Kerr effect and the nonlinear dielectric effect on approaching the critical consolute point

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(Received 4 November 1992)

For the exponent ψ which describes a critical anomaly of the nonlinear dielectric effect (NDE) and the electro-optic Kerr effect (EKE) in critical solutions, theoretical models predict: $\psi_{\mathrm{NDE}}=\psi_{\mathrm{EKE}}=\psi_{\mathrm{theor}}=\gamma-2\beta$. An experiment gave $\psi_{\mathrm{NDE}}\ (\simeq 0.37)<\psi_{\mathrm{theor}}\ (\simeq 0.59)<\psi_{\mathrm{EKE}}\ (\simeq 0.85)$. For all other experimental results, however, the agreement with the theory is good. In this paper it is shown that also both of the above relations may be valid. This result is based on the assumption that the NDE and the EKE exhibit a mixture of both a nonclassical and a classical type of behavior of critical fluctuations. Additionally, a relation was found between the semimicroscopic models for critical solutions and the phenomenological Landau–de Gennes model for the pretransitional effect of the NDE and the EKE in the isotropic phase of nematogens.

PACS number(s): 64.70.Ja, 64.60.−i, 77.22.Ch, 78.20.Fm

I. INTRODUCTION

Binary solutions of limited miscibility of ordinary liquids are an example of a simple, nonsymmetric critical system with properties particularly convenient for an experiment [1–3]. Together with the Ising model and the one-component liquid (the gas-liquid critical point) they belong to the $d=3, n=1$ universality class (d, n are the dimensions of the space and the order parameter, respectively). This has been confirmed by experimental and theoretical studies of almost all basic thermodynamic properties of these solutions [2,3].

Certain discordant elements appeared in studies on dielectric properties. Relatively recently (1979, 1980, and the following years) theoreticians and experimentors were able to determine the value of the critical exponent for the electric permittivity ϵ [4–7]:

$$\epsilon-\epsilon_c \sim t^{1-\alpha}\ , \quad \text{for } T>T_c\ ,\ x=x_c\ , \tag{1}$$

where $t=(T-T_c)/T_c; T_c, x_c$ are the critical temperature and concentration, respectively, $\alpha\simeq 0.11$ is the critical exponent of the specific heat, and ϵ_c is the value of ϵ at the critical consolute point, extrapolated from data far from T_c.

However, the possible influence of important factors such as the frequency of the measuring field, dT_c/dp (p denotes pressure), etc., is almost completely unknown.

A singular situation is found for the nonlinear dielectric properties: electro-optic Kerr effect (EKE) and nonlinear dielectric effect (NDE). The first describes birefringence due to a stationary electric field E [8]:

$$\mathscr{E}^{\mathrm{EKE}}=\frac{1}{\lambda}\frac{n_{\parallel}-n_{\perp}}{E^2}\ , \tag{2}$$

where λ is the wavelength of the light, $n_{\parallel}$ and $n_{\perp}$ are values of the anisotropy (induced by the electric field) of the refractive index in the direction parallel and perpendicular to the direction of the electric field E.

The second, NDE, describes variations in electric permittivity for radio frequencies due to the application of a strong, stationary electric field E [9]:

$$\mathscr{E}^{\mathrm{NDE}}=\frac{\Delta\epsilon}{E^2}=\frac{\epsilon^E-\epsilon}{E^2}\ , \tag{3}$$

where ϵ^E, ϵ are the electric permittivities in the presence and in the absence of the field E, respectively.

