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Effect of the Molecular Interaction Between Anisotropic Molecules on the Optical Kerr Effect. Field-Induced Phase Transition*

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The effect of molecular interaction between anisotropic (prolate) molecules in liquids on the nonlinear refractive index is studied. The model, without the driving term describing the strong optical-field molecular reorientation, is the same as the Maier and Saupe model of the isotropic to nematic phase transition in liquid crystals. The local field corrections are analyzed with the Onsager theory, the average polarizability being given by the Lorentz-Lorenz formula. It is found that the temperature dependence of the nonlinearity is modified and becomes $(T-T_i)^{-1}$ and that the electric field required to achieve a certain nonlinear index change can be very much smaller than required when only molecular reorientation is considered. Under certain restrictive conditions the liquid can be driven into a new ordered phase, similar to a liquid-crystal mesophase.

I. INTRODUCTION

Self-focusing and self-trapping of intense light beams have been recently studied extensively, both theoretically[1-11] and experimentally,[12-24] but discrepancies still remain between the experimental observations and the theoretical explanations or predictions. Self-focusing arises because the refractive index of the medium increases with the intensity of the beam, such that a laser beam shrinks until it is limited by other processes such as diffraction, nonlinear index saturation, etc. This limitation leads to the formation of intense optical filaments or self-trapping of the laser beam.

The intensity dependence of the refractive index is due to the optical Kerr effect, electrostriction, and nonlinear electronic polarizability. It is believed that the Kerr effect gives the most important contribution to the intensity-dependent part of the refractive index. The electrostrictive part, which involves mass transfer, cannot follow the rapid intensity variation of a short laser pulse.

In the optical Kerr effect four main processes can be considered. (i) One involves distortion of the electronic charge distribution; it is not the most important effect in most molecules. (ii) A very important contribution for anisotropic molecules is their tendency to orient in the direction of the laser electric field. This effect, with the nonlinear index saturation, has been studied recently by Brewer *et al.*[24] and by Gustafson *et al.*[11] For nonpolar anisotropic molecules the theory of the molecular orientation with saturation leads to nonlinear index changes larger than observed experimentally, or equivalently to filament diameters smaller than observed experimentally. For CS_2 the experimental small scale filament diameter is of the order of 4 μ, while the theory leads to a diameter of a few tenths of a micron. (iii) The third contribution to the Kerr effect arises from molecular redistribution or clustering under the action of the applied field.[25, 26] Hellwarth[25] has shown that symmetric or nearly symmetric molecules may thus exhibit self-focusing in liquid as easily as asymmetric molecules, and that in general, the molecular redistribution effect may be comparable to and in some cases dominate molecular reorientation. (iv) The fourth part of the Kerr effect is the effect of angular correlation between anisotropic molecules. This effect has previously been considered by Takatsuji.[27]

In this paper we will study this last effect, the angular correlation, with a simple model which describes adequately the liquid-crystal phase,[28, 29] with its high degree of angular correlation, in the absence of an external field. We will show that under certain conditions, anisotropic molecules can undergo a phase transition from the partially aligned phase to a more ordered phase, comparable to the nematic mesophase of a liquid crystal. This phase will occur for a liquid crystal in a small temperature range above the transition temperature. This phase will also occur for some molecular systems which do not show a nematic phase in the absence of the applied field. For most liquids with a positive Kerr constant, no phase transition occurs, but the electric field intensity required to achieve a certain degree of alignment can be an order of magnitude smaller than in calculations with noninteracting molecules. It should be pointed out that in the absence of an external field, anisotropic molecules prefer parallel orientation and have a short range ordering, as shown, for instance, by x-ray scattering in liquids.[30, 31] An applied field induces a birefringence in liquid with anisotropic molecules, via a reorientation of the molecules. In liquid crystals, the molecular interaction is strong enough to create a long-range order which governs the orientation of the molecular axis, which in turn leads to an optically uniaxial liquid. The applied field and the molecular interaction have therefore the same tendency, which can be enhanced and, for instance, lead to an induced mesophase above the zero-field transition temperature of the liquid crystal.

In this paper we will extend the theory of liquid crystals developed by Maier and Saupe[32] to include a strong external optical field. We will assume linear polarizability of the molecules.[33] The local field corrections are formulated following the theory of Onsager, while the average polarizability is determined from the Lorentz-Lorenz formula. In studying the enhancement of self-trapping by a cooperative phenomenon, Freiser and Joenk[34] have briefly considered the same Hamiltonian as here.

II. MOLECULAR ORIENTATION, INFLUENCE OF THE LOCAL FIELD

We consider nonpolar molecules with a symmetry axis, such that the two other axes are equivalent. The molecule orientation[31, 35] is specified by a spherical harmonic of second order,

$$P_2{}^0(\cos\theta) = \tfrac{3}{2}\cos^2\theta - \tfrac{1}{2}.$$

The degree of orientation of a liquid, consisting of such quadrupolar molecules is $S = \langle P_2{}^0(\cos\theta)\rangle$, where θ is the angle between the long molecular axis and the average orientation of the optical axis of the liquid. $S = 1$ means that all the molecules are parallel to the optical axis; $S = -\frac{1}{2}$ means that all the molecules are perpendicular to it and $S = 0$ corresponds to a random orientation as in an isotropic liquid.

