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Theory of the dielectric constant of the smectic phases, and comparison with experiments (*)

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Résumé. — On propose une relation entre la constante diélectrique et les paramètres d'ordres des phases smectiques, dans le cas d'un ou plusieurs dipôles par molécule. On compare la variation avec la température de la constante diélectrique dans différents cas expérimentaux, avec celle prévue par la théorie.

Abstract. — The relation between the order parameters and the static dielectric constant of the smectic phases is investigated here, in the cases of one or more dipoles per molecule. We predict the temperature dependence of the dielectric constant and compare with experimental results.

1. Introduction. — Most of the literature on dielectric properties of liquid crystals is devoted to the nematic phase, whose behaviour in this respect seems well understood [1]. However, data and theory on the dielectric properties of other phases are rather scarce [2].

It is the purpose of this paper to present a theoretical calculation of the static dielectric constant ε in the smectic A, B and C phases, in order to find the connection between ε and the order parameters characteristic of each phase. In the second part of the paper, we compare our results with published values and also with some measurements we performed.

De Jeu *et al.* [2a] have shown that the correlations between the dipolar bonds, usually existing in liquid crystal molecules, are important for the understanding of the dielectric behaviour of the smectic A and B phases. The theory of Maier and Meier [3] valid for the nematic phase, completely neglects these correlations, and thus is not suitable for the smectic phases. Our theoretical approach allows us to describe a suggestive and physically illuminating relation between the dielectric behaviour and the smectic order parameters Ψ and δ , respectively the amplitude of the first harmonic of the density wave and the tilt angle.

2. Theory of the dielectric constant in smectic phases. — We begin by writing down the expression

of the static dielectric tensor in anisotropic media given by Bordewijk [4a] and by Inone and Urano [4b]

$$\varepsilon_i - \varepsilon_i^\infty = \frac{\varepsilon_i}{\varepsilon_i + (\varepsilon_i^\infty - \varepsilon_i) L_i} \frac{4 \pi N}{kT} (\overline{\mu\mu^*})_i \quad (1)$$

Here ε_i^∞ is the dielectric constant for frequencies above the lowest frequency relaxation : μ is the dipolar moment of a reference molecule in its own medium. μ^* is a thermal average dipole moment of the molecules contained inside a sphere of radius R around the reference molecule. L_i are anisotropic shape factors, N is the number of molecules for unit volume, k is the Boltzmann constant, and i is the coordinate index ($i = x, y, z$). The expression $(\overline{\mu\mu^*})_i$ stands for an average [5] of the product $\mu_i \mu_i^*$.

The first approximation is to take $L_i = 1/3$, as it should be in the isotropic case. This is justified by the relatively small anisotropy of the dielectric tensor. This approximation was also used by Maier and Meier [3] in their theory of the dielectric constant of the nematic phase. Thus we write :

$$\varepsilon_i - \varepsilon_i^\infty = \frac{3 \bar{\varepsilon}}{2 \bar{\varepsilon} + \varepsilon_i^\infty} \frac{4 \pi N}{kT} (\overline{\mu\mu^*})_i \quad (2)$$

with $\bar{\varepsilon} = \left(\sum_i \varepsilon_i \right) / 3$. To calculate $(\overline{\mu\mu^*})_i$, we follow Fröhlich's approximations [5] and we assume that one can write

$$(\overline{\mu\mu^*})_i = \overline{\mu_i^2} \left[1 + \sum_k \frac{\mu_i \mu_i^*}{\mu_i^2} \right] \quad (3)$$

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μ_i and μ_i^k are the i -th component of the dipole of the reference molecule and of its k -th nearest neighbour. Clearly the summation in square parentheses of (3) describes the short range dipole-dipole correlations.

2.1 SMECTIC A AND B PHASES. — In order to calculate $\mu_i \mu_i^k$, consider two nearest neighbour molecules in the smectic A phase (Fig. 1). We assume, to simplify the calculation, that the nematic order is well established, which means that the molecules can only be parallel or anti-parallel to the nematic direction (z -axis), analogously to an Ising model. Each nearest neighbour can then flip between two positions, parallel (state $+$) and anti-parallel (state $-$) to the reference molecules. (We assume that this is true even in the SmB phase). The rotational motion around the long axis is assumed to be completely free. If α and α_1 are defined as in figure 1, we have, for the short range correlation factor

$$g_{\parallel} = \sum_k \frac{\overline{\mu_z \mu_z^k}}{\mu_z^2} = \sum_k \frac{\iint (e^{-E_+/kT} - e^{-E_-/kT}) d\alpha d\alpha_1}{\iint (e^{-E_+/kT} + e^{-E_-/kT}) d\alpha d\alpha_1} \quad (4)$$