Both effects exhibit a marked increase on approaching the critical consolute point [9] [in contrast to electric permittivity, relation (1)]. All existing theories describe the shape of their critical effects by the same universal, critical exponent [4,10,11]:

$$\begin{aligned} &\mathscr{E}_c^{\mathrm{NDE}}\simeq A_{\mathrm{NDE}}t^{-\psi}\ ,\\ &\mathscr{E}_c^{\mathrm{EKE}}\simeq A_{\mathrm{EKE}}t^{-\psi}\ ,\\ &\psi=\gamma-2\beta\simeq 0.59\ , \end{aligned} \tag{4}$$

where subscript c denotes the critical part of the given effect, A_{NDE} and A_{EKE} are critical amplitudes, $\gamma\simeq 1.24$ is the critical exponent of susceptibility (osmotic compressibility in this case), and $\beta\simeq 0.325$ is the critical exponent of the order parameter. The values of exponents are for the (3,1) universality class [2,3].

The experiment gave $\psi_{\mathrm{NDE}}\simeq 0.37$ and $\psi_{\mathrm{EKE}}\simeq 0.85$. Hence the following relation is fulfilled:

$$\psi_{\mathrm{NDE}}<\psi_{\mathrm{theory}}<\psi_{\mathrm{EKE}} \tag{5}$$

instead of

$$\psi_{\mathrm{NDE}}=\psi_{\mathrm{theor}}=\psi_{\mathrm{EKE}}\ . \tag{6}$$

The electro-optic Kerr effect and the nonlinear dielectric effect have been also studied experimentally for many other precritical properties predicted by theoretical models. In this case the agreement is excellent.

An attempt is made here to explain the discrepancy between experiment and theory. To present a complete picture, at the beginning, a short description of theoretical predictions and important experimental results are given.

1063-651X/93/48(2)/1136(6)/$06.00

II. THEORETICAL PREDICTIONS

(i) Goulon, Greffe, and Oxtoby [4], using the droplet model, which treats critical fluctuations as drops or an assembly of drops with a concentration profile and a number distribution depending on the distance from T_c, obtained

$$\frac{\Delta\epsilon}{E^2}=\left[\frac{\Delta\epsilon}{E^2}\right]_B+\left[\frac{\Delta\epsilon^{\mathrm{I}}}{E^2}+\frac{\Delta\epsilon^{\mathrm{II}}}{E^2}\right]_C , \quad x=x_c , \quad T=T_c , \tag{7}$$

where indices B and C indicate the noncritical background and the critical effect, respectively.

$$\frac{\Delta\epsilon^{\mathrm{I}}}{E^2}\sim a_1^4 t^{2\beta-\gamma} \tag{8}$$

is the effect associated with elongation of the drops in the electric field;

$$\frac{\Delta\epsilon^{\mathrm{II}}}{E^2}\sim a_2^2 t^{1-2\beta} \tag{9}$$

is the electrostriction effect.

Moreover,

$$a_1^4 \gg a_2^2 . \tag{10}$$

Hence, the critical effect is described as

$$\left[\frac{\Delta\epsilon}{E^2}\right]_C \simeq \frac{\Delta\epsilon}{E^2}-\left[\frac{\Delta\epsilon}{E^2}\right]_B \sim a_1^4 t^{2\beta-\gamma} . \tag{11}$$

The same value of the exponent was predicted for the Kerr effect.

Pyżuk [12] further developed this model and obtained an explicit relation for critical amplitudes as well:

$$\left[\frac{\Delta\epsilon}{E^2}\right]_C \simeq A'\frac{1}{\epsilon^2}\left[\frac{\partial\epsilon}{\partial x}\right]^4\left[\frac{\partial\mu}{\partial x}\right]^2\xi^{-d}=A'\frac{1}{\epsilon^2}\left[\frac{\partial\epsilon}{\partial x}\right]^4\frac{\Gamma^2}{\xi_0^d}t^{d\nu-2\gamma} , \tag{12a}$$

$$\left[\frac{\Delta n}{E^2}\right]_C \simeq \frac{A''}{\lambda}\frac{1}{\epsilon n^2}\left[\frac{\partial\epsilon}{\partial x}\right]^2\left[\frac{\partial n}{\partial x}\right]^2\left[\frac{\partial\mu}{\partial x}\right]^2\xi^{-d}=\frac{A''}{\lambda}\frac{1}{\epsilon n^2}\left[\frac{\partial\epsilon}{\partial x}\right]^2\left[\frac{\partial n}{\partial x}\right]^2\frac{\Gamma^2}{\xi_0^d}t^{d\nu-2} , \tag{12b}$$

