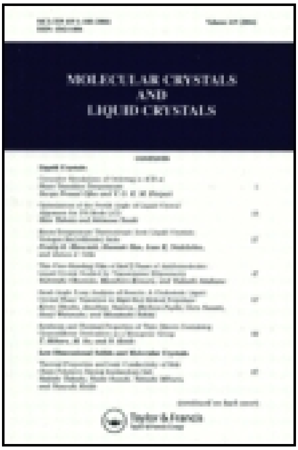

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On the Possibility of a Biaxial Smectic A Phase

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On the Possibility of a Biaxial Smectic A Phase†

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The existence of a uniaxial-biaxial phase transition in a smectic A phase is shown theoretically, based on the more realistic anisotropic pair potential and within the mean field approximation. The resulting phase diagram exhibits successive phase transitions of isotropic-uniaxial nematic-uniaxial smectic A-biaxial smectic A and a uniaxial nematic-uniaxial smectic A-biaxial smectic A triple point. The possible assignment of the predicted biaxial smectic A to some phase classified recently as a smectic C is discussed.

I. INTRODUCTION

It has been known that there are many kinds of smectic phases, which are all characterized by a layer structure. The simplest of them are a smectic A and a smectic C. The center-of-mass positions of molecules for both phases distribute randomly within eacy layer like a two-dimensional liquid. They are conventionally distinguished from each other in that the former is optically uniaxial, while the latter is biaxial. These features are usually interpreted as follows; in a smectic A the averaged long molecular axis (director **n**) is upright to the layer, while it is tilted with respect to the layer normal in a smectic C.

As seen from the recent optical[1] and X-ray diffraction[2-5] measurements, however, there seem to be at least two kinds of smectic C liquid crystals according to the temperature dependence of the smectic layer thickness *d*. Let us provisionally call them smectic C_1 and C_2. The smectic C_1 is composed of usual biaxial smectics like TBBA. The layer thickness *d* decreases drastically

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when temperature is decreased from smectic A-smectic C_1 second order phase transition point.[1,2,5] This clearly indicates the inclination of the director **n** from the layer normal. On the other hand, the layer thickness of the smectic C_2 has no prominent temperature dependence near the smectic A-smectic C_2 transition point.[3-5] This seems to indicate that in spite of the apparent biaxiality the director **n** does not begin to incline just under the transition point.

In order to explain the existence of the smectic C_2 Wulf[6] has demonstrated that a system of long molecules, moving within a planar layer and making a fixed angle with the layer normal, exhibits a second-order transition from a phase with disordered tilt directions (smectic A) to a phase with the tilt directions aligned along some preferred axis (smectic C); whereas the present author[7] has pointed out that the smectic A–C transition in the same system can be regarded as the topological order transition proposed by Kosterlitz and Thouless.[8] Both of them seem rather *ad hoc*, and do not elucidate the existence of such a system itself.

In this paper we will indicate by means of mean-field theory the existence of a uniaxial-biaxial phase transition in a smectic A phase, based on the fact that many liquid crystal molecules are biaxial lath-like objects. We will then discuss the possibility that the smectic C_2 described above may be the biaxial smectic A. Starting from more general anisotropic pair interaction potential in Section II, we will define in Section III some new order parameters which characterize biaxial phases, in addition to usual nematic and smectic order parameters. Then we will derive mean-field theoretic self-consistent equations of the order parameters. Based on the numerical results for the temperature dependence of the order parameters shown in Section IV, we will discuss the biaxial smectic A phase and its application to real systems in Section V.

II. ANISOTROPIC PAIR POTENTIAL

In the well-known Maier–Saupe theory of the nematic state[9] molecules are considered as rod-like uniaxial objects. Most liquid crystal molecules, however, contain rigid planar central part constructed mainly by aromatic rings. This means they are more or less biaxial objects. Hence we should extend the Maier–Saupe theory to more realistic one, and search for biaxial states reflecting the molecular shape.

