Dielectric Relaxation in Liquid Crystals

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DIELECTRIC RELAXATION IN LIQUID CRYSTALS

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Abstract   We present recent progress in the study of
the liquid crystals by dielectric relaxation. First,
we discuss the possible mechanism controlling the rota-
tion of the molecules around a short axis: rotational
diffusion or free volume effect. In the case of phase
transition between Sm A phases, dielectric relaxation
can bring information about the short range order and
also the long range order when a dipole ordered struc-
ture is established.

INTRODUCTION

The nematic ordering, which exists in liquid crystals, per-
mits to distinguish between two types of relaxation, depend-
ing on the relative position of the measuring electric field
and the director. The dielectric spectra are different in
the E//n or the E⊥n configuration (external field respect-
ively parallel or perpendicular to the director n). In this
paper, we shall be concerned only with the E//n relaxation
and we shall first discuss what are the possible mechanisms
associated with this kind of relaxation. Then, we shall
give two examples of dielectric relaxation in the Smectic A
phases. It is known that several Smectic A phases[1] have
been discovered and we shall present results concerning the
passage from the Sm A phase to the Sm A_1 phase, and the
Sm A_2-Sm A_1 transition.

THE E//n RELAXATION

The first studies[2,3] of this relaxation described it in

terms of a rotational diffusion process. They are an exten-
tion of the Debye theory of molecular relaxation in regular
liquids. The flipping of one molecule around a short axis
is seen as a rotational diffusion through many collisions
with the neighbouring molecules hindered by the presence of
the nematic potential. Different methods [2-5] have been pro-
posed to resolve this problem. The relaxation time associa-
ted with the longitudinal component of the dipole moment is
given by $\tau_{//} = g_{//}\tau$, where τ is the relaxation time in the
isotropic phase and $g_{//}$ is the "retardation factor" which
takes into account the nematic potential. (We recall that
the basic picture of the molecules is that of a rod with a
dipole making an angle with the rod axis.) It is shown that
$g_{//} \gg 1$ and this explains the large values of τ experi-
mentally observed. Experimentally, the E//n relaxation
(with the lowest relaxation frequency) is an almost pure
Debye relaxation, but it is not true for the isotropic
liquid. This shows that the situation is more complicated
than the proposed picture.

    de Jeu[6] has compared the theoretical predictions with
the experimental results of the compound 7 C B (p-heptyl-
p-cyanobiphenyl) and he found a good agreement only quali-
tatively. In particular, there is a discrepancy in the slope
of the curve $\ln f_R$ versus $1/T$. A difficulty with this theory
is that $\tau_{//}$ is related to the viscosity of the liquid (it
was proposed[5] to identify this viscosity with γ , the rota-
tional viscosity) and this cannot be useful in the Sm A and
Sm C phases in which this relaxation has been also observed.
Finally we want to note that it is an Arrhenius model, in
which $\tau_{//}$ is expressed as $\tau_{//} = A \exp(W/T)$.   But when one
tries to fit the experimental results with such an expres-
sion, one gets sometimes unrealistic values of A and W. The

interval of temperature for which $\tau_{//}$ is measured is so
small (of the order of $10-20°K$) that the fit with an Arrhenius
law is not unic.

Another interpretation of this relaxation has been re-
cently proposed independently by Zeller[7] and Diogo and
Martins[8]. It is not a collective phenomenon, but a single
particle process by instantaneous jump of the molecule.
Since it is a single particle process, the relaxation occurs
with a well defined relaxation time and it is a pure Debye
relaxation. The process is not related to the nematic po-
tential, but only to the free volume. The relaxation time
$\tau_{//}$ is given by

$$\tau_{//} = B \exp \frac{\theta s^2}{(T - T_o)} \tag{1}$$

If the temperature is much lower than the nematic isotropic
transition temperature T_{NI}, s^2 is practically constant and
(1) reduces to

$$\tau_{//} = B \exp \frac{E}{(T - T_o)} \tag{2}$$

(Vogel-Fulcher law). Zeller has measured $\tau_{//}$ on several
compounds in a large temperature interval, even reaching
the glassy state and (2) was very well verified. The veri-
fication of Diogo and Martins[8] is indirect, since they ana-
lyzed the temperature dependence of τ through that of the
viscosity coefficients of MBBA. They found a very good
agreement by using (1).

It is interesting to note that Buka and Leyvraz[9] pre-
sented a model taking into account the two possible mechan-
isms: instantaneous jump (which can be identified with the
free volume effect) and rotational diffusion, in order to
analyze the results of the compound 8 C B in which the E//n

spectrum exhibits two modes. The relaxation at the lowest
frequency and with the strongest amplitude is attributed to
the first mechanism whereas the second relaxation with the
highest frequency, but much smaller amplitude (only one
length of the first relaxation) is related to the rotational
diffusion. This second relaxation may be difficult to ob-
serve, especially if the molecule has also a transverse di-
pole moment. Their analysis gives support to the interpre-
tation of the E//n relaxation as a free volume effect.