where A', A'' are constants containing certain parameters connected with the model, x is concentration in mole fractions; $\xi=\xi_0 t^{-\nu}$ is the correlation length (ξ_0, ν are its critical amplitude and exponent, respectively), $\chi=\Gamma t^{-\gamma}$ is the critical susceptibility–osmotic compressibility in this case (Γ, γ are its critical amplitude and exponent, respectively). For the (3,1) universality class $\nu\simeq 0.63$, $\gamma\simeq 1.24$ [2,3].

Using scale relations, $\psi=2\gamma-d\nu=\gamma-2\beta$.

(ii) Høye and Stell [10] on the basis of purely microscopic considerations, studying the distortion induced by a strong electric field in the orientationally averaged particle-particle correlations function, obtained

$$\mathcal{E}_C^{\mathrm{NDE}}, \mathcal{E}_C^{\mathrm{EKE}} \sim t^{-\psi}=t^{2\beta-\gamma} .$$

(iii) Recently, Onuki and Doi [11] considered the uniaxiality of the structure factor, caused by dipolar interactions induced in critical fluctuations by an electric field. They obtained

$$\left[\frac{\Delta\epsilon}{E^2}\right]_c \simeq C^2(160\pi k_B T_c)^{-1}\frac{1}{\epsilon_s\epsilon_f}\left[\frac{\partial\epsilon_s}{\partial x}\right]^2\left[\frac{\partial\epsilon_f}{\partial x}\right]^2\xi^{1-2\eta} , \tag{13a}$$

$$\left[\frac{\Delta n}{E^2}\right]_c \simeq 2C^2(480\pi k_B T_c\lambda)^{-1}\frac{1}{\epsilon_s n^2}\left[\frac{\partial\epsilon_s}{\partial x}\right]^2\left[\frac{\partial n}{\partial x}\right]^2\xi^{1-2\eta} , \tag{13b}$$

where C is the constant connected with the model. Indices f and s refer to the given measurement frequency and the stationary electric field, respectively.

Using scaling relations, $\nu(1-2\eta)=2\gamma-d\nu=\gamma-2\beta$.

The critical exponent ψ describes the static behavior of the NDE and the EKE. The experiment is performed by applying a rectangular electric-field pulse of duration τ_D. The static response can be derived if

$$\tau_D \gg \tau_c , \tag{14}$$

where τ_c is the relaxation time of critical fluctuations connected with the application of the field.

In the immediate vicinity of T_c the influence of the increasing value of τ_c on the EKE and the NDE response of the sample to the rectangular impulse of a strong electric field becomes visible. This offers the opportunity of analyzing the dynamic properties of critical fluctuations. This phenomena will be called here the dynamic response. Piazza *et al.* [13], using the dynamic droplet model, obtained a stretched exponential function for the time dependence of the response. Onuki and Doi, using their model [11], constructed a scaling function which indicates the possibility of a nonexponential decay.

III. EXPERIMENTAL RESULTS

A. Kerr effect

The behavior of the electro-optical Kerr effect on approaching the critical consolute point has been studied by Pyżuk and Baranowska (since 1979) [14–16] and recently by Bellini and Degiorgio [13,17,18]. Tests of Pyżuk and Baranowska were conducted for solutions with a difference between the electric permittivities of components $\epsilon_1 - \epsilon_2 < 30$ (1, 2 denote the first and second component of the critical solution, respectively). In Ref. [14] the great difficulties encountered in the proper estimation of the noncritical background effect were pointed out, which may be the main reason of the scatter of ψ_{EKE} values in different solutions. The majority of Pyżuk's results have been recently reanalyzed [16]. The obtained value of the critical exponent is $\psi_{\mathrm{EKE}} \simeq 0.75$.

