Critical phenomena in a liquid in a strong electric field

V. L. Pokrovskiĭ and S. V. Fomichev
L. D. Landau Institute of Theoretical Physics, USSR Academy of Sciences

(Submitted November 20, 1972)
Zh. Eksp. Teor. Fiz. **64**, 1440-1444 (April 1973)

Critical phenomena in liquids in a strong electric field are investigated. It is shown that the behavior of various thermodynamic quantities is determined by a geometric factor which depends on the shape of the surface of the system.

An external electric field **E** polarizes the particles of a gas. The oriented dipoles interact with one another. A dipole-dipole interaction of the density fluctuations develops. These long-range forces can significantly change the behavior of the liquid near the critical point, since they inhibit fluctuations and introduce anisotropy. Specific effects of the long-range forces also appear. In the present article, all these effects are considered in the homogeneous phase region.

To simplify the situation, we shall not consider fluctuations of the electric field **E**, assuming it to be homogeneous and equal to the field outside the sample. This is valid if at the critical point

$$\varepsilon - 1 = 4\pi\chi\rho_c \ll 1 \tag{1}$$

(ϵ is the static dielectric constant, χ the electric susceptibility of the individual particle, ρ_c the critical density). The inequality (1) is satisfied, for many real liquids.

In the spirit of the Landau phase transition theory (see[1]), we write down the thermodynamic potential Φ as a functional of the density $\rho(\mathbf{r})$:

$$\Phi = \Phi_0 + \int\left[\frac{a}{2}(\rho-\rho_c)^2 + \frac{b}{2}(\nabla\rho)^2 - \frac{\mathbf{E}\mathbf{d}(\mathbf{r})}{2}\rho(\mathbf{r})\right]d^3\mathbf{r}$$
$$+\frac{1}{2}\iint \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)\frac{\mathbf{d}(\mathbf{r}_1)\mathbf{d}(\mathbf{r}_2) - 3(\mathbf{d}_1\mathbf{n}_{12})(\mathbf{d}_2\mathbf{n}_{12})}{|\mathbf{r}_1-\mathbf{r}_2|^3}d^3\mathbf{r}_1\,d^3\mathbf{r}_2 + \frac{g}{4!}\int(\rho-\rho_c)^4 d^3\mathbf{r}, \tag{2}$$

where $\rho(\mathbf{r})$ is the local density, $\mathbf{d}(\mathbf{r})$ the dipole moment for a single particle, and

$$a \sim \frac{T-T_c}{\rho_c} + \frac{T_c}{\rho_c^{\,3}}(\rho-\rho_c)^2.$$

In the present work, we shall be interested chiefly in the qualitative change of the character of the critical phenomena in an electric field, and we shall therefore at first limit ourselves to the simplified theory of noninteracting fluctuations, g = 0. The dipole moment per single particle is equal to

$$\mathbf{d}(\mathbf{r}) = \chi\mathbf{E},$$

and (2) can be rewritten in the form

$$\Phi = \Phi_0 + \int\left[\frac{a}{2}(\rho-\rho_c)^2 + \frac{b}{2}(\nabla\rho)^2 - \frac{\chi E^2}{2}\rho\right]d^3\mathbf{r}$$
$$+\frac{1}{2}\iint\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)U(\mathbf{r}_1-\mathbf{r}_2)\,d^3\mathbf{r}_1\,d^3\mathbf{r}_2, \tag{3}$$
$$U(\mathbf{r}) = \chi^2E^2r^{-3}[1-3\cos^2\sphericalangle(\mathbf{E},\mathbf{r})]. \tag{4}$$

Inasmuch as Φ depends quadratically on the density fluctuations in the approximation used, one can calculate the density correlation function in the Fourier representation by the standard technique:

$$G(\mathbf{k}) = \frac{1}{T}\langle\rho_{-\mathbf{k}}\rho_{\mathbf{k}}\rangle = \frac{1}{a+bk^2+U(\mathbf{k})}, \tag{5}$$
$$U(\mathbf{k}) = \chi^2E^2(4\pi\cos^2\theta - 4\pi/3), \tag{6}$$

where θ is the angle between **k** and **E**, which is indeterminate for **k** = 0.

We take particular note of the value

$$U(\mathbf{k}=0) = \chi^2E^2(4\pi N_z - 4\pi/3), \tag{7}$$

where the field **E** is directed along the z axis and N_z is the demagnetization factor in the direction of the z axis:

$$N_z = \frac{1}{4\pi}\int_S\frac{z\,dx\,dy}{r^3}. \tag{8}$$

Integration in (8) is carried out over the surface of the liquid.

