This article was downloaded by:
On: *26 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Uniaxial nematic phase in fluids of biaxial particles

B. Bergersen[a]; P. Palffy-muhoray[b]; D. A. Dunmur[c]
[a] Department of Physics, The University of British Columbia, Vancouver, B.C., Canada [b] Liquid Crystal Institute, Kent State University, Kent, Ohio, U.S.A. [c] Department of Chemistry, The University of Sheffield, Sheffield, England

To cite this Article Bergersen, B. , Palffy-muhoray, P. and Dunmur, D. A.(1988) 'Uniaxial nematic phase in fluids of biaxial particles', Liquid Crystals, 3: 3, 347 — 352
To link to this Article: DOI: 10.1080/02678298808086380
URL: http://dx.doi.org/10.1080/02678298808086380

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

LIQUID CRYSTALS, 1988, VOL. 3, NO. 3, 347–352

Uniaxial nematic phase in fluids of biaxial particles

by B. BERGERSEN
Department of Physics, The University of British Columbia,
Vancouver, B.C. Canada V6T 1W5

P. PALFFY-MUHORAY
Liquid Crystal Institute, Kent State University, Kent, Ohio 44242, U.S.A.

and D. A. DUNMUR
Department of Chemistry, The University of Sheffield, Sheffield S3 7HF, England

(*Received 20 February 1987; accepted 15 October 1987*)

We construct a mean field theory for fluids of biaxial particles interacting via London–van der Waals interactions. This model is shown to belong to a class of systems previously studied by Straley. In the special case when the psueodpotential can be constructed from the invariants of the dielectric susceptibility tensor, the model is shown to be equivalent to that of Freiser and others. A discussion is given of the difference between molecular properties, as obtained in N.M.R. experiments, and bulk properties.

In the absence of external fields, most thermotropic nematics exhibit only bulk uniaxial phases, although biaxial phases have been observed in lyotropics [1, 2]. Very recently, a biaxial phase has been observed [3] in a thermotropic material and also in long chain polymers with nematogenic side groups [4]. Even for uniaxial phases, while bulk properties such as the dielectric and magnetic susceptibilities are uniaxial, molecular properties of the constituents do not typically have cylindrical symmetry.

In the case of N.M.R., where one measures the orientation of molecular segments, biaxial distributions have been observed for some time [5]. There has been some controversy as to whether the dominant mechanism for this is molecular biaxiality [5] or flexibility [6]. A recent study of molecular biaxiality of a dilute solute using U.V. spectroscopy is that of Averyanov *et al.* [7], while we refer to Emsley *et al.* [8] for similar phenomena using N.M.R. A theory which concentrates on the effects of conformational averaging of flexible molecules has been presented by Emsley *et al.* [9]. We wish here to re-examine the role of biaxiality in *rigid* molecules.

The very successful and simple mean field theory of Maier and Saupe [10] assumes that the molecules have cylindrical symmetry, and for this reason their theory only predicts a uniaxial phase. In an elegant paper, Straley [11] constructed a general mean field theory for particles without cylindrical symmetry. He obtained both biaxial and uniaxial solutions, with a biaxial regime separating rod- and disk-like uniaxial phases. In this molecular field approach three anisotropy interaction parameters are introduced. In an alternative Landau approach [12, 13] 11 parameters were used. On the other hand, if the intermolecular interaction is expressible in terms of the three principal molecular polarisabilities, two parameters will describe the anisotropy. We construct a formalism for the case where the dominant interaction is of the

London–van der Waals type. In the most general case our results are equivalent to those of Straley [11]. Under certain assumptions only two anisotropy parameters are required. We give criteria when this is allowed, and in this case our theory becomes equivalent to that of Freiser [14] and Remler and Haymet [15]. The order parameters of Remlet and Haymet [15] are linear combinations of the molecular order parameters. We therefore find it useful to calculate the temperature dependence of each of the two molecular order parameters in the bulk uniaxial phase.