In Ref. [15] Pyżuk confirmed the dependence predicted by relations (12b) and (13b) of the critical amplitude from dielectric properties of the solution:

$$A_{\mathrm{NDE}} \sim \frac{(\epsilon_1 - \epsilon_2)^2 (n_1 - n_2)^2}{\epsilon n^2} , \tag{15}$$

where ϵ, n refer to electric permittivity and refractive index of the critical solution.

Piazza, Bellini, and Degiorgio studied the Kerr effect in critical solutions with a very large difference of electric permittivity of their components, water-lutidine [13] and water-buthoxyethanol [17], where $\epsilon_1 - \epsilon_2$ is about 70. This caused the background effect to be negligible. They obtained $\psi_{\mathrm{EKE}} = 0.88 + 0.03$ and $0.85 + 0.04$ for the first and second solution, respectively.

A similar value of the exponent has been obtained in the nonionic micellar solution C_8E_3-H_2O: $\psi_{\mathrm{EKE}} = 0.88 + 0.04$ [18].

They also conducted experimental studies of the dynamic response [13,19]. The obtained decay rate can be described by the stretched exponential function with parameters in agreement, within the limit of experimental error, with the dynamic droplet model [13]. However, the obtained data, at least in the first approximation, are also in agreement with the Onuki-Doi model [11]. It may be concluded that for the dynamic response further experiments will be crucial. The temperature dependence of the correlation time was described by the critical exponent $y \simeq 1.8$.

B. Nonlinear dielectric effect

The first studies on NDE (since 1978) [20,21] showed a large scatter of the exponent ψ_{NDE} [22]. Systematic studies (since 1983) by the present author in cooperation with Ziolo and Chrapeć showed that the main reason for this scatter was problems with the background effect [22,23]. The NDE and the EKE are very sensitive to a large number of molecular properties and it appears to be impossible to find a general formula for the description of the background effect. Apart from the background, the possibility of the influence of the second power term [relation (9)] and the possible influence of the definition of the distance from the critical point [i.e., for $t = (T - T_c)/T_c$ and $t = (T - T_c)/T$] [23] has also been tested. All these studies showed that near T_c in binary critical solutions the critical behavior is described by a single power term with the exponent [22–25] $\psi_{\mathrm{NDE}} \simeq 0.4$.

Further studies in solutions, where for some molecular reasons,

$$\mathcal{E}_C^{\mathrm{NDE}} \gg \mathcal{E}_B^{\mathrm{NDE}} , \tag{16}$$

and taking into account the correction-to-scaling term, gave [25,26]

$$\psi_{\mathrm{NDE}} = 0.370 + 0.005 .$$

Tests conducted on the tenth solution for which $\epsilon_1 - \epsilon_2$ ranged from 3 to 40 showed that, as predicted by relations (12a) and (13a), the dependence of the critical amplitude on the difference between electric permittivities of the solution constituents [27],

$$A_{\mathrm{NDE}} \sim \frac{(\epsilon_1 - \epsilon_2)^4}{\epsilon^2} , \tag{17}$$

is very satisfactorily fulfilled.

Tests in a homologous series of (nitrobenzene–n-alkanes) critical solutions where $\epsilon_1 - \epsilon_2 \simeq \mathrm{const}$ but electric permittivity of the solution ϵ changed significantly due to variation in critical concentration, showed that also this, more subtle, dependence [28],

$$A_{\mathrm{NDE}} \sim \frac{1}{\epsilon^2} , \tag{18}$$

is in agreement with experiment.

The NDE has also been studied from the point of view of certain general predictions of the theory of critical phenomena. Results of high-pressure studies [29] are in agreement with the smoothness postulate [3]. Studies of the isothermal approaching the critical consolute point in a three-component solution [30] (which allowed the crossover behavior to be avoided) confirmed the prediction of Fisher's renormalization theory [i.e., relation $\psi \to \psi/(1-\alpha)$] [3].

