CRITICAL PHENOMENA IN NONCONDUCTING LIQUIDS IN AN EXTERNAL ELECTRIC FIELD

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An external electric field applied to a pure substance or to a binary mixture modifies the critical properties of the system. We calculate and compare with experiment the changes in the critical parameters of mixtures resulting from the application of the field, and present formulas for the electrohydrostatic effect, namely the height distribution of the density when gravitational and electric fields are simultaneously applied, for cases of parallel-plate and cylindrical capacitors. It is shown that it is impossible to cancel out the action of these two fields on the critical state in the entire volume.

1. IN our earlier papers[1,2] we explained (to the extent that this could be done without resorting to model representations) how the gravitational field affects the properties of a substance in the critical state. We considered two types of critical points, namely the liquid–vapor critical point of a pure substance, characterized by the equations

$$\left(\frac{\partial p}{\partial \rho}\right)_T = \left(\frac{\partial^2 p}{\partial \rho^2}\right)_T = 0, \tag{1}$$

and the critical points of two-component systems (liquid–vapor and liquid–liquid). These states are characterized by the vanishing of the first two derivatives of the chemical potential of each of the components with respect to the molar concentration

$$(\partial \mu_1 / \partial c_1)_{p,T} = (\partial^2 \mu_1 / \partial c_1^2)_{p,T} = 0. \tag{2}$$

The influence of the gravitational field on the behavior of a liquid near the critical points (hydrostatic effect) was observed experimentally already in the last century, at the very start of the studies of the critical state.

The influence of an electric (or magnetic) field on the critical phenomena has been much less investigated. We wish, without resorting to model representations (in the spirit of the papers[1,2]), to consider certain phenomena in which the effect of the electric field on the critical state is manifest, and we confine ourselves only to nonconducting liquids.

2. In the presence of an electric field, the conditions (1) and (2), which define the critical points of single- and two-component systems, are modified. The thermodynamic equation and the stability conditions for dielectrics near the critical point were investigated by Landau and Lifshitz.[3] The critical point of the pure substance in an electric field is defined by the conditions

$$\left(\frac{\partial \mu}{\partial \rho}\right)_{T,E} = \left(\frac{\partial^2 \mu}{\partial \rho^2}\right)_{T,E} = 0; \quad \mu = \mu_0 - \frac{ME^2}{8\pi}\frac{\partial \varepsilon}{\partial \rho}. \tag{3}$$

The chemical potential in formula (3) and throughout the article is referred to one mole of the substance, and M is the molecular weight.

In the absence of a field and at a constant temperature, the change of the chemical potential $d\mu_0$ is determined completely by the change of the pressure $d\mu_0 = Mdp/\rho$, and (3) reduces to (1).

For two-component systems, the critical conditions retain the old form (2), but the chemical potentials in the electric field acquire an addition in the form (3):

$$\mu_i = \mu_i^0 - \frac{v_i E^2}{8\pi}\frac{\partial \varepsilon}{\partial c_i},$$

where ε is the dielectric constant of the mixture, and c_i and v_i are the molar concentration and the molar volume of one of the mixture components.

The change of the critical temperature of the pure substance upon application of an electric field has been calculated in the monograph.[3] The shift of the critical density is likewise calculated:

$$\Delta T = \frac{\rho E^2}{8\pi}\frac{\partial^2 \varepsilon / \partial \rho^2}{\partial^2 p / \partial \rho \partial T},$$

$$\Delta \rho = \frac{E^2/8\pi}{(\partial^3 p / \partial \rho^3)_T}\left\{\frac{\partial^2 \varepsilon}{\partial \rho^2}\left[1 - \frac{\partial^3 p / \partial \rho^2 \partial T}{\partial^2 p / \partial \rho\, \partial T}\right] + \rho \frac{\partial^3 \varepsilon}{\partial \rho^3}\right\}. \tag{4}$$

We present numerical estimates. For fields of 45 kV/cm the energy is $E^2/8\pi \approx 900$ erg/cm^3. The mixed derivative $\partial^2 p/\partial\rho\partial T$ is estimated in [4] and equals $\sim 6p_c/\rho_c T_c$. Then (for a typical critical pressure p_c = 50 atm) $\Delta T/T_c \approx 3 \times 10^{-6} \rho_c^2 (\partial^2 \varepsilon / \partial \rho^2)$. Unfortunately, it is difficult to estimate the derivative $\partial^2\varepsilon/\partial\rho^2$ which, as seen from (4), determines the influence of the electric field on the critical phenomena. If $\rho_c^2(\partial^2\varepsilon/\partial\rho^2) \sim \varepsilon \sim 1$, then $\Delta T/T_c \sim 3 \times 10^{-6}$ and we get $\Delta T \approx 10^{-3}$ deg at $T_c = 300°$.