Let α_i ($i = 1, 2, 3$) be the molecular polarizabilities along the three principal molecular axes. We generalize the isotropic case considered by Kittel [16] and take this polarizability to be due to three orthogonal harmonic oscillators with characteristic frequencies ω_i. The London–van der Waals force between the two molecules a and b will then be of the form

$$U_{ab} = -\frac{\hbar}{4r^6}\sum_{ij}(\omega_i + \omega_j)\alpha_i\alpha_j(3(\mathbf{L}_i^a\cdot\mathbf{R})(\mathbf{L}_j^b\cdot\mathbf{R}) - \mathbf{L}_i^a\cdot\mathbf{L}_j^b)^2 \tag{1}$$

Here $\mathbf{R}$ is a unit vector in the direction of the intermolecular vector $\mathbf{r}$. $\mathbf{L}_i^a$ is a unit vector in one of the principal directions of the molecular polarizability. We use Greek indices to describe components of these vectors in the laboratory frame and employ the summation convention for repeated Greek indices. We define

$$G_{\beta\gamma} = \tfrac{1}{2}(3R_\beta R_\gamma - \delta_{\beta\gamma})/r^3, \tag{2}$$

and rewrite equation (1)

$$U_{ab} = -\hbar\sum_{ij}(\omega_i + \omega_j)\alpha_i\alpha_j L^a_{i\beta}L^b_{j\mu}L^a_{i\gamma}L^b_{j\nu}G_{\beta\mu}G_{\gamma\mu}. \tag{3}$$

In the spirit of the Maier–Saupe theory [10], we make the approximation that the spatial and orientational parts of the pair distribution function are decoupled. Then

$$\langle G_{\beta\mu}G_{\gamma\nu}\rangle = \varrho b(3\delta_{\beta\gamma}\delta_{\mu\nu} - 2\delta_{\beta\mu}\delta_{\gamma\nu} + 3\delta_{\beta\nu}\delta_{\mu\gamma}), \tag{4}$$

with b a constant (of dimension inverse volume per particle) and ϱ is the number density. We define

$$\sigma^{ik}_{\beta\gamma}(a) = \tfrac{1}{2}[3L^a_{i\beta}L^a_{k\gamma} - \delta_{ik}\delta_{\beta\gamma}], \tag{5}$$

with the corresponding order parameter tensor

$$S^{ik}_{\beta\gamma} = \langle\sigma^{ik}_{\beta\gamma}\rangle. \tag{6}$$

We get for the spatially averaged pair interaction

$$\bar{U}_{ab} = -\frac{\varrho b\hbar}{2}\sum_{ij}\alpha_i A_j(3 + \tfrac{4}{9}\sigma^{ii}_{\beta\gamma}(a)\,\sigma^{jj}_{\gamma\beta}(b)), \tag{7}$$

where $A_j = \alpha_j\omega_j$. In mean field theory one averages over orientation of particle b to obtain the single particle orientational pseudopotential

$$\varepsilon = -\frac{\varrho b\hbar}{9}\sum_i\sigma^{ii}_{\beta\gamma}\sum_j(A_i\alpha_j + \alpha_i A_j)S^{jj}_{\gamma\beta}. \tag{8}$$

We write

$$\bar{\alpha} = \tfrac{1}{3}(\alpha_1 + \alpha_2 + \alpha_3), \quad \bar{A} = \tfrac{1}{3}(A_1 + A_2 + A_3). \tag{9}$$

In the principal axis frame of the order parameter tensor $S^{jj}_{\beta\gamma}$, the anisotropic part of the susceptibility tensor is given by

$$\chi_{\beta\gamma} = \sum_j \alpha_j S^{jj}_{\beta\gamma} = \tfrac{3}{2}(\alpha_3 - \bar{\alpha}) \begin{pmatrix} -\tfrac{1}{2}(Q - P) & & \\ & -\tfrac{1}{2}(Q + P) & \\ & & Q \end{pmatrix}$$

$$+ \tfrac{1}{2}(\alpha_1 - \alpha_2) \begin{pmatrix} -\tfrac{1}{2}(D - C) & & \\ & -\tfrac{1}{2}(D + C) & \\ & & D \end{pmatrix}, \tag{10}$$

where

$$\left.\begin{aligned} q &= \tfrac{1}{2}(3\cos^2\theta - 1) = \tfrac{1}{2}[3(L_{3z})^2 - 1], \\ Q &= \langle q \rangle, \end{aligned}\right\} \tag{11}$$