The molecular interaction is treated in the molecular field approximation.[34] The potential energy W_i of molecule i is a function of θ_i, S, and the density or volume and it is required that

$$S_i = \tfrac{1}{2}\langle 3\cos^2\theta_i - 1\rangle = S. \qquad (1)$$

Maier and Saupe[32] considered only the dipole-dipole part of the dispersive or van der Waals forces (R^{-6}) and showed that the single-molecule potential energy W_i can be written,

$$W_i = -(A/V^2)S(1 - \tfrac{3}{2}\sin^2\theta_i), \qquad (2)$$

where A is characteristic of the molecules, proportional to $\bar{\alpha}^2\hbar\omega_0$, where $\bar{\alpha} = \frac{1}{3}(\alpha_1 + 2\alpha_2)$ is the average polarizability of the molecule, α_1 and α_2 being the polarizabilities parallel and perpendicular to the molecular axis, and $\hbar\omega_0$ is a typical electronic energy (i.e., the ionization energy).

The Lorentz formulation of the local field does not take into account any molecular correlation. In the Onsager[36] theory, the polarization of the surrounding molecules is assumed to follow the orientation of the dipole moment of the molecule under consideration, and the induced dipoles of the surrounding molecules react on the original molecule.

To calculate the orientational energy, we decompose the effective field $\vec{F}$ acting on the molecule into two parts: the first part $\vec{G}$ is that field which would be obtained in a spherical cavity containing the molecule,[37] if the molecule were removed, under the condition that the homogeneous field $\vec{E}$ and polarization $\vec{P}$ outside the cavity should remain constant at large distances from the considered molecule. Besides this cavity field, the reaction field $\vec{R}$ is that field due to the additional polarization of the liquid produced by the introduction of the molecule in question into the cavity, with a given direction of its axis. In general $\vec{P}$ has different direction from that of $\vec{F}$, $(\vec{P} = \bar{\bar{\alpha}}\cdot\vec{F})$, so that $\vec{F}$ not only polarizes the molecule but also produces a torque which tends to align the molecule into the field. It is easy to show that

$$\vec{F} = \frac{3\epsilon}{2\epsilon+1}\vec{E} + \frac{2(\epsilon-1)}{2\epsilon+1}\frac{\vec{P}}{a^3}, \qquad (3)$$

where a is the radius of the cavity. Later on in the paper we will consider very strong fields, therefore we should remark here that the expression for $\vec{F}$ is based on the superposition principle and is not correct for all field strengths, since the dielectric constant is a function of the field strength. We will disregard this difficulty in the paper.

If γ_i are the direction cosines of $\vec{E}$ in the molecular axis coordinate system,

$$p_i = \frac{3\epsilon}{2\epsilon+1}\alpha_i\gamma_i E + \frac{2(\epsilon-1)}{(2\epsilon+1)a^3}\alpha_i p_i, \qquad (4)$$

which gives $p_i = \alpha_i{}'\gamma_i E \qquad (5)$

with
$$\alpha_i{}' = \frac{3\epsilon\alpha_i a^3}{(2\epsilon+1)a^3 - 2(\epsilon-1)\alpha_i}. \qquad (6)$$

The orientational energy of the molecule is

$$W_0 = -\frac{1}{2}\vec{G}\cdot\vec{P} = -\frac{1}{2}\frac{3\epsilon}{2\epsilon+1}\sum\alpha_i{}'\gamma_i{}^2E^2. \qquad (7)$$

The induced polarization parallel to the applied field is

$$p_E = \sum p_i\gamma_i = E\sum\alpha_i{}'\gamma^2. \qquad (8)$$

In the following we always assume that the polarizability has a cylindrical symmetry, i.e., $\alpha_2 = \alpha_3$. If we introduce the angle θ between the principal axis and the applied field,

$$p_E = E(\alpha_1{}' - \Delta\alpha'\langle\sin^2\theta\rangle), \qquad (9)$$

where $\Delta\alpha' = \alpha_1{}' - \alpha_2{}'$,

$$\langle\sin^2\theta\rangle = \frac{\int \sin^2\theta\, e^{t\sin^2\theta}\, d\Omega}{\int e^{t\sin^2\theta}\, d\Omega},$$

and $$t=\left(\frac{3}{2}\frac{AS}{V^2}+\frac{1}{4}\frac{3\epsilon}{2\epsilon+1}E^2\Delta\alpha'\right)\frac{1}{kT}. \tag{10}$$

In Eq. (9) we have performed the thermodynamical average, considering the two contributions to the one-molecule Hamiltonian,

$$H=W_i+W_0=-(A/V^2)S(1-\tfrac{3}{2}\sin^2\theta)$$

$$-\frac{3\epsilon}{2\epsilon+1}\frac{E^2}{4}(\alpha_1'\cos^2\theta+\alpha_2'\sin^2\theta). \tag{11}$$