For the critical parameters of binary systems, the shift in the electric field, calculated in accordance with (4), is

$$\Delta T = \frac{v_i E^2}{8\pi}\frac{\partial^2 \varepsilon / \partial c_i^2}{\partial^2 \mu_i / \partial c_i\, \partial T},$$

$$\Delta c_i = \frac{v_i E^2}{8\pi (\partial^3 \mu_i / \partial c_i^3)}\left[\frac{\partial^3 \varepsilon}{\partial c_i^3} - \frac{\partial^2 \varepsilon}{\partial c_i^2}\frac{\partial^3 \mu_i / \partial c_i^2 \partial T}{\partial^2 \mu_i / \partial c_i \partial T}\right]. \tag{5}$$

Debye and Kleboth[5] investigated experimentally the change of the critical opalescence in a binary mixture of trimethyl pentane in nitrobenzene following application of an electric field. This phenomenon was in-

terpreted as a shift of the critical temperature. From the experimental data ($\Delta T = 1.5 \times 10^{-2}$ deg at $E = 45 \times 10^3$ V/cm and $\partial^2\varepsilon/\partial\Phi_i^2 = 28.7$, where Φ_i is the volume fraction) it is possible to obtain the value of the thermodynamically important quantity

$$\left(\frac{\partial^2\mu}{\partial T\,\partial c}\right)_{cr} \approx 10^2 \quad \frac{\text{J}}{\text{mole (mol.frac.)-deg}}$$

If we assume that the dimensional estimates[2] for $(\partial^3\mu/\partial c^3)_{cr} \sim \mu_c/c_c^3$ are valid, then we can assume that the dimensionless value of the quantity $(\partial^2\mu/\partial c\partial T)$ is close to unity. This makes it possible to estimate the shift of the temperatures and of the concentrations for other systems. In particular, for the He^3–He^4 mixture, for which $\mu \sim 20 - 40$ J/mole, the shift turns out to be very small—smaller than 10^{-3}–10^{-4} deg.

3. An external electric field, like a gravitational one, leads to a redistribution of the density over the height of the vessel (electrohydrostatic effect). The intensity of the electric field should satisfy Maxwell's equation (without sources) div D = 0, i.e., the result depends on the geometry of the experiment. We confine ourselves to cases of a parallel-plate (height H) and cylindrical capacitors (inside and outside radii r_1 and r_2):

$$E_{\text{par. pl.}} = \frac{A}{\varepsilon}, \quad A = (\varphi_1 - \varphi_2)\Big/\int_0^H \frac{dz}{\varepsilon(\rho)},$$
$$E_{\text{cylind.}} = \frac{C}{\varepsilon r}, \quad C = (\varphi_1 - \varphi_2)\Big/\int_{r_1}^{r_2} \frac{dr}{r\varepsilon(\rho)}. \tag{6}$$

The condition that the chemical potential of the pure substance be constant in external gravitational and electric fields (at T = const) is

$$\frac{1}{\rho}dp + g\,dz - d\left(\frac{E^2}{8\pi}\frac{d\varepsilon}{d\rho}\right) = 0. \tag{7}$$

Expanding the chemical potential (3) in terms of the deviations of the density from its critical value, we obtain from (7)

$$\frac{1}{2}\left\{\frac{1}{\rho}\frac{\partial^3 p}{\partial\rho^3} - \frac{\partial^3}{\partial\rho^3}\left[\frac{E^2}{8\pi}\left(\frac{\partial\varepsilon}{\partial\rho}\right)\right]\right\}_{cr}(\rho - \rho_c)^2 d\rho + g\,dz - d^*\left(\frac{E^2}{8\pi}\frac{\partial\varepsilon}{\partial\rho}\right) = 0, \tag{8}$$

where we put $dA = d^*A + (\partial A/\partial\rho)d\rho$.

In a parallel-plate capacitor, the electric field does not depend on the coordinates

$$d^*\left(\frac{E^2}{8\pi}\frac{\partial\varepsilon}{\partial\rho}\right) = 0$$

and from (8) we obtain the same height distribution of the density as in [1], but the characteristic parameter determining the $\rho(z)$ dependence turns out to depend on the applied potential difference.

In the case of a cylindrical capacitor, the density at the given height (z = const) varies along the radius, just as in the case of centrifuging.[1)] Substituting (6) in (8) we obtain, after simple transformations

$$\left[\frac{\varepsilon^2}{6\partial\varepsilon/\partial\rho}\frac{\partial^3}{\partial\rho^3}\left(\frac{\partial\varepsilon/\partial\rho}{\varepsilon^2}\right)\right]_{cr}(\rho - \rho_c)^3 = \ln\frac{F(r, r_0)}{F(r_0, r)}, \tag{9}$$

where

$$F(r, r_0) = r^2\left[\left(\frac{\partial^3 p}{\partial\rho^3}\right)_{cr}\frac{r_0^2}{2\rho_c} - \frac{C^2}{16\pi}\frac{\partial^3}{\partial\rho^3}\left(\frac{\partial\varepsilon/\partial\rho}{\varepsilon^2}\right)_{cr}\right]$$

r_0 is the radius at which the critical conditions are realized.