E_+ and E_- are the dipole energies of the two states of the molecule, $+$ or $-$ relative to each other (the smectic energy does not play a role since it is the same for the two states). E_+ and E_- depend on all the angles α , α_1 , γ and θ . We shall expand the exponentials in (4) in powers of E_{\pm}/kT and retain only the first two terms. This is not always a justifiable approximation but it simplifies enormously the calculations. We get, after integration on α and α_1 :

$$g_{\parallel} = - \frac{\mu^2 \cos^2 \beta}{kT} \sum_k \frac{(1 - 3 \sin^2 \gamma_k)}{r_k^3}. \quad (5)$$

The sum in (5) is a function of T , though γ_k and r_k .

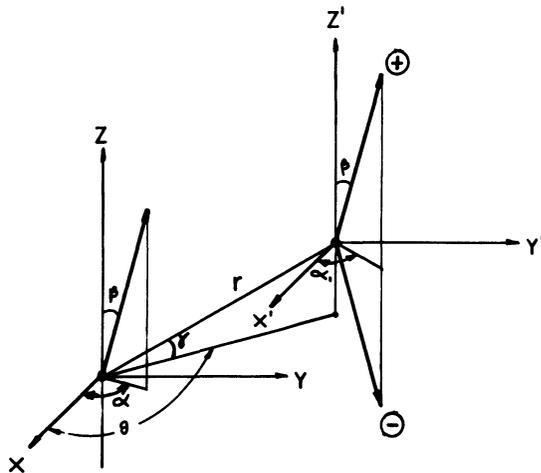


Fig. 1. — Respective positions of two neighbour molecules in the smectic A phase. The two molecules are not necessarily in the smectic layer.

In the smectic B phase we can assume a perfect smectic order, which means $\gamma_k = 0$ for every k ; the lattice in the layer is hexagonal and if r is the mean distance between molecules we have :

$$g_{\parallel} = - \frac{6 \mu^2 \cos^2 \beta}{r^3 kT}. \quad (6)$$

Note that expression (6) is very similar to that of de Jeu *et al.* [2], obtained by a different method.

If the smectic order is not perfect, we have to calculate the quantity

$$\sum_k (1 - 3 \sin^2 \gamma_k) / r_k^3,$$

using a specific model of the short range order. It is a rather difficult task, in particular because this order is not well known and it seems that even the number of nearest neighbours changes from the nematic state to the smectic state [6]. In ref. [7], we have proposed another approach. This sum is a single function of the smectic order parameter Ψ . It means that we assume that the short range order is directly related to the long range order. This is a mean field assumption and it will be checked by comparison with the experimental results. For symmetry reasons, we assume that the sum in (5) is an even function of Ψ . Thus we write

$$g_{\parallel} = - f(\Psi^2) \frac{\mu^2 \cos^2 \beta}{kT}. \quad (7)$$

The complete formula for $\varepsilon_{\parallel} = \varepsilon_z$ is now :

$$\varepsilon_{\parallel} - \varepsilon_{\parallel}^{\infty} = \frac{3 \bar{\varepsilon}}{2 \bar{\varepsilon} + \varepsilon_{\parallel}^{\infty}} \frac{4 \pi N}{kT} \times \mu^2 \cos^2 \beta \left[1 - f(\Psi^2) \frac{\mu^2 \cos^2 \beta}{kT} \right] \quad (8)$$

Ψ should take the value 0 at the smectic A-nematic transition and approach 1 at lower temperature in the smectic B phase.

For ε_{\perp} we can calculate $\varepsilon_x = \varepsilon_y$ (valid in the smectic A) and we have :

$$g_{\perp} = 2 \sum_k \frac{\iint \cos \alpha \cos \alpha_1 (e^{-E_+/kT} + e^{-E_-/kT}) d\alpha d\alpha_1}{\iint (e^{-E_+/kT} + e^{-E_-/kT}) d\alpha d\alpha_1}. \quad (9)$$

As above, in the case of ε_{\parallel} , we expand the exponentials as follows : $e^{-E_{\pm}/kT} \sim 1 - E_{\pm}/kT$, and we get :

$$g_{\perp} = \frac{\mu^2 \sin^2 \beta}{2 kT} \sum_k \frac{(1 - 3 \cos^2 \theta_k \cos^2 \gamma_k)}{r_k^3} \quad (10)$$

after integration.

