\perp} \cong \frac{V}{2} H^2 (\chi - \chi_0)(D_c - D_a)\chi \qquad (3)$$

where $D_c$ and $D_a$ are demagnetizing factors in the directions of respectively the smaller and larger semiaxes.

The largest energy difference occurs for highly asymmetrical ellipsoids, when a $\gg$ c; in this case $D_a = 0$ and $D_c = 4\pi$ for oblate and $D_c = 2\pi$ for prolate ellipsoids. This condition is approximately verified already for $a \cong 10c$.

For $\Delta U_{form} \gg kT$ orientational effects due to form anisotropy may be observed. Taking the largest possible value for $\Delta U_{form}$ and the typical values obtained for lyomesophases the necessary condition at room temperature is $H^2 V \sim 1$ ($G^2\text{cm}^3$). This means that for the usual values of **H** only macroscopic particles may present orientational effects due to shape anisotropy individually.

However, if we consider $M$ micellar units elastically coupled, with a degree of correlation among micelles expressed by $S_{\text{ext}}$, orientation of the bulk sample could occur for $S_{\text{ext}}MV \sim 10^{-6}\text{cm}^3$, a condition that can be satisfied by the macroscopic samples investigated.

### II.3. Comparison of molecular and form anisotropy effects

Elastic coupling is the mechanism that makes possible diamagnetic orientation due to molecular or form anisotropies. To decide whether the two processes may compete or have converging effects it is necessary to compare $\Delta U_{\text{mol}}$ with $\Delta U_{\text{form}}$.

Admitting that the volume $V$ of the micelle can be approximated to $NV_0$, the ratio between the energy differences due to molecular and shape anisotropy is

$$\frac{\Delta U_{\text{mol}}}{\Delta U_{\text{form}}} = \frac{S_{\text{int}}\Delta_{\chi}}{(\bar{\chi} - \chi_0)(D_c - D_a)\bar{\chi}} \tag{4}$$

As it has been seen in the previous item $\Delta\chi \sim \bar{\chi} - \chi_0$ and as $\bar{\chi}$ is very small ($\sim 10^{-6}$) it results for highly assymmetrical ellipsoids

$$\Delta U_{\text{mol}}/\Delta U_{\text{form}} \cong 10^5 S_{\text{int}}$$

Therefore $\Delta U_{\text{mol}} \gg \Delta U_{\text{form}}$ except in the case of almost completely uncorrelated molecules, when $S_{\text{int}}$ goes to zero. This would be the case for anisotropic molecules in the isotropic liquid state.

An estimate of typical values for the order parameters can be made from order parameters of the $C$-$D$ bonds obtained from NMR studies of amphiphilic molecules with deuterated methylene groups. For nematic lyotropics typical values for oriented samples[8,10] allow an estimate of $S_{\text{mol}} \cong 0.1 - 0.2$; the values obtained from lipid[17,32] and phospholipid[17] bilayers can be used to estimate $S_{\text{int}} \cong 0.2 - 0.4$. Therefore, it is possible to estimate also $S_{\text{ext}} \cong 0.5 - 0.6$.

These estimates for the order parameters allow some conclusions to be drawn:

- the order parameter that characterizes the nematic order ($S_{\text{ext}}$) has similar values for lyotropics as for thermotropic nematics, even if the correlation among individual molecules is smaller in lyotropics.
- the effect of the shape anisotropy of the micelles is negligible in front of the molecular diamagnetic anisotropy of the methylene groups.
- the estimated anisotropy of the hydrocarbon chains leads to $\Delta\chi_{\text{eff}}/\bar{\chi} \cong$

1–2%. Experimental results of $\Delta\chi_{\mathrm{eff}}$ and $\bar{\chi}$ are necessary to verify if the diamagnetic anisotropy is due only to the methylene groups or polar heads and ions are also giving a contribution.