Maier–Saupe pair interaction is the simplest anisotropic interaction. Let us assume that constituent molecules are centrosymmetric. Then more general and realistic anisotropic interaction potential between two molecules, α and β, can be written as[10]

$$V^{an}(\alpha\beta) = -J(r^{\alpha\beta}) \sum_m (-1)^m Q_{2m}(\Omega^\alpha) Q_{2,-m}(\Omega^\beta), \tag{2.1}$$

where $r^{\alpha\beta} = |\mathbf{r}^{\alpha} - \mathbf{r}^{\beta}|$, Ω is the Euler angle, and molecular multipolar moments in a spherical representation $Q_{lm}(\Omega)$ in the space-fixed coordinate system is given by

$$Q_{lm}(\Omega) = \sum_{m'} D^{(l)}_{m'm}(\Omega) Q_{lm'}, \tag{2.2}$$

in terms of those referred to axes fixed in the molecules, Q_{lm}. $D^{(l)}_{m'm}$ are the elements of the representations of the rotation group.

From the molecular shape we can always choose the principal axes of molecules so that $Q_{2,\pm1} = 0$ and $Q_{22} = Q_{2,-2}$ is real. Therefore we need only $D^{(2)}_{00}$, $D^{(2)}_{02}$, $D^{(2)}_{20}$ and $D^{(2)}_{22}$ which are given in some textbooks of quantum mechanics.[11] For axially symmetric molecules ($Q_{22} = 0$), the anisotropic interaction (2.1) can be easily shown to reduce to that of Maier and Saupe.

III. MEAN FIELD AND ORDER PARAMETERS

Based on the anisotropic pair potential (2.1), let us formulate order parameters with resort to mean field approximation. The mean field for the pair potential (2.1) which each molecule "feels" is given by

$$V_1(\mathbf{r},\Omega) = -n \sum_{m} (-1)^m Q_{2m}(\Omega) \int d\mathbf{r}' J(r') \langle Q_{2,-m}(\mathbf{r} - \mathbf{r}') \rangle^{or}, \tag{3.1}$$

where $n = N/V$ (N the total number of molecules, and V the system volume). The local order parameter $\langle Q_{2m}(\mathbf{r}) \rangle^{or}$ in (3.1) is written as

$$\langle Q_{2m}(\mathbf{r}) \rangle^{or} = \int d\Omega Q_{2m}(\Omega) f_1(\mathbf{r},\Omega), \tag{3.2}$$

where self-consistent center-of-mass position and orientation distribution function $f_1(\mathbf{r},\Omega)$ is

$$f_1(\mathbf{r},\Omega) = \frac{\exp\{-\beta V_1(\mathbf{r},\Omega)\}}{\dfrac{1}{V}\displaystyle\iint d\mathbf{r}\, d\Omega \exp\{-\beta V_1(\mathbf{r},\Omega)\}}. \tag{3.3}$$

Hence we have a set of self-consistent Eqs. (3.1)–(3.3) for the mean field and order parameters. Since it is very difficult to solve these equations directly, we will simplify the problem and make some assumptions in the following.

By means of an appropriate choice of the laboratory frame of reference due to the symmetry of the problem we can put

$$\langle Q_{2,\pm1}(\mathbf{r}) \rangle^{or} = 0; \langle Q_{20}(\mathbf{r}) \rangle^{or}, \langle Q_{22}(\mathbf{r}) \rangle^{or} = \langle Q_{2,-2}(\mathbf{r}) \rangle^{or}, \text{ real.}$$

For convenience' sake let us put in Eq. (2.2)

$$Q_{20} = Q \cos \Xi, \; Q_{22} = Q_{2,-2} = 2^{-1/2} Q \sin \Xi. \tag{3.4}$$

Ξ is considered as a molecular parameter which represents the biaxiality of the constituent molecule. Anticipating the existence of a uniaxial-biaxial smectic A transition, we extend McMillan's theory of nematic-smectic A phase transition,[12] and write the order parameters as follows,

$$\langle Q_{20}(\mathbf{r})\rangle^{or} = Q\left(\eta_c + 2\sigma_c \cos\frac{2\pi z}{\mathrm{d}}\right), \tag{3.5a}$$

$$\langle Q_{22}(\mathbf{r})\rangle^{or} = \langle Q_{2,-2}(\mathbf{r})\rangle^{or} = 2^{-1/2}Q\left(\eta_s + 2\sigma_s \cos\frac{2\pi z}{\mathrm{d}}\right). \tag{3.5b}$$