In the smectic B phase, we again assume $\gamma_k = 0$ for every k and g_{\perp} reduces to

$$g_{\perp} = \frac{3}{2} \frac{\mu^2 \sin^2 \beta}{r^3 kT} \sum_k (1 - 3 \cos^2 \theta_k). \quad (11)$$

Now, since the molecules are ordered in a hexagonal two dimensional lattice, we get

$$g_{\perp} = \frac{3}{2} \frac{\mu^2 \sin^2 \beta}{r^3 kT}. \quad (12)$$

Here, also, we find an expression analogous to that of de Jeu *et al.* [2], but with the difference that the ratio g_{\parallel}/g_{\perp} is equal to $4/\text{tg}^2 \beta$ while de Jeu *et al.* found $g_{\parallel}/g_{\perp} = 2/\text{tg}^2 \beta$. Again we assume that the sum in (10) is related to the smectic order parameter Ψ . Thus the final formula for ϵ_{\perp} is

$$\epsilon_{\perp} - \epsilon_{\perp}^{\infty} = \frac{3 \bar{\epsilon}}{2 \bar{\epsilon} + \epsilon_{\perp}^{\infty}} \frac{4 \pi N}{kT} \frac{\mu^2 \sin^2 \beta}{2} \times \left[1 + h(\Psi^2) \frac{\mu^2 \sin^2 \beta}{kT} \right]. \quad (13)$$

Although, we have no exact expressions for the functions $f(\Psi^2)$ and $h(\Psi^2)$ relating the short range order implied in the expressions of g_{\parallel} and g_{\perp} to the long range order, we can look for the qualitative behaviour of these functions. If we assume that the number of nearest neighbours is the same in the smectic phases A and B, and is equal to six, we see that for decreasing T , the r_k 's and the γ_k 's decrease also. This means that the quantity $\sum (1 - 3 \sin^2 \gamma_k)/r_3 = f(\Psi^2)$ increases if Ψ increases. However, for g_{\perp} , we have

$$h(\Psi^2) = \sum (1 - 3 \cos^2 \theta \cos^2 \gamma_k)/r_k^3$$

and there is a competition between the variation of r_k^3 and that of $\cos^2 \gamma_k$ with temperature. Thus, it is difficult to conclude definitely about the T dependence of $h(\Psi^2)$. Now near the SmA-N transition, we can expand f and h around $\Psi^2 = 0$, if the transition is of second order, or weakly of first order, we have, in the molecular field approximation,

$$f(\Psi^2) \simeq f(0) + f'_0 \Psi^2 = f(0) + f'_0 K(T_0 - T) \quad (14)$$

$$h(\Psi^2) \simeq h(0) + h'_0 \Psi^2 = h(0) + h'_0 K(T_0 - T)$$

where we write $\Psi^2 \sim K(T_0 - T)$. Thus we expect a linear variation of $f(\Psi^2)$ and $h(\Psi^2)$ with T very near T_0 .

2.2 SMECTIC C PHASE. — Now the dielectric tensor has three principal axes, since the C phase is biaxial (see figure 2). We define direction 1 to be in the smectic layer, and perpendicular to the molecular axis, or direction 3. Direction 2 is then defined by being perpendicular to directions 1 and 3. Directions

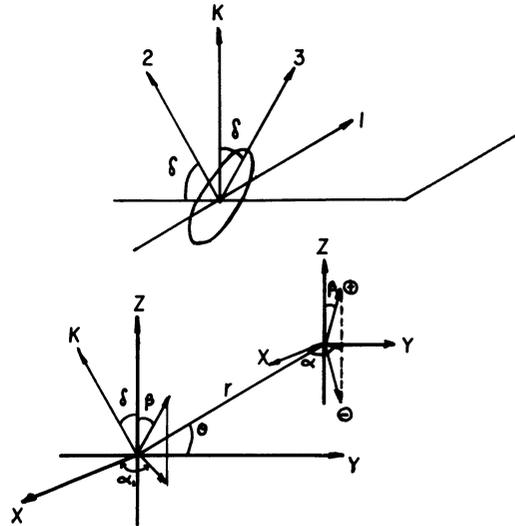


Fig. 2. — Respective positions of two neighbour molecules in the smectic C phase and definition of the principal axes. The plane xy is not the smectic layer, but the two molecules are in the same smectic C layer.