E^2 has been assumed averaged over an optical period. We can rewrite

$$p_E=E(\bar{\alpha}'+\tfrac{2}{3}\Delta\alpha' S). \tag{12}$$

This relation, along with $P=(\epsilon-1)E/4\pi$ yields an equation for ϵ, which could be used to study the self-focusing of a light beam.[4,11]

Since our main concern here is not to calculate the dielectric constant of the liquid but mainly the nonlinear index change we can simplify the expression for α', first by replacing α_i in the denominator by $\bar{\alpha}$. Then if we identify the volume of the cavity containing one molecule with the volume per molecule in the liquid $(4\pi a^3 N/3=1)$, we can write

$$\alpha_i'=\alpha_i\frac{3\epsilon}{2\epsilon+1}\left(1-\frac{8\pi N}{3}\bar{\alpha}\frac{\epsilon-1}{2\epsilon+1}\right)^{-1}. \tag{13}$$

Although Close *et al.*[21] gave an expression for $\Delta\epsilon$ free of the error, it is customary[11] to assume that the Lorentz-Lorenz expression for the average polarizability yields an explicit formula for the dielectric constant, namely

$$\bar{\alpha}=[(\epsilon-1)/(\epsilon+2)]a^3. \tag{14}$$

This assumption leads to large errors. From (12) we see that $\Delta\epsilon$, the nonlinear dielectric-constant change, involves $S(t)$ and that we cannot obtain an explicit expression for all field strengths. Provided $\Delta\epsilon\ll\epsilon$, we can write

$$\delta\alpha_i'=\alpha_i(B/4\pi)\Delta\epsilon,$$

$$B=(3-8\pi N\bar{\alpha})[2\epsilon_0+1-\tfrac{8}{3}\pi N\bar{\alpha}(\epsilon_0-1)]^{-2}/4\pi, \tag{15}$$

where ϵ_0 is the field free dielectric constant [with (14), $B=4\pi/3$]. In terms of B we have

$$\Delta\epsilon=\tfrac{8}{3}\pi\Delta\alpha'\Delta S(1-B\bar{\alpha}-\tfrac{2}{3}BS_K\Delta\alpha)^{-1}, \tag{16}$$

where $\Delta S=S-S_K$, and S_K is the value fo the orientation factor in the absence of field. If the liquid is isotropic $S_K=0$. Expression (16) is quite different from the equivalent derived by Gustafson *et al.*[11] (with $B=4\pi/3$). In the following no explicit use of (16) will be made and to facilitate comparisons with other papers we will write $\alpha_i'=(\epsilon+2)\alpha_i/3$ as derived from (13) and (14). However in a quantitative study, expressions (15) and (16) should be used.

In this paper the validity of these approximations will not be analyzed further. The influence of the shape and volume of the cavity could be analyzed following the generalization of Onsager's formulation by Scholte.[37]

With these approximations (10) reads

$$t=\left(\frac{3AS}{2V^2}+\frac{1}{4}E^2\Delta\alpha\,\frac{\epsilon(\epsilon+2)}{2\epsilon+1}\right)\frac{1}{kT}. \tag{17}$$

and $$\langle\sin^2\theta\rangle=1-F'(t)/F(t), \tag{18}$$

where

$$F(t)=\int_0^1 e^{tu^2}du=\sum_{n=0}^{\infty}\frac{t^n}{(2n+1)n!}. \tag{19}$$

By integration by parts, we see that

$$F'(t)=[e^t-F(t)]/2t \tag{20}$$

and therefore

$$S=\tfrac{1}{2}-3/4t+3e^t/4tF(t). \tag{21}$$

$F(t)$ is a confluent hypergeometric function $F(\frac{1}{2}|\frac{3}{2}|t)$ also known as the Dawson integral, and is tabulated.[38] From (19) and (21) it is easy to find two useful expansions of $S(t)$ for large and small t. They read

$$S(t)=\begin{matrix}1-3/2t+0(1/t^2)\\ \\ \frac{2}{15}t+\frac{4}{315}t^2-\frac{8}{4725}t^3-\frac{16}{31185}t^4+0(t^5).\end{matrix} \tag{22}$$

The negative t^3 term leads to an inflection point. $S(t)$ is given in Fig. 1 as a function of the energy parameter t. The most interesting feature of $S(t)$, namely its inflection point is not apparent on Fig. 1 and on other more qualitative figures will be exaggerated. S enters in the expression for t,

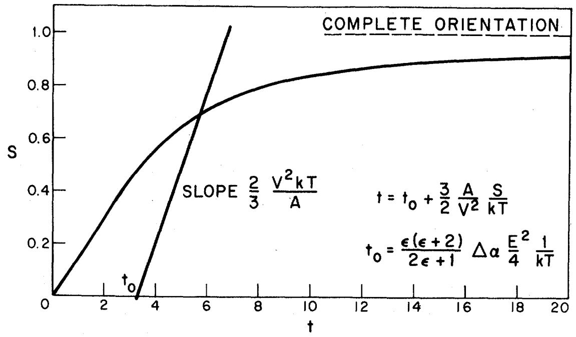

FIG. 1. The molecular orientation function $S=\langle\frac{3}{2}\cos^2\theta\rangle-\frac{1}{2}$ versus energy parameter t. The value of the molecular orientation for a field E at a temperature T is at the intersection of $S(t)$ and the straight line of slope $2V^2kT/3A$ passing through t_0.