        We can give a direct verification of (1) from our
measurements of τ or $f_R = 1/(2\pi\tau)$ of three compounds of
the serie p-pentoxy-benzylidene alkylaniline: 50.6, 50.7 and
50.8, in their "fluid" phases: nematic, Smectic A and Smec-
tic C. We tried to fit the experimental results by the ex-
pression (1). We do not know S, but Hardouin et al.[10]
measured the diamagnetic susceptibility anisotropy $\Delta\chi$, which
is proportional to S. We found an excellent fit taking for
the three compounds the same value of the difference
$T_{NI} - T_o = 140^\circ K$, as shown on Fig.1. The value of T_o we
found ($T_o \simeq 213^\circ K$) is very near the value determined by
other researchers on different compounds and mixtures (T_o is
found between $225^\circ K$ and $170^\circ K$).

        We show also on the Fig.2 the variation of the relaxa-
tion frequency f_R ($\ell n f_R$ versus $1/T$) of the compound "DB8Cl"
(octylphenyl 2-chloro-4-(p-cyanobenzoyloxy) benzoate) which
exhibits the following sequence of phases: nematic-Sm A_2-
Sm C_2 - Sm S_2. (for details see reference 11 and 12). We
see clearly that the results are not consistent with an
Arrhenius law. However, the fit with (2) (S is practically
constant in the temperature range considered) is very good
as it is shown on Fig.3.

        Thus, we have the feeling that the E//n relaxation is
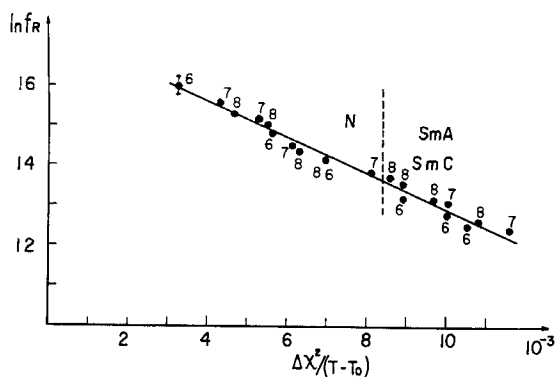
FIGURE 1. $\ln f_R$ versus $(\Delta\chi)^2/(T - T_o)$ for the compounds 50.6, 50.7 and 50.8. $T_{NI} - T_o = 140°K$.

very likely controlled by the free volume. In a physical way, we can say that in this picture the probability for a molecule to change the direction of its long axis by 180° decreases with T because of the increase of the nematic order and there is less and less room for a molecule reversal. In the rotational diffusion picture, the reversal takes place through the nematic barrier and consequently it is an activated energy process.

DIELECTRIC RELAXATION IN THE SMECTIC A PHASES

The dielectric relaxations in the Sm A phase may exhibit very different behaviour in accordance with the fact that there are several types of Sm A phases[1] (Sm A_1, Sm A_2, Sm $\tilde{A}$, Sm A_d). Here we want to discuss the very special situation of the compound "T8" (4-n-octyloxybenzoyloxy-4"-cyano stilbene) which exhibits two reentrant phases: a nematic one and a smectic A one[13]. This compound has very particular
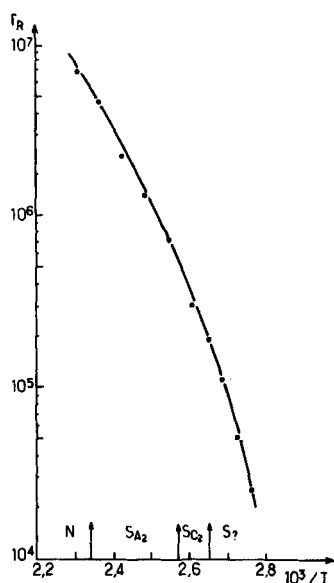
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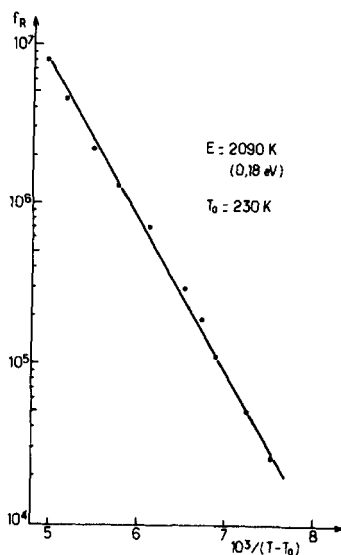FIGURE 2. ℓnf_R versus
1/T for DB8Cl.