x, y, z are fixed with the reference molecule (Fig. 2), and we have the equivalence $1 \rightarrow y, 2 \rightarrow -x$ and $3 \rightarrow z$. The calculation is simpler when we use the xyz reference frame. Figure 2 also shows the position of the two molecules. The molecules are in the smectic layer, and their long axis forms an angle δ with the xy smectic phase. δ is the tilt angle of the C phase. We finally define k as a unit vector, perpendicular to the smectic layer. The components of r are easily calculated and we get $r = |r| (-\sin \theta \cos \delta, \cos \theta, \sin \theta \sin \delta)$. In calculating the different correlation factors g_i we suppose that, as in the smectic A and B phases, there is a rotational motion of the molecules around their long axis. This is in agreement with the general belief [8] and it is contrary to the model of McMillan [9].

For the z direction we get :

$$g_z = \sum_k \frac{\iint (e^{-E_+/kT} - e^{-E_-/kT}) d\alpha d\alpha_1}{\iint (e^{-E_+/kT} + e^{-E_-/kT}) d\alpha d\alpha_1} = \frac{\mu^2 \cos^2 \beta}{r^3 kT} \sum_k (1 - 3 \sin^2 \theta_k \sin^2 \delta). \quad (15)$$

We assume here that the smectic and nematic orders are complete. Thus there are 6 nearest neighbours, and we get

$$g_z = - \frac{6 \mu^2 \cos^2 \beta}{r^3 kT} \left(1 - \frac{3}{2} \sin^2 \delta \right) \quad (16)$$

g_z now depends on the tilt angle δ and in particular its absolute value begins to decrease if δ increases, and becomes zero for $\sin^2 \delta_1 = 2/3$ ($\delta_1 \approx 54^\circ$). For $\delta > \delta_1$ the correlation factor g_z becomes positive.

In general, the tilt angle of the known smectic C phases is smaller than 54° and therefore we expect only to observe a decrease of the absolute value of g_z on going from the smectic A to the smectic C phase. For the y direction (direction 1), we have

$$g_1 = \sum_k \frac{\iint \sin \alpha \sin \alpha_1 (e^{-E_+/kT} + e^{-E_-/kT}) d\alpha d\alpha_1}{\iint (e^{-E_+/kT} + e^{-E_-/kT}) d\alpha d\alpha_1} \quad (17)$$

or

$$g_1 = \sum_k \frac{\mu^2 \sin^2 \beta}{4 r^3 kT} (1 - 3 \cos^2 \theta_k) = \frac{3}{2} \frac{\mu^2 \sin^2 \beta}{r^3 kT} \quad (18)$$

g_1 is identical with g_\perp of the smectic B phase. For the x direction (direction 2) we have :

$$g_2 = \sum_k \frac{\iint \cos \alpha \cos \alpha_1 (e^{-E_+/kT} + e^{-E_-/kT}) d\alpha d\alpha_1}{\iint (e^{-E_+/kT} + e^{-E_-/kT}) d\alpha d\alpha_1} \quad (19)$$

which yields, after integration :

$$g_2 = -\frac{\mu^2 \sin^2 \beta}{2 r^3 kT} \sum_k \left(1 - \frac{3}{2} \cos^2 \delta\right) \quad (20)$$

or, since there are 6 nearest neighbour molecules :

$$g_2 = -3 \frac{\mu^2 \sin^2 \beta}{r^3 kT} \left(1 - \frac{3}{2} \cos^2 \delta\right). \quad (21)$$

In order to compare with our experimental results we need to calculate the mean value $(g_1 + g_2)/2 = g_\perp$, which is

$$g_\perp = \frac{3}{4} \frac{\mu^2 \sin^2 \beta}{r^3 kT} (3 \cos^2 \delta - 1). \quad (22)$$

Thus, g_\perp decreases if δ increases and becomes zero for the same angle $\delta_1 \sim 54^\circ$ at which $g_z = 0$. We can summarize as follows :

In the smectic A (or B) phase the correlation is more important than in the nematic phase. However, in the smectic C phase the role of the correlation becomes less important (compare (6) with (16), and (12) with (22)). We expect that the dielectric anisotropy $\varepsilon_{\parallel} - \varepsilon_{\perp}$ in the smectic C phase will be smaller than in the smectic A phase and even than in the nematic phase.