and there is therefore a self-consistent condition which is exhibited by the construction of S on Fig. 1. S is the intersection of $S(t)$ and the straight line of slope $\frac{2}{3}(V^2/A)kT$ passing through

$$t_0=[\epsilon(\epsilon+2)/(2\epsilon+1)]\Delta\alpha E^2/4kT.$$

In this paper we consider only prolate molecules, $\Delta\alpha>0$. For oblate molecules ($\Delta\alpha<0$) the $S(t)$ does not show an inflection point.

At this point we see the difference between this calculation and a molecular-field calculation in the theory of ferromagnetism. In ferromagnetism we deal with dipoles and the ordering parameter is $S=\langle P_1{}^0(\cos\theta)\rangle$. The function $S(t)$ is then a Langevin function (if we consider classical spins; the quantum case with the Brillouin functions is qualitatively equivalent), which does not have an inflection point. This difference leads to the absence of first-order phase transition in ferromagnetism.

From (16), (17), and (22) we can get an expansion of Δn, the nonlinear index of refraction change ($\Delta n=\Delta\epsilon/2n_0$) in powers of E^2:

$$\Delta n=n_2E^2+n_4E^4+\cdots. \tag{23}$$

To the lowest order in the field we calculate

$$S=\tfrac{2}{15}t_0/I+\cdots, \tag{24}$$

where $I=1-A/5V^2kT$, and therefore

$$n_2=\frac{2\pi}{15}\frac{n}{2n^2+1}\left(\frac{n^2+2}{3}\right)^3\frac{N(\Delta\alpha)^2}{IkT}. \tag{25}$$

{It is customary to refer n_2 to the local field, therefore (25) should be divided by $[(n^2+2)/3]^2$}. As will be discussed in (43) and following, this expression shows a $(T-T_i)^{-1}$ temperature dependence of n_2 and the Kerr coefficient, different from the usual T^{-1}. From a measurement of $n_2(T)$ we could calculate $\Delta\alpha$ and T_i ($A/V^2kT_i=5$, the physical significance of T_i will be shown in the next section). We have here the enhancement of n_2 described by Freiser and Joenk.[34] From (25) we see that the index of refraction diverges when $T=T_i$. In the next section we will see that a phase transition has occurred. It actually occurs for smaller molecular interaction or higher temperature at a value of the parameter $A/V^2kT_K=4.54$. The expression (25) is strictly valid only for much smaller values of this parameter A/V^2kT.[39]

III. INFLUENCE OF THE MOLECULAR INTERACTION

When $A=0$, aside from the treatment of the local field correction, our analysis is the same as previous analyses with saturation of the alignment. Let us now consider the influence of the molecular interaction.

We consider first the case $E=0$ to reproduce the theory of nematic mesophases developed by Maier and Saupe. Let us label the slope $p=\frac{2}{3}kTV^2/A$ by its temperature. It is easy to show that phase stability requires $dS/dT<p$. In Fig. 2 we can distinguish the following possibilities:

(i) $T<T_i$, $A/V^2kT>5$, where T_i labels the slope of the tangent at the origin of $S(t)$. The only stable phase is an ordered phase $S>S_i=0.6147$; T_i represents the lowest temperature at which a disordered phase can be supercooled.

(ii) $T_i<T<T_n$, where T_n labels the tangent at $S(t)$ passing through the origin. $A/V^2kT_n=4.4876$ and $S_n=0.3235$. We have two possible stable phases. We will show in the next section that a Maxwell type of construction gives the temperature of this first-order phase transition. T_n represents the highest temperature at which an ordered phase can be superheated.

(iii) $T>T_n$. The disordered phase is the only possible phase.

On Fig. 2 we have also indicated the slope of the inflection point ($A/V^2kT_c=4.330$, $S_c=0.2143$) which is crucial when we study the interacting molecules under the influence of the driving field. In that case we carry out the same analysis considering a straight line through

$$t_0=[\epsilon(\epsilon+2)/(2\epsilon+1)]\Delta\alpha E^2/4kT.$$

Given a substance characterized by A at a fixed temperature, the molecular orientation as a function of the field (i.e., as the self-focusing develops) is given by changing t_0, keeping the slope fixed. There is now a new and very interesting