As seen from the foregoing estimates, the influence of the electric field is small and, expanding the logarithmic term in (9), we get

$$\rho = \rho_c + \left[\frac{3C^2}{4\pi}\frac{\partial\varepsilon/\partial\rho}{\varepsilon^2}\frac{\rho_c}{(\partial^3 p/\partial\rho^3)_{cr}}\right]^{1/3}\left(\frac{1}{r^2} - \frac{1}{r_0^2}\right)^{1/3}. \tag{10}$$

The electrohydrostatic effect takes place also for a binary mixture. The condition for the equilibrium of each of the components of the mixture in the gravitational and electric fields has, for a thermostatically controlled system, the form

$$v_i\,dp + M_i g\,dz + \frac{\partial\mu_i^0}{\partial c_i}dc_i - d\left(\frac{v_i E^2}{8\pi}\frac{\partial\varepsilon}{\partial c_i}\right) = 0. \tag{11}$$

Eliminating dp from the two equations (11) with i = 1, 2, and using the equilibrium condition with respect to the particle numbers (the Gibbs-Duhem rule), we obtain after simple transformations

$$\left[M_1 - v_1\frac{M_1c_1 + M_2c_2}{v_1c_1 + v_2c_2}\right]g\,dz + \frac{1}{2}\left[\frac{\partial^3\mu_1^0}{\partial c_1^3} - \frac{\partial^3}{\partial c_1^3}\left(\frac{v_1E^2}{8\pi}\frac{\partial\varepsilon}{\partial c_1}\right)\right]_{cr}(c_1 - c_{1c})^2\,dc_1 - \frac{v_1v_2c_2}{v_1c_1 + v_2c_2}\frac{\partial\varepsilon}{\partial c_1}\frac{E\,dE}{2\pi} = 0. \tag{12}$$

For a parallel-plate capacitor E = const and the distribution of the concentration over the height of the vessel has the same form as in the absence of an electric field,[2] but with modified values of the coefficients (see (8)). It was noted in [2] that the hydrostatic effect can be used to separate mixtures. It is seen from (12) that when the components have definite dielectric properties the electric field can intensify or weaken the separation effect.

In the case of a cylindrical capacitor, the variation of the concentration along the radius (at a given height z) is determined by substituting (6) in (12) and integrating the differential equation (12). The result is perfectly analogous to (9).

4. To estimate the derivatives of the dielectric constant of the mixture with respect to the concentration, which enter in our formulas, it is necessary to make use of model representations. The well-known Clausius–Mosotti formula can be written in the form[6]

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \sum_k \frac{\varepsilon_k - 1}{\varepsilon_k + 2}c_k; \quad \sum_k c_k = 1, \tag{13}$$

where the summation is over the types of substances contained in the mixture.

If the differences between the dielectric constants are small compared with each of them, then[3]

$$\varepsilon^{1/3} = \sum_k \varepsilon_k^{1/3}c_k, \quad \sum_k c_k = 1. \tag{14}$$

The derivatives of interest to us, determined from (13) and (14), are

1)We note the following curious possibility. When $T < T_c$ and in a sufficiently strong electric field we can obtain in a cylinder an angular meniscus in a horizontal plane.

$$\frac{d\varepsilon}{\partial c_1}=\frac{(\varepsilon+2)^2}{3}\left[\frac{\varepsilon_1-1}{\varepsilon_1+2}-\frac{\varepsilon_2-1}{\varepsilon_2+2}\right],$$

$$\frac{\partial^2\varepsilon}{\partial c_1^2}=\frac{2}{9}(\varepsilon+2)^3\left[\frac{\varepsilon_1-1}{\varepsilon_1+2}-\frac{\varepsilon_2-1}{\varepsilon_2+2}\right]^2; \qquad (13')$$

$$\frac{\partial\varepsilon}{\partial c_1}=3\varepsilon^{2/3}(\varepsilon_1^{1/3}-\varepsilon_2^{1/3}),$$

$$\frac{\partial^2\varepsilon}{\partial c_1^2}=6\varepsilon^{1/3}(\varepsilon_1^{1/3}-\varepsilon_2^{1/3})^2, \quad \frac{\partial^3\varepsilon}{\partial c_1^3}=6(\varepsilon_1^{1/3}-\varepsilon_2^{1/3})^3. \qquad (14')$$

We note that for $\varepsilon \approx 1$ these two approaches lead to close results.

5. We have assumed so far that the electric field is homogeneous over the height of the vessel or is proportional to $1/r$ in the cylindrical case. The question arises, however, whether it is possible to choose an electric field that varies with height, say in such a manner as to balance the gravitational field. Such a prospect would be very attractive, for one could get rid of the influence of the force of gravity in experiments near the critical point. To compensate for the gravitation field, the electric field must be directed upward and vary like $E^2 \sim z$. However, from the solution of Maxwell's equations it follows that such a compensation (in the absence of space charges) can be realized only at points lying on a single plane located halfway between the electrode of the parallel-plate capacitor or along one axis (for a cylindrical capacitor).

The influence of a magnetic field on critical phenomena can be analyzed in perfect analogy. Experiments with an electric (or magnetic) field (shift of the critical parameters in the fields, height distribution of the density, change of the scattering of light in the field, etc.) would make it possible to determine a number of important parameters characterizing the critical state of pure substances and of mixtures.

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