The final formulas for ε_{\parallel} and ε_{\perp} in the smectic C phase are :

$$\varepsilon_{\parallel} - \varepsilon_{\parallel}^{\infty} = \frac{3 \bar{\varepsilon}}{2 \bar{\varepsilon} + \varepsilon_{\parallel}^{\infty}} \frac{4 \pi N}{kT} \mu^2 \cos^2 \beta \times \left[1 - \frac{6 \mu^2 \cos^2 \beta}{r^3 kT} \left(1 - \frac{3}{2} \sin^2 \delta\right)\right] \quad (23a)$$

and

$$\varepsilon_{\perp} - \varepsilon_{\perp}^{\infty} = \frac{3 \bar{\varepsilon}}{2 \bar{\varepsilon} + \varepsilon_{\parallel}^{\infty}} \frac{4 \pi N}{kT} \frac{\mu^2 \sin^2 \beta}{2} \times \left[1 + \frac{3}{4} \frac{\mu^2 \sin^2 \beta}{r^3 kT} (3 \cos^2 \delta - 1)\right]. \quad (23b)$$

2.3 MOLECULE WITH MORE THAN ONE DIPOLE. —

Until now, we assumed that the molecule has only one dipole μ , making an angle β with the long axis. In fact, in several cases, there are more than one dipole. We can show that if the molecule has n dipoles, $\mu_1, \mu_2, \dots, \mu_n$, making the angles $\beta_1, \beta_2, \dots, \beta_n$ with the long axis and being free to rotate independently around the long axis, we have to modify eqs. (22) and (23) in the different phases. In the isotropic liquid, μ^2 has to be replaced by $\sum_i \mu_i^2$, and in the smectic A phase :

$$\mu^2 \sin^2 \beta \quad \text{by} \quad \mu_s^2 = \sum_i \mu_i^2 \sin^2 \beta_i$$

and

$$\mu^2 \cos^2 \beta \quad \text{by} \quad \mu_c^2 = \left(\sum_i \mu_i \cos \beta_i\right)^2$$

(In the calculation we neglected the correlations.) Thus the formulae (8), (13) and (23) given above hold, if we replace $\sin^2 \beta$ and $\cos^2 \beta$ by :

$$s^2 = \frac{\mu_s^2}{\sum_i \mu_i^2} = \frac{\sum_i \mu_i^2 \sin^2 \beta_i}{\sum_i \mu_i^2} \quad (24)$$

$$c^2 = \frac{\mu_c^2}{\sum_i \mu_i^2} = \frac{\left(\sum_i \mu_i \cos \beta_i\right)^2}{\sum_i \mu_i^2} \quad (25)$$

with this definition, the sum $s^2 + c^2$ is not equal to 1, since

$$s^2 + c^2 = 1 + 2 \frac{\sum_{i,j} \mu_i \mu_j \cos \beta_i \cos \beta_j}{\sum_i \mu_i^2}.$$

3. Experimental results. — 3.1 SMECTIC A AND B PHASES. —

In ref. [7] where a short version of our theory has been presented, we have used the results of ref. [1] on heptylazoxybenzene. In this material we can easily deduce the quantities $(1 + g_{\parallel})$ and $(1 + g_{\perp})$ in its smectic A phase. As already explained by de Jeu *et al.* [1], and in agreement with our theoretical results, g_{\parallel} is found negative, i.e. the parallel correlation is of antiferroelectric type and g_{\perp} is found positive, i.e. the perpendicular correlation is of ferroelectric type. In figure 3, we have drawn the temperature variation of the quantities $|g_{\parallel}| T$ and $g_{\perp} T$, which are respectively proportional to $f(\Psi^2)$ and $h(\Psi^2)$. We see that they have the same qualitative

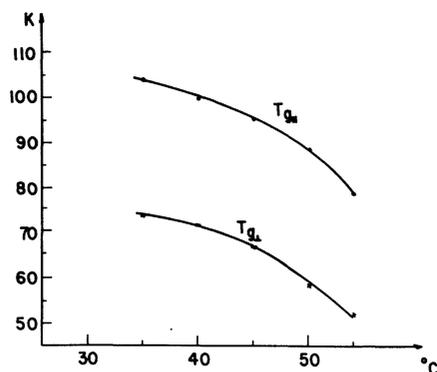


Fig. 3. — Variation with T of the quantities $T|g_{||}$ and Tg_{\perp} in the smectic A phase of heptylazoxybenzene.

behaviour and the correlations are more and more important, as T decreases, i.e. when the smectic order parameter increases. For the compound heptylazoxybenzene, the SmA-N transition is almost of second order and in accordance with eq. (14), the derivatives $f'(0)$ and $h'(0)$ are finite, at 54 °C.