FIGURE 3. ℓnf_R versus
$1/(T - T_o)$.

dielectric relaxation in the $E//n$ configuration. Two re-
laxations[14] are observed: each characteristic of one of the
two Sm A phases. This is consistent with the fact that the
high temperature phase is a Sm A_d phase, and that at low
temperature is a Sm A_1 phase. In the reentrant nematic
phase both relaxations can be observed with amplitudes de-
pending on the temperature.

It is possible to suppress[15] the reentrant phase by

adding the compound "T5NO2" to "T8" and we have only the
nematic and Sm A phases. It is important to note that there
is no phase transition between the Sm A phases, but only
gradual passage from the Sm A_d to the Sm A_1 phase by de-
creasing the temperature. Near the concentration in T5 NO2
for which the reentrant just disappears, the layer thick-
ness of the Sm A phase decreases with T with a slight in-
crease in the slope around 140°C. The question is whether
the coexistence of the two relaxations is an intrinsic pro-
perty of the reentrant nematic phase. We were very sur-
prised when we discovered that for the mixture 0.75 T8 –
0.25 T5 NO2, which does not exhibit the reentrant nematic
phase, we effectively observed two relaxations.[16]

In Fig.4, we show the Cole-Cole plot at different tem-
peratures and we see that one relaxation disappears when
the temperature decreases. We have a situation of a gradual
passage from one kind of Sm A phase to another (something
analogous to the gradual passage from a "liquid" to a "gas"
in a fluid above its critical point) but with the possibi-
lity to have two different short range orders. The main
difference between the Sm A_d phase and the Sm A_1 phase is
the value of ℓ, the layer thickness: in the Sm A_1 phase
it is equal to the molecular length $d = \ell$, and in the Sm A_d
phase we have $\ell > d$. In this last case, it is frequently
assumed that two molecules can form a dimer of length ℓ,
with core overlapping. The passage from the Sm A_d phase to
the Sm A_1 phase does not take place by a continuous varia-
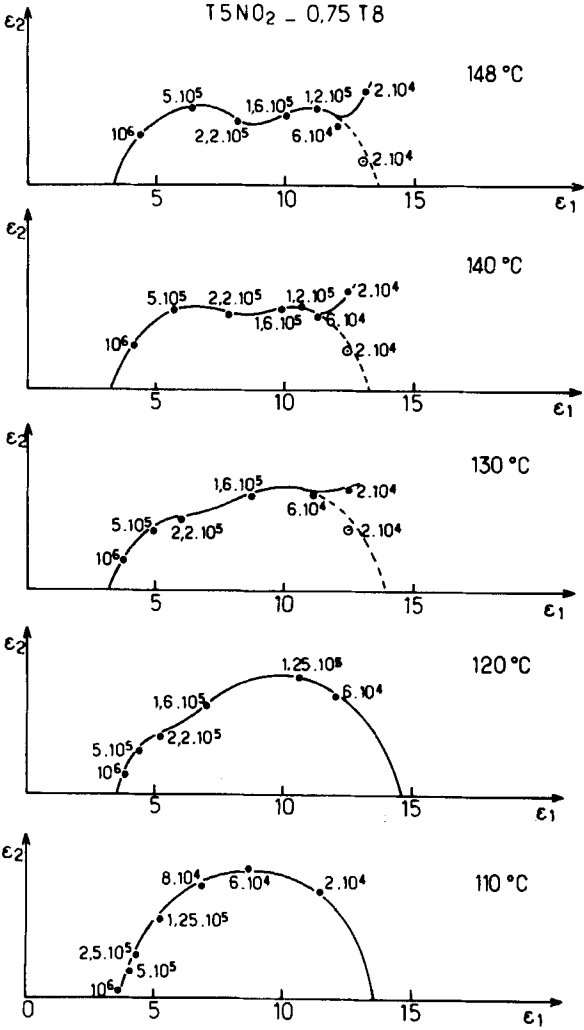tion of the overlapping in a dimer, but by a more complica-
ted process.

FIGURE 4. Cole-Cole diagrams of a T8-T5 NO2 mixture, showing the two relaxations.

DIELECTRIC RELAXATION IN DIPOLE ORDERED STRUCTURES

In liquid crystal, it is possible to observe a very special effect when a dipole modulated structure exists. This effect is not special to liquid crystals and in principle it is possible to observe it in crystals with incommensurate modulated structure. The first mention of this effect was made by Zeks et al.[17] in their theory of the dielectric relaxation in the ferroelectric Smectic C* phase. The effect consists in the appearance of an induced non-uniform modulation by influence of a spatially uniform electric field. It is not a trivial effect and we shall consider as an example the Sm A_2 or Sm $\tilde{A}$ phases, which both have a modulated structure with a k – vector parallel to the z direction. The spatial wavelength of the modulated polarization is double to the layer thickness.