$$\left.\begin{aligned} p &= \tfrac{3}{2}\sin^2\theta\cos 2\phi = \tfrac{3}{2}[(L_{3x})^2 - (L_{3y})^2], \\ P &= \langle p \rangle, \end{aligned}\right\} \tag{12}$$

$$\left.\begin{aligned} d &= \tfrac{3}{2}\sin^2\theta\cos 2\psi = \tfrac{3}{2}[(L_{1z})^2 - (L_{2z})^2], \\ D &= \langle d \rangle, \end{aligned}\right\} \tag{13}$$

$$\left.\begin{aligned} c &= \tfrac{3}{2}[(1 + \cos^2\theta)\cos 2\phi\cos 2\psi - 2\cos\theta\sin 2\phi\sin 2\psi], \\ &= \tfrac{3}{2}[(L_{1x})^2 - (L_{2x})^2 - (L_{1y})^2 + (L_{2y})^2], \\ C &= \langle c \rangle. \end{aligned}\right\} \tag{14}$$

Equation (10) shows that even for uniaxial samples ($P = C = 0$) different susceptibilities will exhibit different temperature dependencies (the experimental evidence for this has been recently reviewed by Bunning *et al.* [17]). We note that, in principle, it should be possible to extract the temperature dependence of Q and D from independent measurements of, say, the dielectric and magnetic susceptibilities. Equation (10) and its implications do not appear to be generally known in the literature. The order parameters Q, P, C and D are related to S, T, U and V of Straley [10] by $Q = S$, $P = 3/2T$, $D = 3/2U$, $C = 3V$.

We get for the orientational pseudopotential in the principal axis frame

$$\varepsilon = -\tfrac{1}{2}\varrho b\hbar(\alpha_3 - \bar{\alpha})(A_3 - \bar{A})(\tfrac{1}{2}(3Qq + Pp) - \tfrac{1}{2}(\delta + \Delta)\tfrac{1}{2}(3Qd + Pc + 3Dq + Cp)$$
$$+ \tfrac{1}{2}(\delta\Delta)(3Dd + Cc)), \tag{15}$$

where

$$\Delta = \frac{A_2 - A_1}{3(A_3 - \bar{A})}, \quad \delta = \frac{\alpha_2 - \alpha_1}{3(\alpha_3 - \bar{\alpha})}. \tag{16}$$

The relevant part of the free energy per particle then becomes

$$f = -k_B T \ln\left(\frac{1}{8\pi^2}\int \exp(-(\varepsilon - \tfrac{1}{2}\langle\varepsilon\rangle)/k_B T)\sin\theta\, d\theta\, d\phi\, d\psi\right). \tag{17}$$

The prefactor, δ and Δ are in principle independent parameters and the pseudopotential (equation (15)) is of the general form suggested by Straley [11]. In his book de Gennes [18] argued that the free energy should be expressible in terms of the invariants of the susceptibility tensor (10) which has two independent anisotropy parameters. We note that this is only possible if the three characteristic frequencies in equation (1) take on the same value $\omega_i = \omega_0$. Then $A_i = \omega_0 \alpha_i$ and $\delta = \Delta$, and our model becomes equivalent to that of Freiser [14]. Although the interactions responsible for liquid-crystalline behaviour will differ from equation (1) (we have omitted steric effects), our argument demonstrates that in general *three* anisotropy parameters are needed to describe the interaction between rigid biaxial particles in mean field theory.

The Landau expansion in the special case $\delta = \Delta$ has been studied by Freiser [14]. He showed that for $\delta = 1/3$ (which in our model corresponds to one of the principal susceptibilities being equal to the mean susceptibility) there is a critical point. This point is the end point of two second order lines separating the biaxial phase from rod-like and disk-like nematic phases. In the general case $\delta \neq \Delta$ the Landau expansion becomes more complicated and we plan to discuss this question elsewhere. We mention, however, that when account is taken of the fact that the density may change at the transition, the uniaxial to biaxial transition may be first order. The uniaxial–biaxial transition in a rod–disk mixture was recenty found [19] to be first order for similar reasons.