It should be interesting to compare our theoretical results with a material exhibiting the smectic A and smectic B phases to study the behaviour of the functions $f(\Psi^2)$ and $h(\Psi^2)$. In particular we expect that they will be constant in the smectic B phases. Thus we performed dielectric measurements on Ethyl p-[(p-Methoxybenzylidene)-amino] cinnamate (EMBAC), commercially available from Eastman Kodak. This material is not an ideal candidate since it is extremely difficult to get pure enough (see ref. [10] for difficulties and pitfalls) and it decomposes easily. Thus in each measurements the material was used only once.

The experimental set-up is described in ref. [11] and we used a bridge with a sensitivity higher than 10^{-2} pF. It is known that the alignment of the molecules is difficult in the smectic phases, but we think we achieved a good alignment for the following reason.

When the aligning magnetic field (~ 2000 G) was perpendicular to the measuring electric field (measurements of ϵ_{\perp}) we never observed dielectric relaxation in the megahertz range. This relaxation is easily observed when magnetic and electric fields are parallel, and corresponds to the rotation of the molecules around their short axis. The previous observation does not ensure that in the parallel configuration, the sample is really homeotropic. But by direct observation with polarized light of the sample between crossed polarizers, we confirm the good alignment. In figure 4 we show $\epsilon_{||}(T)$ and $\epsilon_{\perp}(T)$ of EMBAC as measured as functions of temperature at 100 kHz, which is well below the first parallel relaxation frequency for $T > 70$ °C. $\epsilon_{||}(T)$ and $\epsilon_{\perp}(T)$ present opposite behaviour in the whole smectic region (B and A), the former increasing and the latter decreasing with T . The two actually cross near the A-B transition temperature, giving rise to an anisotropy reversal. $\epsilon_{||}$ decreases again in the nematic phase with a large

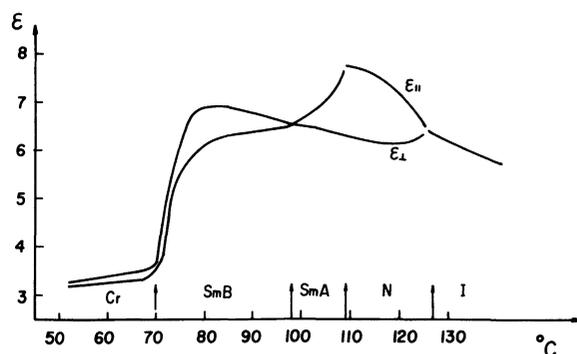


Fig. 4. — $\epsilon_{||}(T)$ and $\epsilon_{\perp}(T)$ of EMBAC at decreasing T .

discontinuity in the slope at the A-N transition temperature. All the transitions are very weakly of first order. We note that the T -dependence of ϵ_{\perp} in the smectic A and B phases is indistinguishable from linear, mostly because of the relatively small range of temperatures and the fact that ϵ_{\perp} varies slowly. This means that we cannot verify the theoretical prediction given by eq. (13). However, we can use the data for $\epsilon_{||}$ and calculate the quantity $c^2(1 + g_{||})$ from eq. (8), in the following manner.