η_c and σ_c are, respectively, the usual nematic and smectic order parameters, while η_s and σ_s are regarded as the nematic biaxial and smectic biaxial order parameters, respectively. We can designate a phase with nonzero σ_s a biaxial smectic A, because nonzero $\langle Q_{22}\rangle^{or}$ corresponds in the cartesian representation to the biaxial order parameter. From this treatment, therefore, we will get five states; isotropic (abbreviated as I; $\eta_c = \eta_s = \sigma_c = \sigma_s = 0$), uniaxial nematic (uN; $\eta_c \neq 0$, $\eta_s = \sigma_c = \sigma_s = 0$), biaxial nematic (bN; $\eta_c \neq 0$, $\eta_s \neq 0$, $\sigma_c = \sigma_s = 0$), uniaxial smectic A (uSA; $\eta_c \neq 0$, $\sigma_c \neq 0$, $\eta_s = \sigma_s = 0$) and biaxial smectic A (bSA; $\eta_c \neq 0$, $\eta_s \neq 0$, $\sigma_c \neq 0$, $\sigma_s \neq 0$).

Substituting (3.5a,b) into (3.2), we have for the mean field

$$\begin{aligned} V_1(\mathbf{r},\Omega) = -\,JQ\Bigg\{&\left(\eta_c + \alpha\sigma_c \cos\frac{2\pi z}{\mathrm{d}}\right)Q_{20}(\Omega) \\ &+ \left(\eta_s + \alpha\sigma_s \cos\frac{2\pi z}{\mathrm{d}}\right)2^{-1/2}[Q_{22}(\Omega) + Q^*_{22}(\Omega)]\Bigg\}, \end{aligned} \tag{3.6}$$

where we put

$$J = n\int \mathrm{d}\mathbf{r}\; J(r),$$

$$J_1 = n\int \mathrm{d}\mathbf{r}\; J(r)\cos\frac{2\pi z}{\mathrm{d}} = \frac{1}{2}\alpha J.$$

The molecular parameter α introduced firstly by McMillan[12] is related to the length of aliphatic chains attached to the central aromatic kernel.

Taking spatial average for the local order parameters (3.5), we obtain self-consistent equations of the order parameters

$$\eta_c = \frac{1}{V}\iint \mathrm{d}\mathbf{r}\;\mathrm{d}\Omega\, Q^{-1}Q_{20}(\Omega)f_1(\mathbf{r},\Omega), \tag{3.7a}$$

$$\eta_s = \frac{1}{V}\iint \mathrm{d}\mathbf{r}\;\mathrm{d}\Omega\, 2^{-1/2}Q^{-1}\{Q_{22}(\Omega) + Q^*_{22}(\Omega)\}f_1(\mathbf{r},\Omega), \tag{3.7b}$$

$$\sigma_c = \frac{1}{V}\iint \mathrm{d}\mathbf{r}\;\mathrm{d}\Omega\, Q^{-1}Q_{20}(\Omega)\cos\frac{2\pi z}{\mathrm{d}}f_1(\mathbf{r},\Omega), \tag{3.7c}$$

$$\sigma_s = \frac{1}{V}\iint \mathrm{d}\mathbf{r}\ \mathrm{d}\Omega 2^{-1/2} Q^{-1}\{Q_{22}(\Omega) + Q^{*}_{22}(\Omega)\} \cos \frac{2\pi z}{\mathrm{d}} f_1(\mathbf{r},\Omega), \tag{3.7d}$$

where $f_1(\mathbf{r},\Omega)$ is given by Eq. (3.3) in which use should be made of Eq. (3.6) for the mean field $V_1(\mathbf{r},\Omega)$.