Following the studies of the transient electric birefringence (TEB) [13] investigations of the dynamic response, based on the NDE, have been performed. Also in this case the decay rate could be well described by the stretched exponential function. However, for unknown reasons, the exponent describing the temperature dependence of the correlation time was only about 1.3 [31].

All the above studies were conducted at the frequency of a weak measuring field of 5–6.7 MHz. Pyżuk [32] studied the critical effect in critical solutions of monoalkanes at the frequency of 1–1.5 MHz. In this case again: $\psi_{\mathrm{NDE}} = 0.4 - 0.37$.

C. The isotropic phase of nematogens

The phenomenological Landau–de Gennes model predicts for the NDE, the EKE, and also the light scattering and Cotton-Mouton effect the same classical (mean-field) behavior, with the exponent $\gamma = 1$ [3,33–35]:

$$\mathcal{E}_c^{\mathrm{EKE}} = \frac{1}{3\lambda a n} \frac{\Delta n_a \Delta \epsilon_a^s}{T - T^*} , \quad \mathcal{E}_c^{\mathrm{NDE}} = \frac{2}{3a} \frac{\Delta \epsilon_a^s \Delta \epsilon_a^f}{T - T^*} , \tag{19}$$

for $T > T^c$, $T^* = T^c - \Delta T$, where T^c is the clearing temperature, T^* is the temperature of a hypothetical, continuous phase transition, ΔT is the value of the discontinuity of the phase transition, a^{-1} is the amplitude of susceptibility, and $\Delta \epsilon_a$ and Δn_a are the anisotropies of electric permittivity and the refractive index, respectively. The indices s and f refer to the zero-frequency limit and the measurement frequency, respectively.

The agreement with the experiment seems to be very good [3,33–36]. Some discrepancies appear for nematogens which contain a large, permanent dipole moment [34,37].

IV. A PROPOSED EXPLANATION OF THE DISCREPANCY BETWEEN THEORY AND EXPERIMENT

Beysens and co-workers [38,39] studied light scattering and the miscibility in binary, critical solutions under shear flow condition. They ascertained that the magnitude of elongation of critical fluctuations has a significant influence on observed critical properties.

For $S\tau<1$ they obtained

$$\gamma \simeq 1.24 \quad \text{and} \quad \beta \simeq 0.34 \ , \tag{20a}$$

i.e., nonclassical values. For $S\tau>1$ they obtained

$$\gamma \simeq 1 \quad \text{and} \quad \beta \simeq 0.5 \ , \tag{20b}$$

i.e., classical (mean-field) values, where S is the shear rate and τ is the relaxation time.

An explicit connection between relations (20) and the magnitude of deformation of fluctuations is found after multiplying both sides by ξ. Such behavior was predicted earlier by the hydrodynamic model of Kawasaki [40].

The entry into regime (20b) means that fluctuations and correlation length become anisotropic, with uniaxial symmetry:

$$\xi=(\xi_{\parallel},\xi_{\perp},\xi_{\perp}) \ , \tag{21}$$

where $\parallel$ and $\perp$ denote the long and the short axis of the ellipsoid.

The shortness of $\xi_\perp$ is the reason that the system crosses over the Ginzburg criterion [41] and becomes classical. However, this does not take place for $\xi_\parallel$, which means that along the parallel direction the critical properties may still be nonclassical. It seems that the Kerr effect and the nonlinear dielectric effect may be used to study properties of critical fluctuations in both directions.