Substituting (6) and (7) in (5), we find:

$$G(\mathbf{k}) = \frac{1}{a' + bk^2 + 4\pi\chi^2E^2k_z^2/k^2}, \tag{9}$$
$$G(\mathbf{k}=0) = \frac{1}{a' + 4\pi\chi^2E^2N_z}. \tag{10}$$

The difference between a and a′ is essentially connected with the renormalization of the chemical potential $\delta\mu = -\chi E^2/2$ due to interaction of the dipoles with the mean field. The theoretical consequences of this renormalization were considered by Voronel' and Giterman.[2] Debye and Kleboth[3] observed the decrease of T_c in an electric field experimentally. The self-consistent field theory replaces the quantity a in Eqs. (9), (10) with the quantity $a' = a + g\bar{\varphi}^2/2$, where $\bar{\varphi}$ is found from the equation

$$a\bar{\varphi} + {}^1/_6 g\bar{\varphi}^3 = \delta\mu. \tag{11}$$

The density correlation function (10) is identical in form with the correlation function of the dipole moments in uniaxial ferroelectrics in the region of applicability of the Landau theory.[4,5] However, the physical situation is quite different, since the anisotropy parameter in the case considered is the electric field, which can be changed arbitrarily. In coordinate space the correlation function G(r) is also an anisotropic function of the angle ψ between the vectors **r** and **E**. In particular, for $\psi = \pi/2$ right at the critical point $T = T_c'$, $\bar{\rho} = \rho_c'$ ($\bar{\rho}$ is the mean density), we have

$$G(r) = \frac{1}{4\pi b\rho_c}\frac{1}{r}\exp\left\{-\left(\frac{\pi}{b}\right)^{1/2}\chi Er\right\}.$$

In the direction parallel to the field **E**, at distances $(r/r_c)^2 \gg 4\pi\chi^2E^2/a'$, where $r_c = (b/a')^{1/2}$ is the correlation radius in the absence of field, we have for G(r)

$$G(r) = \frac{2\chi^2E^2}{\rho_c a'^2}\frac{1}{r^3}$$

instead of the exponential decay from the Ornstein-Zernike theory. Such a slow decay of the correlation function is a consequence of the long-range dipole-dipole interaction and leads to a dependence of the behavior of the various thermodynamic quantities on the shape of the surface near the critical point.

In the range of fields which will be defined below (see (20)), departures from Pascal's law are insignificant (the change in the pressure is of the order of $\rho_c \chi E^2/2$) and therefore the concept of the volume compressibility of the liquid has meaning.

Near the critical point we have:

$$-\frac{\bar{\rho}^2}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{V}\left(\frac{\partial N}{\partial \mu}\right)_{T,P} = \frac{1}{T}\sum_{\mathbf{r}'}\langle(\rho(\mathbf{r})-\rho_c)(\rho(\mathbf{r}')-\rho_c)\rangle. \quad (12)$$

It is not obvious beforehand that the volume compressibility will not depend on the choice of the point r in (12) in the presence of long-range dipole-dipole interaction. In order to show this, we write down the equation which the correlation function

$$G(\mathbf{r}, \mathbf{r}') = V\langle(\rho(\mathbf{r}) - \rho_c)(\rho(\mathbf{r}') - \rho_c)\rangle / T.$$

satisfies. It has the form

$$aG(\mathbf{r},\mathbf{r}') - b\Delta_r G(\mathbf{r},\mathbf{r}') + \int G(\mathbf{r}_1,\mathbf{r}')U(\mathbf{r}-\mathbf{r}_1)d^3\mathbf{r}_1 = V\delta(\mathbf{r}-\mathbf{r}'). \quad (13)$$

Integrating (13) over $\mathbf{r}'$, we obtain the equation

$$aK(\mathbf{r}) + \int K(\mathbf{r}_1)U(\mathbf{r}-\mathbf{r}_1)d^3\mathbf{r}_1 - b\int \Delta_r G(\mathbf{r},\mathbf{r}')d^3\mathbf{r}' = 1 \quad (14)$$

for the quantity

$$K(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{r}'} G(\mathbf{r},\mathbf{r}').$$

The second integral in (14) has the order $1/L^2$, where L is a characteristic dimension of the system and vanishes in the limit $L \to \infty$. By virtue of the fact that

$$\int U(\mathbf{r}-\mathbf{r}_1)d^3\mathbf{r}_1 = \text{const} = U(\mathbf{k}=0),$$

Eq. (14) has a solution of the form

$$K(\mathbf{r}) = \text{const} = 1/[a + U(0)]$$

and we get the following expression for the volume compressibility:

$$-\frac{\bar{\rho}^2}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{a' + 4\pi\chi^2E^2N_z} = G(\mathbf{k}=0). \quad (15)$$

At the critical point itself, the compressibility has a finite value, which depends on the geometry of the system.