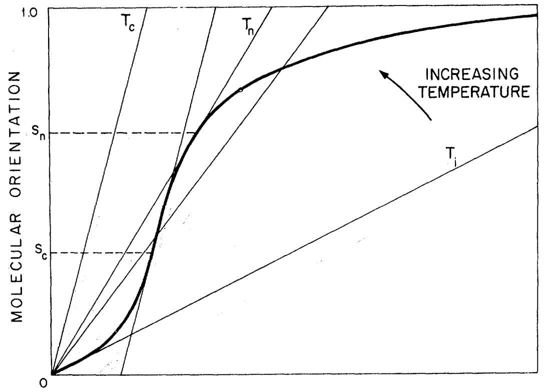

FIG. 2. The molecular orientation in a liquid crystal at a given temperature is, according to the theory of Maier and Saupe, at the intersection of $S(t)$ and $S=2kV^2Tt/3A$. (i) $T<T_i$ the ordered phase is stable; (ii) $T_i<T<T_n$ the ordered and disordered phases coexist; (iii) $T>T_n$ the disordered phase is stable. The parameter A/V^2kT, which measures the molecules ability to be ordered, takes the following values: $A/V^2kT_i=5$, $A/V^2kT_n=4.4876$, $A/V^2kT_c=4.3303$, where T_c labels the slope at the inflection point. The orientation factors are $S_i=0$, $S_n=0.3235$, $S_c=0.2143$.

range of temperature as seen on Fig. 3.

(iv) $T_n < T < T_c$. For a certain value of the field an ordered and a disordered phase can coexist. The field induces a first-order phase transition and extends the domain of the ordered phase from T_n to T_c. In our formalism this extension of the domain is, independent of the molecular system, $T_c/T_n = 1.036$. T_c is a critical point. Above T_c it is impossible to induce a phase transition regardless of the value of the field. The maximum field required to induce this phase transition is given by

$$t_{0c} = [\epsilon(\epsilon+2)/2\epsilon+1)]\Delta\alpha E_c^{\,2}/4kT = 0.0680. \quad (26)$$

Since in our discussion we have disregarded any consideration of relaxation time, the analysis is valid for ac and dc fields, but for dc fields $E_c^{\,2}/4$ should read $E_c^{\,2}/2$. If we substitute in (26) physical constant for CS_2, $E_c \sim 8.7\times10^4$ esu. This critical field will be much smaller for nematic liquids, but since most such liquids are strongly polar, the formalism has to be modified if we consider a dc field. If we consider an ac field, we should take into account the orientational relaxation time. For most liquids in which self-focusing and self-trapping have been observed, the relaxation time is such that ordering by a laser pulse could be achieved.[24,40] This point will be discussed later in Sec. IV.

To carry out further the discussion of the equation of state of the anisotropic liquid in the presence of the external field we now calculate, the internal energy, the entropy, the free energy, and the Gibbs function. It is very easy to find the different expressions; we just have to avoid double counting when considering the molecular interaction in the molecular field approximation. The internal energy per molecule is

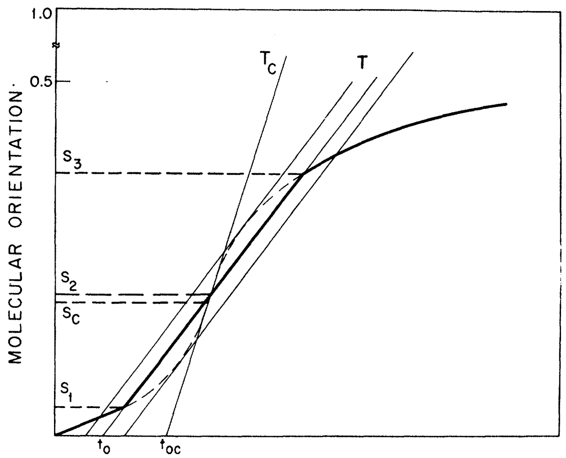

FIG. 3. Construction of the value of the molecular orientations when both the collective interaction and the driving field are considered. In contrast to Fig. 2, the straight line goes through t_0. Only the case $T_n < T < T_c$ which leads to a field-induced first-order transition is considered in this figure.

$$U = -\frac{1}{2}\frac{A}{V^2}S^2 - \frac{\epsilon(\epsilon+2)}{2\epsilon+1}\Delta\alpha\frac{E^2}{4}(\bar{\alpha}+\frac{2}{3}S\Delta\alpha). \quad (27)$$

The orientational entropy of the system is

$$S = -\tfrac{1}{3}(2S+1)tkT + k\ln F(t). \quad (28)$$

Therefore the free energy per molecule can be written

$$F = \frac{A}{2V^2}S(S+1) - \frac{\epsilon(\epsilon+2)}{2\epsilon+1}E^2\alpha_2 - kT\ln F(t). \quad (29)$$

In the absence of an external field, the nematic to isotropic phase transition occurs with a volume change, and one should therefore consider the Gibbs function $G = F + PV$. If we label the two phases i (isotropic or less ordered) and n (nematic or ordered) we have

$$G = G_n - G_i = F_n - F_i + F_i(V_n, T) - F_i(V_i, T) + P(V_n - V_i). \quad (30)$$

But

$$F_i(V_n, T) - F_i(V_i, T) = \int_{V_i}^{V_n}\left(\frac{\partial F_i}{\partial V}\right)_T dV = -\int_{V_i}^{V_n} P_i(V, T)dV. \quad (31)$$