Recently, the Freiser model has been studied by Remler and Haymet [15]. They considered a pseudopotential of the form

$$\varepsilon = -\tfrac{1}{2}\varrho b\hbar\omega_0(\alpha_3 - \bar{\alpha})^2 B_{\beta\gamma} b_{\gamma\beta}, \tag{18}$$

where, in the principal axis frame, the order parameter can be written

$$B = \begin{pmatrix} -\tfrac{1}{2}(\Omega - \Lambda) & & \\ & -\tfrac{1}{2}(\Omega + \Lambda) & \\ & & \Omega \end{pmatrix}, \tag{19}$$

with

$$\Omega = Q + \delta D = \langle q + \delta d \rangle = \langle \omega \rangle, \tag{20}$$

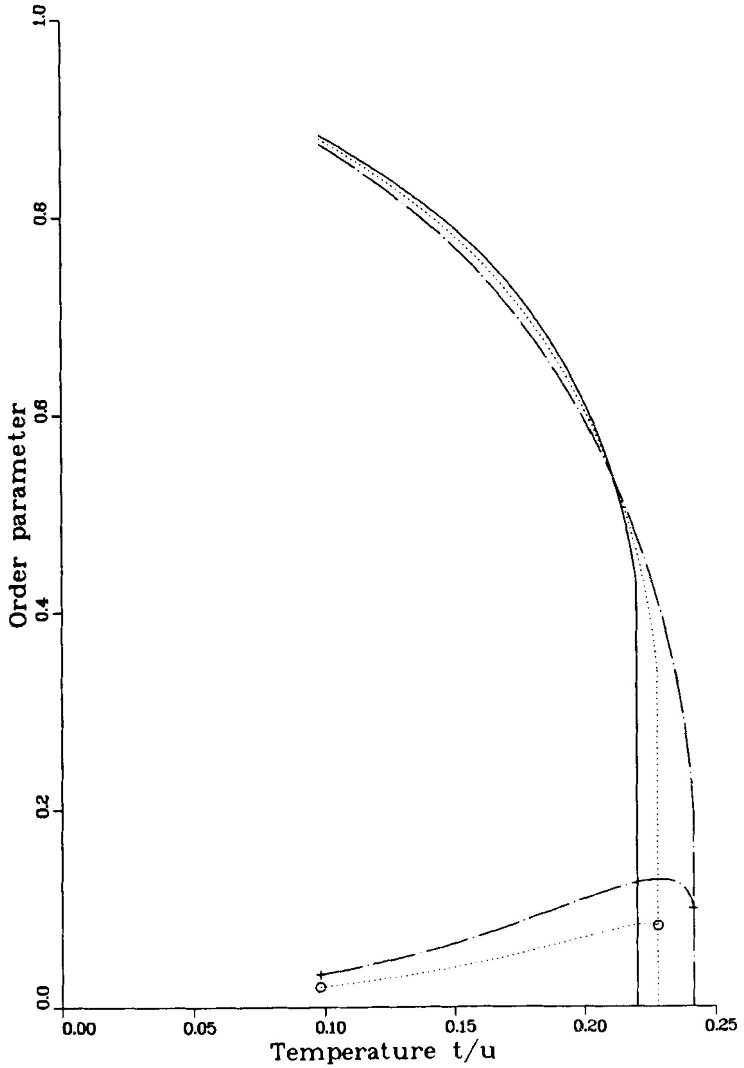
$$\Lambda = P + \delta C = \langle p + \delta c \rangle = \langle \lambda \rangle. \tag{21}$$

The order parameters of Remler and Haymet [15] are $A_0 = \Omega$ and

$$A_2 = \frac{2\Lambda}{3(1 + 2\delta)}, \tag{22}$$

while their anisotropy parameter is $r = (3/2)^{1/2}\delta$. We note that the order parameters Ω and Λ contain the material constant δ which is different for different types of susceptibility. We have therefore found it useful to recalculate Q and D for the special case $\delta = \Delta$. We have solved the self-consistent equations which result from minimizing the free energy.

These integrals were expressed as single integrals over complex error functions, and were evaluated using an adaptive Romberg routine. The temperature dependence of the order parameters Q and D defined in equations (11) and (13) is shown in the figure for the same values of the anisotropy parameter. The transition temperature increases with δ if $u = 3\varrho b\hbar\omega_0(\alpha_3 - \alpha)$ is kept constant. This differs from [15], where a different unit of temperature is used.