In order to describe a modulated structure, we consider the free energy functional of Landau. This functional has a minimum for a modulated polarization P(z) which is the "order parameter". For example, we can choose the following expression:[18]

$$F = \frac{1}{V} \int [\frac{A}{2}P^2(z) + \frac{B}{6}P^4(z) - K(\frac{\partial P}{\partial z})^2 + (\frac{\partial^2 P}{\partial z^2})]dz \qquad (3)$$

We develope the function P(z) in a Fourier serie

$$P(z) = \sum_{-\infty}^{+\infty} P_k e^{-ikz} \qquad (4)$$

and we look for the values of the P's and the k's which give the minimum value for F. It is possible to show[19] that the exact solution can be very well approximated by taking only two terms in the serie. Therefore:

$$P(z) = P_k(e^{+ikz} + e^{-ikz}) \qquad\qquad (5)$$

From the minimization procedure we get $k = K/2\lambda$ and $P^2_k = (A + K^2/4\lambda)/2B$. As usual in the Landau theory, A is linearly dependent on T, $A = A_0(T - T_0)$. Thus we can write $A + K^2/4\lambda = A_0(T - T_c)$. The preceding results show that $P_k \neq$ only if $T < T_c$. There is a second order phase transition between the modulated $Sm\ A_2$ phase and a $Sm\ A_1$ phase (the "disordered phase").

Now, if one applies an external uniform electric field E parallel to the z direction, we can write

$$P(z) = P_k(e^{ikz} + e^{-ikz}) + p(z) \qquad\qquad (6)$$

where $p(z)$ is the induced polarization. Without loss of generality, we write $p(z) = \Sigma p_q e^{iqz}$ and we repeat the minimization procedure with the new $P(z)$. One could think that $p(z)$ will reduce to p_0 (q=0). However, when one introduces (6) in (3), one sees, besides the terms P^2_k, P^4_k, and the terms p^2_0, new terms like $P^2_k p_0 p_{\pm 2k}$ (we neglect the p^4_q, since we can admit that the field is small). This indicates that there is a coupling between the uniform induced polariza tion p_0 and the induced modulation $p_{\pm 2k}$, with a wave vector double to that of the basic structure. Clearly, this coupling disappears for $T \geqslant T_c$, when $P_k = 0$.

Now, we take the case of an electric field which varies with the time accordingly to $E = E_0 e^{i\omega t}$ and we expect two relaxations associated to the two components of the induced polarization p_0 and $p_2 = p_{\pm 2k}$. The complete derivation of the properties of two relaxations is given in ref. 18 and we report the results.

The characteristic frequency ω_0 (associated with p_0) is larger than ω_2 (associated with p_2). Above T_c, there is

only relaxation of ω_1 (it is that we discussed above in the first section) and ω_o (below T_c) is the continuation of ω_1 (above T_c). In principle, the curve $\omega_o(T) - \omega_1(T)$ may exhibit a change of slope at the Sm A_2 - Sm A_1 transition, but it is experimentally found that it is a very weak effect difficult to observe. The variation of ω_2 with T is not known since it is dependent on a friction coefficient Γ_2, which has an unknown temperature dependence. But it is very likely that ω_2 decreases with T.

The amplitudes A_1 and A_2 behave very differently. If A_o decreases slowly with T, A_2 (which is null above T_c) increases if T decreases following $(T_c - T)^2$.

There are few experimental results concerning the E//n relaxations in the Sm A_2 phase. However, we can show the results of Druon et al.[20] on the mixture of DB6 (4-n-hexyl-phenyl-4'-cyanobenzoyloxybenzoate) and C5 (4-cyanobenzoy-loxy-4'-pentylstilbene).
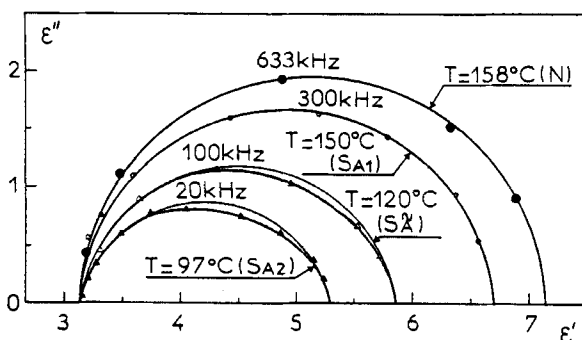

FIGURE 5. Cole-Cole diagrams of a mixture DB6 + C5, showing the change in shape in the Sm A_2 and Sm $\tilde{A}$. (From ref. 20).

As one can see from the Fig.5, they observed in the Sm $\tilde{A}$ and Sm A_2 phases two relaxations, with all the above features. In particular, the amplitude of the mode 2 is low and increases if T decreases. We have also observed a second relaxation, which corresponds very likely to the new mode 2, in the Sm A_2 phase of the compound DB8Cl[12].

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