Let χ_i be the isothermal compressibility of the less ordered phase. Then

$$\Delta G_{n,i} = \Delta F_{n,i} + (\Delta V)^2/2\chi_i V_i\,. \quad (32)$$

At the equilibrium of the two phases $\Delta G = 0$, and ΔV can be calculated from

$$P = -\left(\frac{\partial U}{\partial V}\right)_S. \quad (33)$$

In the case $E = 0$,

$$\Delta V = \chi_i V_i \Delta P = (A/V_n^{\,2})S^2\,. \quad (34)$$

From this we can write an expression which relates $\Delta V/V_n$, S, and T at the transition point, and knowing ΔV and T we can calculate S. Maier and Saupe have determined S for a number of nematic liquids using this method. In this paper we will neglect volume changes, assuming they have no time to occur. For this very reason we have neglected electrostriction and heating. We see here that these effects can be coupled to the Kerr effect through the redistribution of the molecules.

At the phase transition, the free energy of the two phases are equal if we neglect any volume change. Then

$$F_n = F_i \quad (35)$$

which reads,

$$(A/2V^2)S_i(S_i+1) - kT\ln F(t_i) = (A/2V^2)S_n(S_n+1) - kT\ln F(t_n), \qquad (36)$$

where t_i and t_n are given by (17).

If $E=0$, since $S_i=0$ and $F(t_i)=1$, (36) reduces to

$$\tfrac{1}{2}(A/V^2)S(S+1) - kT\ln F(3AS/2kTV^2) = 0. \qquad (37)$$

This equation has only one root,

$$S_K = 0.4292, \quad A/V^2kT_K = 4.541. \qquad (38)$$

At T_K we have coexistence of the two phases. In the temperature range $T_K - T_n$ the nematic phase is superheated.

For $T_K < T < T_c$, there is a pair of values of T and E^2 for which there is a phase transition, and a coexistence line which represents an inhomogeneous phase. At the critical point

$$t_c = 1.46, \quad S_c = 0.2143, \qquad (39)$$

the characteristics of the two phases are undistinguishable. In Fig. 4 we show the coexistence curve $S(T)$, between T_K and T_c. It is (very nearly) a symmetrical curve ($S_i + S_n \approx 2S_c$). Around T_c, $\Delta S \propto (\Delta T/T_c)^{1/2}$. All these results are very similar to the results given by the van der Waals equation of state for a fluid. In Fig. 5 we show the complete isotherm diagram. We see that S and $\Delta\alpha|E|^2/kT$ play roles similar to V amd P of the liquid-gas system. The part of the diagram which corresponds to $T < T_i$ and $|E|^2 < 0$ is reminiscent of a solid or well-ordered phase.

The presence of the field has extended the range of existence of the nematic phase from T_K to T_c.

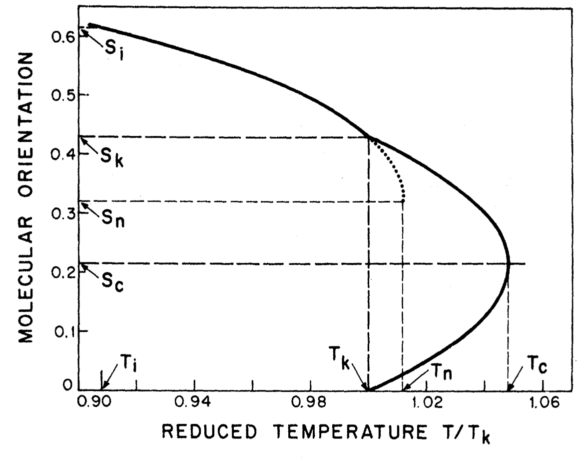

FIG. 4. Phase diagram of a liquid crystal. In the absence of an orienting field the liquid crystal undergoes a first-order phase transition at T_K. With an electric field an ordered phase exists in the range $T_K - T_c$. The dotted curve corresponds to a superheated phase.