## References

1. K. D. Lawson and T. J. Flaut, *J. Am. Chem. Soc.*, **89**, 5489 (1967); P. J. Black, K. D. Lawson and T. J. Flaut, *J. Chem. Phys.*, **50**, 542 (1969).
2. R. C. Long, Jr. and J. H. Goldstein, *J. Mag. Res.*, **23**, 519 (1976).
3. K. Radley, L. W. Reeves and A. S. Tracey, *J. Phys. Chem.*, **80**, 174 (1976).
4. F. Fujiwara, L. W. Reeves, M. Suzuki and J. A. Vanin, in *Solution Chemistry of Surfactants*, ed. K. L. Mittal (Plenum, N.Y., 1979) vol. 1, p. 63.
5. L. Q. Amaral, C. A. Pimentel, M. R. Tavares and J. A. Vanin, *J. Chem. Phys.*, **71**, 2940 (1979); L. Q. Amaral and M. R. Tavares, *Mol. Cryst. & Liq. Cryst. Let.*, **56**, 203 (1980).
6. J. Charvolin, A. M. Levelut and E. T. Samulski, *J. Physique Lett.*, **40**, L-587 (1979).
7. A. M. Figueiredo Neto and L. Q. Amaral, *Mol. Cryst. & Liq. Cryst.*, **74**, 109 (1981).
8. F. Y. Fujiwara and L. W. Reeves, *Can. J. Chem.*, **56**, 2178 (1978); *J. Phys. Chem.*, **84**, 653; 662 (1980); B. J. Forrest and L. W. Reeves, *Chem. Rev.*, **81**, 1 (1981); *Mol. Cryst. Liq. Cryst.*, **58**, 233 (1980).
9. K. Radley and A. Saupe, *Mol. Cryst. Liq. Cryst.*, **44**, 227 (1978); *Mol. Phys.*, **35**, 1405 (1978); L. J. Yu and A. Saupe, *J. Am. Chem. Soc.*, **102**, 4879 (1980).
10. J. Charvolin and Y. Hendrikx, Proc. Conf. Liquid Crystals of 1 and 2 Dimensional Order and their Applications, ed. W. Welfrich and G. Heppke (Springer Series in Chem. Phys. 1980); *J. Physique Let.*, **41**, L-601 (1980).
11. N. Boden, K. Radley and M. C. Holmes, *Mol. Phys.*, **42**, 493 (1981).
12. L. W. Reeves and F. Y. Fujiwara, private communication.
13. V. Luzzati, in "*Biological Membranes*," ed. D. Chappman (Academic Press, 1968), pp. 71–123; V. Luzzati and A. Tardieu, *Ann. Rev. Phys. Chem.*, **25**, 79–94 (1974).
14. F. M. Menger, *Acc. Chem. Res.*, **12**, 111 (1979).
15. B. Cabane, *J. Physique*, **42**, 847 (1981).
16. P. Fromhertz, *Chem. Phys. Let.*, **77**, 460 (1981).
17. J. Seelig, *Quart. Rev. Biophys.*, **10**, 353 (1977); H. Schindler and J. Seelig, *Biochem.*, **14**, 2283 (1975).
18. P. G. de Gennes, *The Physics of Liquid Crystals*, (Claredon Press, Oxford, 1974), p. 79.
19. E. B. Priestley, P. J. Wojtowics and P. Cheng, *Introduction to Liquid Crystals* (Plenum Press, 1975).
20. F. T. Hong, *J. Collid. Interface Sci.*, **58**, 471 (1977).
21. I. Sakurai, Y. Kawamura, A. Ikegami and S. Iwayanagui, *Proc. Natl. Acad. Sci. USA*, **77**, 7232 (1980).
22. K. Lonsdale, *Proc. Royal Soc.*, **A171**, 541 (1939).
23. E. F. Bates, *Modern Magnetism* (Cambridge, 1939).
24. A. H. Morrish, *The Physical Principles of Magnetism* (John Wiley & Sons, 1966).
25. A. Pacault, J. Hoarau and A. Marchand, in Ad. Chem. Phys., ed. I. Prigogine (Interscience, 1961) vol. III, pp. 171–238.
26. L. N. Mulay, *Magnetic Susceptibility* (Interscience, 1963).
27. J. Falgueirettes and P. Delord, in *Liquid Crystals & Plastic Crystals*, ed. G. W. Gray and P. A. Winsor (John Wiley & Sons, N.Y., 1974) vol. 2, 62.
28. A. de Vries, *J. Chem. Phys.*, **56**, 4489 (1972).
29. J. A. Stratton, *Electromagnetic Theory* (McGraw-Hill, New York, 1941).
30. J. A. Osborn, *Phys. Rev.*, **67**, 351 (1945).
31. E. C. Stoner, *Phil. Mag.*, **36**, 803 (1945).
32. B. Mely, J. Charvolin and P. Keller, *Chem. Phys. Lipids*, **15**, 161 (1975).