Internal energy U and entropy S are given, within the mean field approximation, by

$$U = -\frac{1}{2}NJQ^2\{\eta_c^2 + \eta_s^2 + \alpha(\sigma_c^2 + \sigma_s^2)\}, \tag{3.8}$$

$$TS = -NJQ^2\{\eta_c^2 + \eta_s^2 + \alpha(\sigma_c^2 + \sigma_s^2)\} + Nk_BT \ln Z, \tag{3.9}$$

where

$$Z = \frac{1}{8\pi^2 V}\iint \mathrm{d}\mathbf{r}\ \mathrm{d}\Omega \exp\{-\beta V_1(\mathbf{r},\Omega)\}. \tag{3.10}$$

From them we can calculate free energy $F = U - TS$.

IV. NUMERICAL RESULTS

As seen from (3.3) and (3.6), Eqs. (3.7) are very complicated transcendental integral equations. We can solve them only numerically. We used Shimpson formula in order to calculate four-fold integral, and obtained various order parameters self-consistently by the iteration procedure.

In Figure 1 is shown the typical example of the numerical results for the temperature dependence of the order parameters with appropriate values of the molecular parameters α and Ξ. In the figure reduced temperature means $t = T/T_{NI}$, where T_{NI} is the nematic-isotropic phase transition temperature. The arrows indicate various phase transition points. This figure clearly shows the existence of the biaxial smectic A phase.

Rounding effects seen near the bSA-uSA and uSA-uN second order transition points arise from the roughness of the numerical calculation.

Next we show in Figure 2 the resulting phase diagram in the case of the molecular parameter $\alpha = 0.7$. In the figure the phases were determined by comparing their free energy values. In this case we have four phases—I, uN, uSA and bSA. It should be noted that there exists uN-uSA-bSA triple point. The uN-uSA transition line has a tendency to come down when decreasing the value of α, as shown firstly by McMillan.[12] The I-uN transition line should approach to $t = 1.0$ when sin Ξ reduces to zero. The apparent difference shows the error of the numerical calculations.

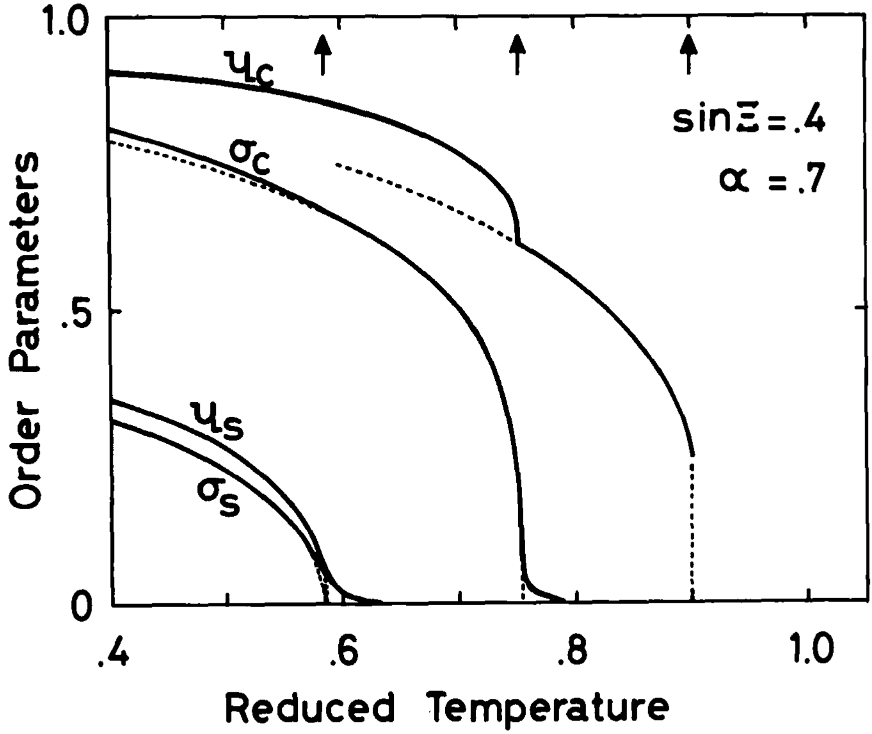

FIGURE 1 Temperature dependence of the order parameters in the case of molecular parameters $\alpha = 0.7$ and $\sin \Xi = 0.4$.