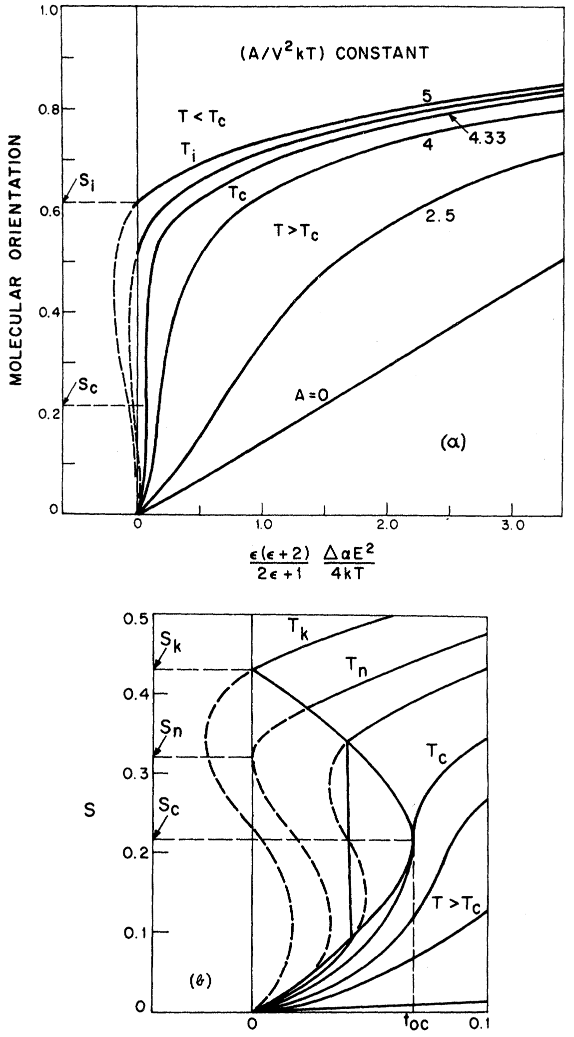

FIG. 5. (a) Isothermal molecular orientation in a liquid of anisotropic molecules versus orientational electric field parameter t. The isotherms are labeled by the parameter A/V^2kT. No angular correlation between molecules corresponds to $A=0$. (b) The scale of the electric field parameter is greatly expanded to show the critical region and the coexistence curve.

It is easy to show that for small fields, the increase of the transition temperature is given by

$$\frac{\Delta T}{T_K} = \frac{\epsilon(\epsilon+2)}{2\epsilon+1}\,\Delta\alpha\,\frac{E^2}{kT_K}\,\frac{4}{3S_K}\,\frac{V^2kT_K}{A}, \qquad (40)$$

or

$$\frac{\Delta T}{T_K} = 0.6841\,\frac{\epsilon(\epsilon+2)}{2\epsilon+1}\,\Delta\alpha\,\frac{E^2}{kT_K}. \qquad (41)$$

If we substitute values for CS_2, we find $\Delta T/T_K = 10^{-9}\,E^2$ esu., and we see that only fields of the order of the internal molecular field can induce a significant modification of the molecular system.

From this discussion we see that substances which are nearly nematic (i.e., that freeze just before they undergo an isotropic to nematic phase transition) can show an induced mesophase in a small temperature range ($T_c/T_K \simeq 1.05$) above their freezing point. This rules out a phase transition in CS_2, at room temperature, since its freezing temperature is − 112°C. For most anisotropic molecules the molecular interaction lowers the value of the field required to achieve a certain alignment. The ratio of the fields required with and without molecular interaction is as large as 27, which occurs for $T = T_c$ near $S = S_n$.

There is another aspect of the molecular interaction which was touched upon earlier [see Eq. (24)] which is also important. If we expand the molecular alignment to lowest order in the field we get

$$S = I^{-1}\left\{\tfrac{2}{15}b + b^2\left[\tfrac{4}{315} + \tfrac{16}{15}a/I + \tfrac{16}{315}\tfrac{1}{225}(a/I)^2\right] + \cdots\right\}, \tag{42}$$

where

$$I = 1 - A/5V^2kT = 1 - T_i/T, \tag{43}$$

and

$$b = \frac{\epsilon(\epsilon+1)}{2\epsilon+1}\,\frac{E^2}{4}\,\frac{\Delta\alpha}{kT}, \quad a = \frac{3A}{2V^2kT}, \quad \frac{1}{15}\,\frac{a}{I} = \frac{T_i}{2(T-T_i)}. \tag{44}$$

From this we see that the Kerr coefficient has a $(T - T_i)^{-1}$ temperature dependence. An experimental study of this temperature dependence would determine T_i and therefore the strength of the molecular interaction. A glance at Fig. 5 indicates that (42) is certainly not valid above T_K. This new temperature dependence had already been pointed out by Freiser and Joenk, and should have been expected since we have introduced in the model a cooperative phenomenon.

IV. DISCUSSION AND SUMMARY

We have seen that the molecular interaction has three main effects on molecules with anisotropic polarizability tensor.

(i) The temperature dependence of the Kerr constant is modified from T^{-1} to $(T - T_i)^{-1}$, where T_i is a temperature, very often smaller than the freezing temperature, which gives a measure of the molecular interaction, T_i is the limiting temperature at which the liquid shows an isotropic phase.

(ii) The electrical field required to achieve a certain molecular alignment is smaller for interacting molecules than for free molecules.

(iii) For substances which are nematic or nearly so ($T_i \simeq$ freezing temperature) there is a small temperature range in which a field-induced mesophase exists.

Let us first consider this last aspect in more detail. In a Kerr cell configuration, as the transition occurs, a droplet of more ordered liquid will appear in the cell. This droplet will grow and its longest axis will orient itself parallel to the field.[37] In the present formulation there is no surface energy and a comparison with vortices in type-II superconductors[41] is of limited interest. If however a refinement of the theory leads to filaments, they will be parallel to the electrical field. Shen, Au Yang, and Cohen[9] have given a theory of self-trapped filaments with a phenomenological theory for a two-phase dielectric which is parallel to the theory of vortices in type-II superconductors. Such a purely energetic theory should also lead to filaments parallel to the field. Instead of a uniform field let us now consider a self-trapping experiment. The laser beam, propagating in the nonlinear liquid, is self-focused into the cell and as the field reaches the critical value a droplet of ordered liquid is formed. Then the beam, in the shadow of the droplet (acting as a lens), is further focused and one can imagine the development of a filament parallel to the laser propagation. With our formulation such transition is ruled out for most nonlinear liquids, since this new phase can only exist in a limited temperature range below the critical temperature which for these nonlinear liquids is below the freezing temperature. Perhaps a better formulation of the molecular interaction which would include molecular redistribution and angular correlation could lead to a phase transition in a larger class of liquids or in a more important temperature range.