According to the definition [relation (2)], the Kerr effect compares properties of critical fluctuations in two directions: perpendicular and parallel to the strong electronic (forcing) field, which are described by nonclassical $\xi_\parallel$ and classical $\xi_\perp$ components of the correlation length. The consequences of such an assumption may be tested. According to relations (12) and (13),

$$\begin{aligned}\mathcal{E}^{\rm EKE} &\sim \xi^{-d}\chi^2=\xi_0^{-3}\Gamma^2 t^{3\nu}t^{-2\gamma}\\ &=\xi_0^{-3}\Gamma^2 t^{\nu(x)}t^{\nu(y)}t^{\nu(z)}t^{-2\gamma} \ .\end{aligned} \tag{22}$$

For the stationary electric field acting in the direction x one may expect that for the critical exponent ν [relation (20), [3]], $\nu(x)=\nu_\parallel=\nu^{\rm nonclassical}\simeq 0.63$ and $\nu(y)=\nu(z)=\nu_\perp=\nu^{\rm classical}=0.5$. Hence for the Kerr effect, the critical exponent ψ has a value of

$$\begin{aligned}\psi_{\rm EKE}&=2\gamma-(\nu_\parallel+2\nu_\perp)\\ &\simeq 2\times 1.24-(0.63+2\times 0.5)=0.85 \ .\end{aligned} \tag{23}$$

The obtained value, $\psi_{\rm EKE}(\text{theor})\simeq 0.85$, is in a very good agreement with the experimental result of Bellini and Degiorgio [17]:

$$\psi_{\rm EKE}(\text{expt})=0.85\pm 0.04 \ .$$

As regards the nonlinear dielectric effect, an important difference between the NDE and the EKE should first be noted. The Kerr effect considers the system only in the anisotropic state, caused by a stationary electric field. The nonlinear dielectric effect compares the properties of the isotropic (without a field) and anisotropic (with a strong, stationary, electric field) states of the liquid. Additionally, the weak measuring field is parallel to the strong, stationary one:

$$\mathcal{E}^{\rm NDE}=\frac{\epsilon^E-\epsilon}{E^2}=\frac{\epsilon_\parallel-\epsilon}{E^2} \ . \tag{24}$$

This leads to the conclusion that the classical properties of the correlation length should not influence the properties of the NDE directly, as for the EKE [relations (22) and (23)]. However, relations (12) and (13) may be transformed to [42]

$$\mathcal{E}^{\rm NDE}\sim \xi^{-d}\chi^2=\xi^{-d}\chi\chi\sim\langle \Delta M^2\rangle_v\chi \ , \tag{25}$$

where $\langle \Delta M^2\rangle_v$ contains the coefficient $(1/\epsilon)^2(d\epsilon/dx)^4$ (fluctuations of the order parameter M for critical solutions are connected with the concentration fluctuations in this case).

In relation (25), one of the susceptibilities is included in the $\langle \Delta M^2\rangle_v$ term. This susceptibility is linked with ξ and is responsible for the appearance of critical fluctuations, in the isotropic and anisotropic states of the critical solution. Hence, it would appear that it should be of the same nature. The second susceptibility describes the possibility of shrinking of fluctuations by a force acting perpendicularly to the lines of the field, i.e., in the classical direction, described by $\xi_\perp$. This means that the exponent ψ describing the temperature increase of NDE has the following form:

$$\begin{aligned}\psi_{\rm NDE}&=\gamma^{\rm nonclassical}+\gamma^{\rm classical}-d\nu\\ &\simeq 1.24+1.02-3\times 0.63=0.37 \ ,\end{aligned} \tag{26}$$

where in the classical value of γ the logarithmic correction [3,43], very probably near the crossover frontier, has been included.

The values obtained, $\psi_{\rm NDE}(\text{theor})\simeq 0.37$, is in very good agreement with the experimental result [26]:

$$\psi_{\rm NDE}(\text{expt})=0.370\pm 0.005 \ .$$

It is noteworthy that, in a very approximate way, relation (25) may be commented as follows: In the isotropic state of the solution, due to fluctuations of the order parameter, critical fluctuations appear. This is described by the correlation length and one of the susceptibilities. Next, due to the action of a strong electric field, these fluctuations are oriented along the lines of forces of a strong electric field. This process is connected with the force acting perpendicularly to lines of the field and is described by the second susceptibility. Naturally, the fluctuations are in a fluid state, which means that the process of orientation has to be implemented rather by "reshaping" than by real orientation, as one should expect, for instance, for the nematic fluctuations in the isotropic phase of liquid-crystal materials. However, taking into account that the exponent ψ describes the static behavior for which condition (14) is fulfilled, only the first (a fluctuation in the isotropic solution) and the last (an elongated fluctuation in the anisotropic solution) is observed—except for the region in the immediate vicinity of T_c.