V. DISCUSSION

We have shown the existence of the uniaxial-biaxial smectic A phase transition within the mean field approximation. From Figure 2, however, it seems difficult for the biaxial smectic A to exist unless constituent molecules have strong molecular biaxiality Ξ. This may be why we have never confirmed the existence of biaxial nematic and smectic A phases experimentally, in spite of some theoretical suggestions for the biaxial nematics.[10,13] In the case of large molecular biaxiality we have biaxial smectic A phase which follows uniaxial smectic A via second order phase transition. When increasing molecular biaxiality Ξ more, uniaxial nematic phase changes directly to the biaxial smectic A via first order transition, as seen in Figure 2.

The biaxial smectic A phase has macroscopic biaxiality in optical property, but it does not have prominent temperature dependence of the layer thickness. Therefore we cannot distinguish it from the smectic C_2 described in Sec. I, by macroscopic optical, X-ray diffraction or miscibility methods. Hence we

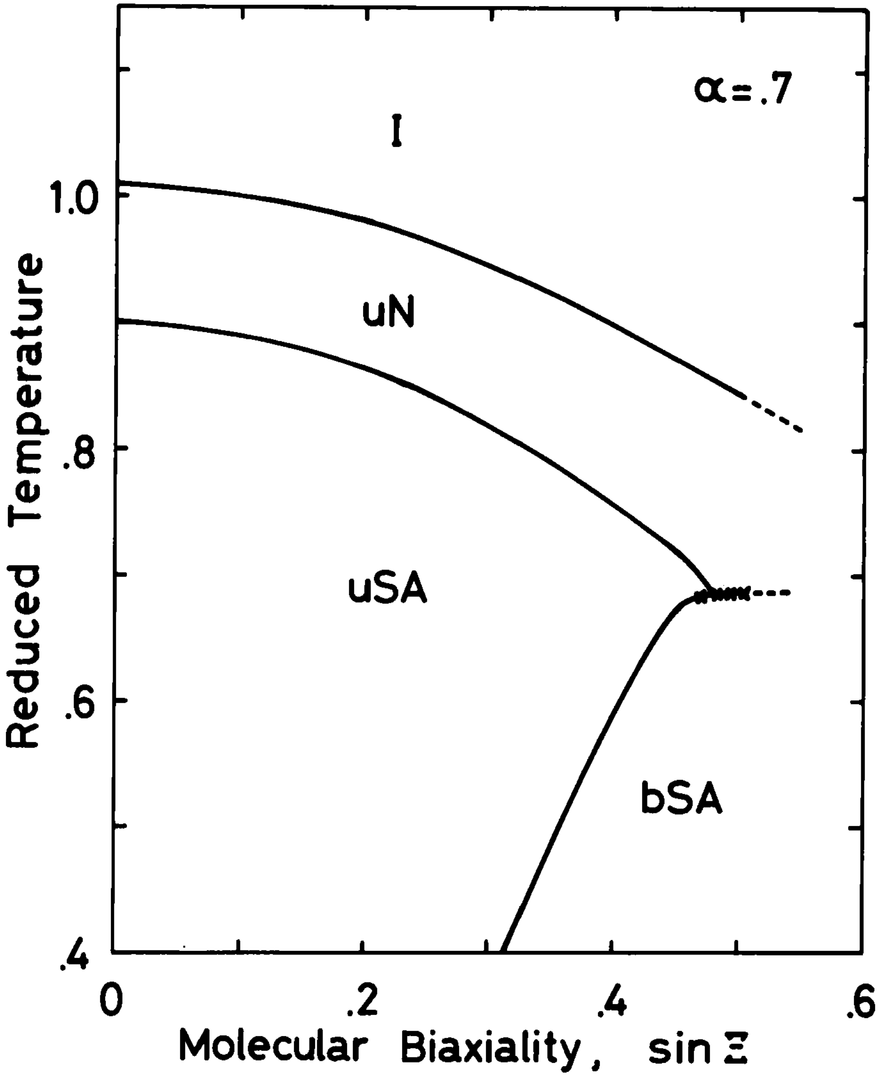

FIGURE 2 Phase diagram as a function of the molecular parameter Ξ in the case of $\alpha = 0.7$. The crosses on the line indicate first-order transition. The I-uN transition line is also first-order.