The diffusion coefficient of the dissolved material in the solution near the critical mixing point is connected with the density correlation function in the following way:[6]

$$D = \frac{1}{3}\int G(\mathbf{r})F(\mathbf{r})d^3\mathbf{r} \Big/ \int G(\mathbf{r})d^3r = \frac{2T}{3\eta}\frac{1}{G(\mathbf{k}=0)}\int G(\mathbf{k})\frac{1}{\mathbf{k}^2}\frac{d^3\mathbf{k}}{(2\pi)^3}, \quad (16)$$

where $F(\mathbf{r}) = T/2\pi\eta r$ and η is the viscosity of the solvent. Using (9), (10),.we find

$$D = D_0\left(\frac{\sqrt{a'}}{2\sqrt{\pi}\chi E} + N_z\frac{2\sqrt{\pi}\chi E}{\sqrt{a'}}\right)\operatorname{arcsh}\frac{2\sqrt{\pi}\chi E}{\sqrt{a'}}, \quad (17)$$

where $D_0 = T(a/b)^{1/2}/6\pi\eta$ is the diffusion coefficient in the absence of field.

In an electric field, the diffusion coefficient increases and no longer goes to zero at the critical point (as it does in the absence of field), but has a logarithmic singularity there. The extinction coefficient[7] for scattering of natural light is determined by the density correlation function $G(\mathbf{q})$ for $q \neq 0$ ($\mathbf{q} = \mathbf{k} - \mathbf{k}'$ is the scattering vector) and, near the critical point in the electric field, has the form

$$dh = \frac{T_c\omega^4}{32\pi^2c^4}\left(\frac{\partial\varepsilon}{\partial\rho}\right)_T^2\left\{a' + 2\frac{b\omega^2}{c^2}(1-\cos\vartheta) + 4\pi\chi^2E^2\left[\sin\frac{\vartheta}{2}\cos\theta + \sin\theta\cos\frac{\vartheta}{2}\cos\varphi\right]^2\right\}^{-1}(1+\cos^2\vartheta)\sin\vartheta\, d\vartheta\, d\varphi, \quad (18)$$

where ϑ is the angle of scattering between the vectors $\mathbf{k}$ and $\mathbf{k}'$ and θ is the angle between the direction of the incident wave (vector $\mathbf{k}$) and the vector $\mathbf{E}$. Anisotropy of the critical opalescence with respect to the angle φ arises at high fields, when the angle θ is not equal to zero. For $\theta = 0$, Eq. (18) is simplified:

$$dh = \frac{T_c\omega^4}{32\pi^2c^4}\left(\frac{\partial\varepsilon}{\partial\rho}\right)_T^2\frac{(1+\cos^2\vartheta)\sin\vartheta\, d\vartheta\, d\varphi}{a' + 2[b\omega^2/c^2 + \pi\chi^2E^2](1-\cos\vartheta)}. \quad (19)$$

It is seen from (18), (19) that suppression of critical opalescence takes place in an electric field, especially for low frequencies $\omega \lesssim c\chi E/r_c\sqrt{a'}$.

The fields at which a change begins in the critical behavior of the quantities mentioned are determined from the relation

$$4\pi\chi^2E^2/a' \sim 1 \quad (20)$$

and have the order

$$E \sim (10^6 - 10^7)\left\{\frac{T - T_c'}{T_c'} + \left(\frac{\bar{\rho}-\rho_c}{\rho_c}\right)^2\right\}^{1/2} \text{ [V/cm]}.$$

These fields are located on the boundary of minimal breakdown fields for the corresponding liquids, so that observation of these phenomena is possible in principle.

The interaction of fluctuations for small g can be taken into account in the same way as was done in the work of Larkin and Khmel'nitskiĭ[5]. Summation of parquet diagrams leads in the first place to a logarithmic renormalization of the quantity a' in Eqs. (15), (17), (18). Moreover, in Eq. (18), the dependence on frequency changes but slightly. However, all the qualitative conclusions remain in force.

[1] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics), Nauka, 1964 [Addison-Wesley, 1971].

[2] A. V. Voronel' and M. Sh. Giterman, Zh. Eksp. Teor. Fiz. 55, 2459 (1968) [Soviet Phys.-JETP 28, 1306 (1969)].

[3] P. Debye and K. Kleboth, J. Chem. Phys. 42, 3155 (1965).

[4] M. A. Krivoglaz, Fiz. Tverd. Tela 5, 3439 (1963) [Soviet Phys.-Solid State 5, 2526 (1964)].

[5] A. I. Larkin and D. E. Khmelnitskiĭ, Zh. Eksp. Teor. Fiz. 56, 2087 (1969) [Soviet Phys.-JETP 29, 1123 (1969)].

[6] R. A. Ferrel, Phys. Rev. Lett. 24, 1169 (1970).

[7] L. D. Landau and E. M. Lifshitz, Elektrodinamika sploshnykh sred (Electrodynamics of Continuous Media) Gostekhizdat, 1957 [Addison-Wesley, 1959].

Translated by R. T. Beyer
160