In the isotropic liquid phases, we assume the validity of the Onsager formula

$$\epsilon - \epsilon_{\infty} = \left(\frac{3\epsilon}{2\epsilon + \epsilon_{\infty}} \right) \frac{4\pi N\mu^2}{3kT} \quad (26)$$

which neglects the short range correlation. At least at high enough temperature this assumption should be justified. In (26), two parameters are unknown: ϵ_{∞} and $K = (4\pi N\mu^2)/k$. (It is again difficult to fit (26) in the narrow temperature range of our experimental results.) We choose for ϵ_{∞} the value 2.5, a value lower than the dielectric constant in the crystal phase (Fröhlich [3] suggested taking $\epsilon_{\infty} \approx \epsilon(T=0)$), and we get from (26) $K \simeq 1100$ K, taking the experimental value of ϵ at 140 °C. It may appear that the choice of $\epsilon_{\infty} = 2.5$ is somewhat arbitrary, but we have verified that the results we get and the conclusions we draw are not affected by the exact value of ϵ_{∞} , as long as it is taken between 2 and 3, which are very reasonable bounds. From expression (8), we calculate the quantity $c^2(1 + g_{||})$ using the experimental results for $\epsilon_{||}$ and $\bar{\epsilon} = (\epsilon_{||} + 2\epsilon_{\perp})/3$ and the values of ϵ_{∞} and K above. The results are presented in table I. We see that $c^2(1 + g_{||})$ increases with T , which means that $g_{||}$ increases, because it is the only quantity which depends on T . In figure 5, we plot the quantity $A = Tc^2(1 + g_{||})$ as a function of T . According to the expression (6) and (7) of $g_{||}$, in the smectic B and A phase, we must have

$$A = c^2 T - f(\Psi^2) \frac{\mu^2 c^2}{k}. \quad (27)$$

In the smectic B phase $f(\Psi^2)$ should be constant, because the smectic order in layers should be good,

Table I. — Correlation factor $c^2(1 + g_{\parallel})$ of EMBAC in the smectic phases. In the SmA phase ($T > 98$ °C) $\varepsilon_{\parallel} > \bar{\varepsilon}$ and in the SmB phase ($T \leq 98$ °C) $\varepsilon_{\parallel} < \bar{\varepsilon}$.

T °C	ε_{\parallel}	$\bar{\varepsilon}$	$c^2(1 + g_{\parallel})$
108	7.53	6.77	0.458
106.5	7.25	6.68	0.432
105	7.10	6.67	0.417
102	6.78	6.59	0.385
100	6.65	6.56	0.372
98	6.55	6.55	0.360
95	6.45	6.58	0.348
92	6.44	6.65	0.345
90	6.42	6.67	0.340
88	6.40	6.71	0.337
85	6.375	6.73	0.332

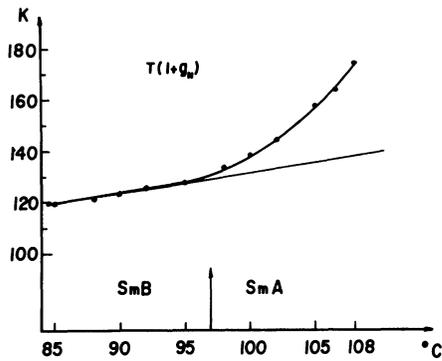


Fig. 5. — $A = Tc^2(1 + g_{\parallel})$ as a function of T . In the smectic B phase ($T < 98$ °C), the theory predicts that $A(T)$ is a straight line as observed.

with $\Psi \approx 1$; $A(T)$ is therefore a straight line, as we can see in figure 5. In the smectic A phase, $A(T)$ increases with T faster than linearly (figure 5), and from (27) it follows that $f(\Psi^2)$ decreases if T increases (or with decreasing Ψ). This result is expected from the ideas expressed above. We can calculate a quantity B which is directly related to $f(\Psi^2)$ in the following way :

$$B = \frac{\mu^2 c^4}{k} \{ f(\Psi^2) - f[\Psi(108 \text{ °C})] \}. \quad (28)$$

Although the SmA-N transition is of first order, it is very nearly of second order, thus we can assume that $\Psi(108 \text{ °C}) \approx 0$. In figure 6, we show B as function of T . Below 98 °C, B is constant as expected since the material is in the SmB phase. Near 108 °C (SmA-N transition) $B(T)$ can be approximated by a straight line, in agreement with the expressions (14). This gives support to our basic assumption that the correlation factor is a function of the second power of Ψ . From figure 5 we get $c^2 \sim 0.95$. But we cannot conclude that $s^2 \sim 0.05$. If this were true, ε_{\perp} would be much lower than the value observed since as explained above, $s^2 + c^2$ may be larger than 1.