would like to point out the possibility that the smectic C_2 recently classified as smectic C^{3-5} may be biaxial smectic A.

In principle we have a means of distinguishing biaxial smectic A with smectic C. The biaxial smectic A phase can have point disclinations with half-integral index in addition to those with integral index, while the smectic C can only have the latter.

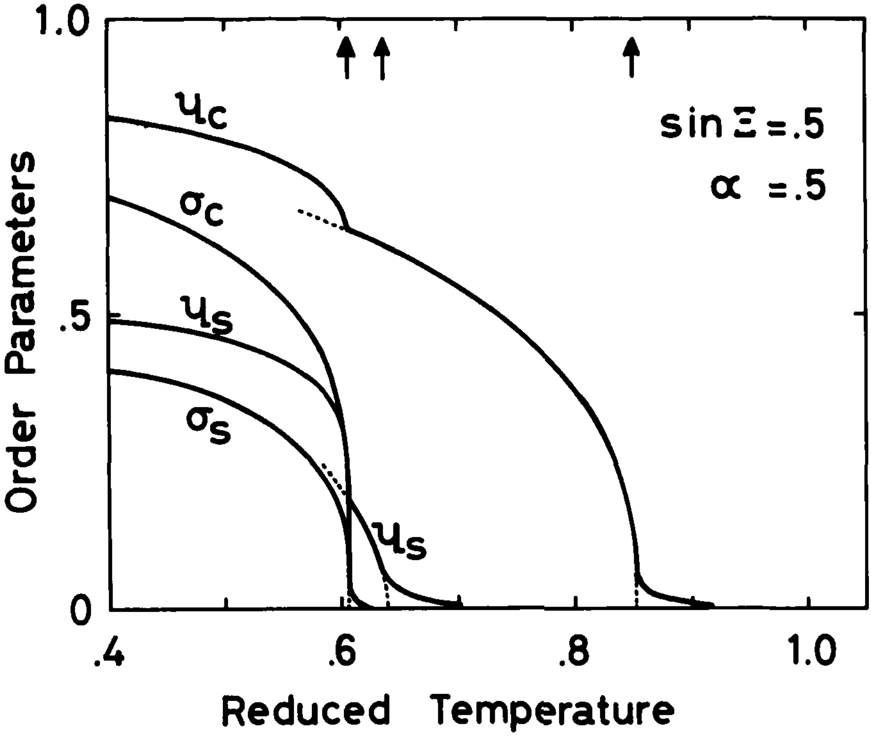

FIGURE 3 Temperature dependence of the order parameters with $\alpha = 0.5$ and sin $\Xi = 0.5$.

It should be noted that within this theory there exists biaxial nematic phase, although in Figure 2 it does not appear. In the case of smaller $\alpha(\alpha = 0.5)$ we have successive transition of bSA–bN–uN–I, as seen in Figure 3.

Finally numerical calculations should be proceeded for various α values. It seems very interesting to elucidate the properties and behaviors of the uN–uSA–bSA triple point. Moreover we hope some *ad hoc* experiments will be done for the detailed properties of the smectic C_2 compared with the usual smectic C_1.

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