As was shown in Secs. II and III, from the theoretical point of view the behavior of the electro-optic Kerr effect and the NDE in critical mixtures and in the isotropic phase of nematogents are described quite separately. However, taking into account relation (25) and the fact that nematic fluctuations are "naturally" anisotropic and stiff, so that more real orientation takes place, it may be written as

$$\mathcal{E}^{\mathrm{NDE}} \sim \langle \Delta M^2 \rangle_v \chi = \Gamma^* \frac{\Delta\epsilon_a \Delta\epsilon_a}{T - T^*} , \qquad (27)$$

where instead of T_c the temperature T^* has been introduced.

The above relation is in full agreement with the results of the mean-field Landau–de Gennes model [33] [relation (19)]. The lack of the coefficient $\frac{2}{3}$ may be due to the fact that in averaging fluctuations of the order parameter in critical solutions, three independent directions must be taken into account, while for describing nematic fluctuations in the isotropic liquid it is sufficient to have two independent coefficients [33].

V. CONCLUSIONS

Studies reported here are based on two assumptions. First, due to the elongation of critical fluctuations in a strong electric field their properties are classical for the $\xi_\perp$ direction and nonclassical for the $\xi_\parallel$ direction. Second, the nonlinear dielectric effect and electro-optic Kerr effect are able, in a different way, to detect this difference.

These assumptions make is possible to explain all the relations between experimental results and predictions of theoretical models mentioned in the Introduction and Sec. III. The values of critical exponents ψ_{NDE} and ψ_{EKE} obtained are in very good agreement with experimental results. All these facts suggest that the Kerr effect and the NDE, because of their sensitivity to classical and nonclassical properties, could become valuable and very interesting tools for studying critical fluctuations in solutions of limited miscibility.

Another interesting result is the possibility of a unified description of the nonlinear dielectric effect and the Kerr effect for critical solution of ordinary liquids and for the isotropic phase of liquid-crystal materials. In this latter case of particular interest appears to be the relation between the semimicroscopic models for critical solutions and the phenomenological Landau–de Gennes model. For instance, relation (25) helps in understanding the reasons for the same, mean-field, behavior of the NDE, the EKE, and light scattering on approaching the isotropic-nematic transition in the isotropic phase of liquid-crystal materials.

Critical fluctuations may give a large, positive contribution to the observed value of the NDE (even of the order of 10^{-14} $\mathrm{m^2\,V^{-2}}$) [27]. In liquids where there are no critical effects, the permanent dipole moment is negligible, molecular interactions virtually do not exist and no intramolecular rotations take place (for instance, in solvents like CCl_4, alkanes, etc., or in noble gases) the significant influence to the NDE gives statistical fluctuations of polarizability [9,44–46]. In fact, this is the smallest effect which may be observed by the NDE (of the order 10^{-20} $\mathrm{m^2\,V^{-2}}$). Its value is proportional to the molecular polarizability α_m and isothermal compressibility k_T (i.e., susceptibility χ) [43]:

$$\mathcal{E}^{\mathrm{NDE}} \sim \alpha_m^2 \chi . \qquad (28)$$

The similarity of relations (25) and (28) shows that, at the qualitative level, it is justifiable to speak of a unified description of the NDE also for critical and noncritical fluctuations.

ACKNOWLEDGMENTS

The author would like to thank J. Zioło for help, support, and discussions and V. Degiorgio, R. Piazza, and T. Bellini for their criticism. The author is also grateful to P. G. de Gennes for his opinion. The author was supported by a grant from the International Centre for Theoretical Physics, Trieste, Italy, under the Training Programme in Italian Laboratories.

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