Temperature dependence of the order parameters Q and D for $\delta = 0$ (full curve), $\delta = 0{\cdot}1633$ (dotted curve, this value of δ corresponding to $r = 0{\cdot}2$ in [14]), and $\delta = 0{\cdot}25$ (chained curve). The upper curves represent the order parameter Q, the lower curves plot D.

The susceptibility (equation (10)) for biaxial particles contains two order parameters even in the bulk uniaxial case. For this reason the anisotropy associated with different susceptibilities will exhibit different temperature dependencies. This may account, at least in part, for the observed difference in temperature dependence of magnetic and electric susceptibilities (birefringence) [17]. Similarly, the ratio $(S_{xx} - S_{yy})/S_{zz}$ depends on temperature even in the case of rigid biaxial molecules in qualitative agreement with recent results of Wu *et al.* [20].

We have shown by a counter example that the free energy is not in general expressible in terms of the invariants of a single susceptibility. We have thus explained the difference between the more general formulation of Straley [11] and that Freiser [14].

This work was supported by the Natural Sciences and Engineering Research Council of Canada. We are grateful for discussions with A. Buka, E. Burnell, B. Frisken, J. Gleeson, M. Gingras, P. W. Holdsworth, A. Reid and S. R. Sharma.

References

[1] Yu, L. J., and Saupe, A., 1980, *Phys. Rev. Lett.*, **45**, 1000.
[2] Saupe, A., Boonbrahm, P., and Yu, L. J., 1983, *J. Chim. phys.*, **80**, 7.
[3] Malthete, J., Liebert, L., Levelut, A.-M., and Galerne, Y., 1986, *C. r. Séanc. Acad. Sci., Paris* II, **303**, 1073.
[4] Hessel, S., and Finkelmann, H., 1986, *Polym. Bull.*, **15**, 349.
[5] Bos, P. J., Pirs, J., Ukleja, P., and Doane, J. W., 1977, *Molec. Crystals liq. Crystals.*, **40**, 59.
[6] Deloche, B., and Charvolin, J., 1980, *J. Phys. Lett., Paris*, **41**, 39.
[7] Averyanov, E. M., Gunyakov, V. A., Korets, A. Ya., and Shabanov, V. F., 1986, *Optika Spektrosk.*, **60**, 66.
[8] Emsley, J. W., Hashim, R., Luckhurst, G. R., and Shilstone, G. N., 1986, *Liq. Crystals*, **1**, 437.
[9] Emsley, J. W., Luckhurst, G. R., and Stockley, C. P., 1982, *Proc. R. Soc.* A, **381**, 117.
[10] Maier, W., and Saupe, A., 1958, *Z. Naturf.* (*a*), **13**, 564; 1959, *Ibid.*, **14**, 882; 1960, *Ibid.*, **15**, 287.
[11] Straley, J. P., 1974, *Phys. Rev.* A, **10**, 1881.
[12] Allender, D. W., and Lee, M. A., 1984, *Molec. Crystals liq. Crystals*, **110**, 331.
[13] Allender, D. W., Lee, M. A., and Hafiz, N., 1985, *Molec. Crystals liq. Crystals*, **124**, 45.
[14] Freiser, M. J., 1971, *Molec. Crystals liq. Crystals*, **14**, 165.
[15] Remler, D. K., and Haymet, A. D. J., 1986, *J. phys. Chem.*, **90**, 5426.
[16] Kittel, C., 1971, *Introduction to Solid State Physics*, 4th edition, Advanced topic B (Wiley), p. 700.
[17] Bunning, J. D., Crellin, D. A., and Faber, T. E., 1986, *Liq. Crystals*, **1**, 37.
[18] de Gennes, P. G., 1974, *The Physics of Liquid Crystals* (Clarendon).
[19] Sharma, S. R., Palffy-Muhoray, P., Bergersen, B., and Dunmur, D. A., 1985, *Phys. Rev.* A, **32**, 3752.
[20] Wu, B. G., Ziemnicka, B., and Doane, J. W., *J. chem. Phys.* (to be published).