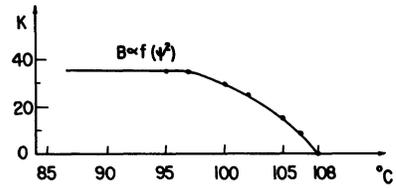


Fig. 6. — $B = (\mu^2 c^4/k) [f(\Psi^2) - f(0)]$ as a function of T ; for $T \leq T_{AN}$, $f(\Psi^2) - f(0) \propto \Psi^2$ and B directly proportional to Ψ^2 . In the mean field approximation, $\Psi^2 \propto (T_c - T)$ and B is a straight line.

3.2 SMECTIC C PHASE. — There are very few measurements of the dielectric permittivity in the smectic C phase. Maier and Meier [12] have measured ε_{\parallel} and ε_{\perp} of diheptyloxy-azoxybenzene (DHAB) at various frequencies. We repeated those measurements, with results shown in figure 7. These are in general agreement with Maier and Meier's, but our values of ε_{\parallel} are slightly above theirs. We note the strong discontinuities of both ε_{\parallel} and ε_{\perp} , observed at the SmC-Cr transitions, which indicate the freezing of the rotational motion of the molecules as with EMBAC. The decrease of ε_{\parallel} with T in the SmC phase is due to the presence of the parallel relaxation, which occurs in the SmC phase between 20 kHz and 200 kHz. However, with the help of the Cole-Cole plot we estimate that the static value of ε_{\parallel} is equal to 3.95 and does not depend on T . Thus, in the SmC range ε_{\parallel} and ε_{\perp} , are constant and this may be explained by the fact that at the transition from the N phase to the SmC phase two orderings appear together : the smectic ordering in layers, and the tilt angle. We saw, in the previous section, that each ordering gives opposite contributions to the correlation factors g_{\parallel} and g_{\perp} . However, we note a net increase of ε_{\parallel} at the SmC-N transition and this means that due to the large value of the tilt angle $\delta = 45^\circ$ [11] (δ is independent of T), the effect of the tilting is dominant and this gives an increase in ε_{\parallel} .

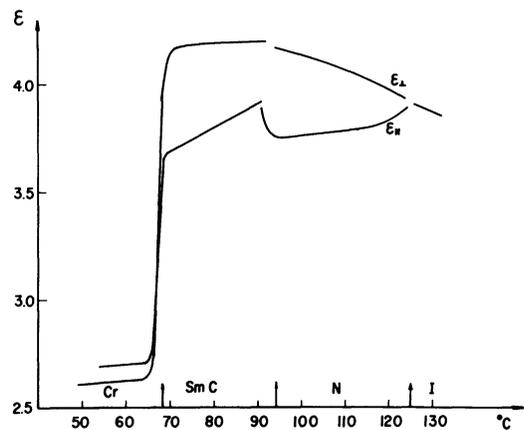


Fig. 7. — $\varepsilon_{\parallel}(T)$ and $\varepsilon_{\perp}(T)$ of DHAB. The frequency is 200 kHz and the temperature is decreasing.

In ref. [11], we measured the three values of the dielectric tensor. In particular we found $\varepsilon_1 = 4.24$, and $\varepsilon_2 = 4.14$ at 90°C , i.e. $\varepsilon_2 < \varepsilon_1$. The difference between these two values comes essentially from the different correlation factors g_1 (see (18)) and g_2 given by (21). For $\delta = 45^\circ$, we see that $g_2 < g_1$, in agreement with our experimental results. We note also that $g_1 > 0$ and $g_2 < 0$ i.e. the correlations are of ferroelectric type only in the direction 1 which is parallel to the layer planes (see figure 2).

4. Conclusion. — In our theoretical study of the dielectric permittivity of liquid crystals in their smectic phases we were able to show its relation with the order parameters. Our approach takes into account only the correlation between neighbouring molecules. For the smectic A and B phases, our results are analogous to those of de Jeu *et al.* (refs. [2a] and [2b]) but their method is more complicated and physically less evident. The comparison between the two methods shows clearly that the essential part of the correlation

is given by neighbouring molecules. We have also proposed a functional dependence of the correlation factor with the smectic order parameter Ψ .

We also extended our theory to the smectic C phase when there are three different components of the permittivity tensor. This was possible due to the simplicity of the method proposed here. In this case, we found an explicit dependence of the three correlation factors on the tilt angle. In particular, g_1 is positive and independent of δ . The correlation factor in the layer is equal to that obtained in the case of the smectic B phase.

By comparison with the experimental results, we showed the correctness of our approach in the smectic A and B phase, and results in the smectic C phase give support for the theory.

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