For most liquids, in which self-trapping and focusing have been observed, the experiments were done above the critical temperature, but we see on Fig. 5 that the molecules have nevertheless a collective behavior when they are partially aligned, the extent of this collective behavior being more important the closer the liquid is to its critical point. This collective behavior is analogous to a temperature and field-dependent relaxation time, and during the lifetime of a self-trapped filament it is perhaps impossible to reach saturation of the alignment.[40] Brewer *et al.*[24] have extensively discussed the size and lifetime of small scale trapped filaments. The filaments are destroyed after 10^{-10} sec by heating, expansion, or instabilities. The relaxation time of the anisotropy, measured from Rayleigh-wing scattering or calculated from $\tau = 4\pi a^3\eta/3kT$, where η is the viscosity, is of the order of 10^{-11} sec for most relevant liquids. The n_2 coefficient in CS_2 and nitrobenzene are also of the same magnitude and yet the small scale filaments are, respectively, 4 and 12 μ in diameter. If the results of Fig. 5 were used in the calculation of Gustafson *et al.*,[11] the same submicron diameter would be predicted, since nothing prevents complete saturation. The difference between CS_2 and nitrobenzene may come from the molecular interaction. The liquids freeze at − 112 and 5°C, respectively, and although it may be unwarranted to identify the freezing point with T_K, they are related. At the freezing point a three-dimensional ordering sets in, at T_K a one-dimensional ordering occurs.[42] We can assume that at room-temperature nitrobenzene is much closer than CS_2 to its critical point. This will mean that P_{min} (as defined by Gustafson *et al.*[11]) is much smaller for nitrobenzene than for CS_2, and also that the effective relaxation time of nitrobenzene is longer. In ferroelectrics[43] above the Curie point the loss tangent deteriorates as $(T - T_c)^{-1}$. We may speculate[44, 34] here that the effective relaxation time for the anisotropy is $\tau_{\mathrm{eff}} = \tau T(T - T_i)^{-1}$. This would lead to a greater deterioration of the relaxation time for nitrobenzene than for CS_2 and makes τ_{eff} of the order of the filament duration. If this speculation is true, a careful study of the temperature dependence of the small scale filaments in nitrobenzene is very important. Equally important would be a more complete study of the thermodynamics of the system in which the adiabatic heating of the liquid, as the ordering is increased, is considered. In the preceding discussion we have assumed that nitrobenzene was a prolate molecule, which is only an approximation. The difference in filament sizes between CS_2 and C_6H_6 was explained by Reichert and Wagner[45] by the difference between prolate and oblate molecules and nitrobenzene was assumed approximately oblate, but in view of the polarizabilities the molecule is more prolate than oblate.

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[39] The expression for n_2 we just derived is different from the usual expression; this is due to the different treatment of the local field correction. Brewer *et al.*[24] give

$$n_2^B = \frac{(n^2+2)^2}{6n}\,\frac{4\pi N}{3}\,\frac{1}{45}\,\frac{(\Delta\alpha)^2}{kT}\ .$$

In an experiment measuring the optical Kerr constant n_2 is measured, which means that $(\Delta\alpha)^2/I$ and $(\Delta\alpha)_B{}^2$ can be deduced from (25) and $n_2{}^B$ and we have,

$$(\Delta\alpha)^2/I = (\Delta\alpha)_B{}^2(2n^2+1)(n^2+2)/9n^2 .$$

Therefore in a dilute system where $I \simeq 1$ the two values of $\Delta\alpha$ are the same. But in general the value of $\Delta\alpha$ deduced from (25) is smaller than the value deduced from $n_2{}^B$. If we now consider the index change in the limit of complete saturation, the expression deduced from both treatments of the local field are the same (when $S_K = 0$) and given by (15) with $S = 1$. This means that Δn will be smaller in our formulation and part of the discrepancy between theory with complete molecular alignment and experiments will be removed. From the approximate relationship,[3] which gives the index change in a diffraction-limited self-trapped filament of diameter d ($\Delta n \approx n_0 \times (1.22\lambda/n_0 d)^2/8$), one finds for CS_2, $\Delta n \approx 0.005$. Gustafson *et al.*[11] calculating from an expansion like (25) give a saturation value $\Delta n = 0.58$, which is certainly too much of a difference to be accounted for by $(\Delta\alpha)^2/I$. A more exact treatment of the local field, considering (15) and (16) instead of (14), would lift part of the discrepancy.

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