INTERNAL FIELD GRADIENT IN INHOMOGENEOUS SYSTEMS WITH VARIOUS FILLING DENSITIES, WHICH ARE IN THE CRITICAL STATE

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On the basis of the fluctuation theory of phase transitions and the theory of gravitational effect, the gradient of an internal field in an inhomogeneous system near its critical point (CP) has been demonstrated to depend on the density of the system filling. The results obtained are corroborated by the experimental studies of the altitude dependence of the scattered light intensity in such systems.

For studying the critical state of the substance [1, 2], the methods that use the phenomenon of gravitational effect [3] are applied successfully. For example, this phenomenon has been earlier used in a series of works [4–7] to study the equation of state in a wide vicinity of the CP and the properties of liquid systems along three critical directions: the critical isochore, the critical isotherm, and the phase interface. It is the gravitational effect phenomenon that enables one to study the critical indices γ, δ, and β, as well as the amplitudes of the equations of state along the critical directions specified above, in the same experimental run, provided that the experimental chamber is filled with the substance only once.

While studying the gravitational effect in the CP vicinity [8–10], a number of new features in the behavior of spatially inhomogeneous liquids, as compared with the behavior of homogeneous systems, have been revealed. In works [8–10], it has been shown that if the system is close to its CP, the variation of the internal field $\Delta U = \Delta\mu(h) = (\mu - \mu_c)/\mu_c$ in the direction of the gravitational field of the Earth considerably exceeds the altitude-connected variation of the hydrostatic pressure $h = \rho_c g z/p_c$: $\Delta\mu = (10 \div 100)h$. Here, ρ_c, p_c, and μ_c are the critical values of density, pressure, and chemical potential, respectively; z is the altitude reckoned from the level, at which the substance possesses the critical density; and g is the gravitational acceleration.

It was revealed that the gradient of this field $dU/dh = d\mu/dh$ depends on the height of the system L. It has been shown for the first time that if the height increases, the gradient $d\mu/dh$ decreases rather than increases. The conclusions drawn were explained on the basis of the fluctuation theory of phase transitions (FTPT) [1, 2] and the theory of gravitational effect [4].

This work aimed at studying the influence of the system filling density on the magnitude of the internal field gradient.

Consider an inhomogeneous system in a gravitational field at the critical temperature T_c of the substance and various densities of filling: $\overline{\rho_1} = \rho_c$, $\overline{\rho_2} > \rho_c$, and $\overline{\rho_3} < \rho_c$. Provided the filling density $\overline{\rho_1} = \rho_c$, the phase interface disappears at the half-height level of the system; at $\overline{\rho_2} > \rho_c$ or $\overline{\rho_3} < \rho_c$, the phase interface disappears in the top or the bottom part of the system, respectively.

In those three cases, taking into account the results of works [1,4], the fluctuation part of the thermodynamic potential of the inhomogeneous system can be expressed in the form [10]

$$F_{\mathrm{FI}}(\overline{\rho_1} = \rho_c) = 2S \int\limits_0^{\frac{L}{2}} C_0 R_e^{-3}(\Delta\mu) dz =$$

$$= S \int\limits_0^{L} C_0 (d_0 \Delta\mu^{\xi})^3 dz = \frac{V C_0}{3\xi + 1} d_0^3 \left(\frac{d\mu}{dh}\right)^{3\xi} \left(\frac{L}{2}\right)^{3\xi},$$

$$F_{\mathrm{FI}}(\overline{\rho_2} > \rho_c, \overline{\rho_3} < \rho_c) =$$

$$+S\int\limits_0^L C_0 R_e^{-3}(\Delta\mu)dz = \frac{VC_0}{3\xi+1}d_0^3\left(\frac{d\mu}{dh}\right)^{3\xi}L^{*3\xi}. \quad (1)$$

Here, S is the cross-section area of the system, and $L^* = \rho_c gL/p_c$. Let us mix the inhomogeneous systems together. Then, the fluctuation energy of such homogeneous but now nonequilibrium systems at critical ($\overline{\rho_1} = \rho_c$) and noncritical ($\overline{\rho_{2,3}} \neq \rho_c$) fillings is equal to

$$F_{\mathrm{FH}}(T_c, \overline{\rho_1} = \rho_c) = 0,$$

and

$$F_{\mathrm{FH}}(T_c, \overline{\rho_2} > \rho_c, \overline{\rho_3} < \rho_c) = VC_0 d_0^3 \Delta\mu(\rho_2, \rho_3)^{3\xi} =$$

$$= \frac{VC_0}{(3\xi)^{3\xi/(3\xi-1)}}d_0^3\left(\frac{d\mu}{dh}\right)^{3\xi}L^{*3\xi}. \quad (2)$$

respectively.

After some time, the homogeneous nonequilibrium system goes to the equilibrium state, which is spatially inhomogeneous over the altitude. In so doing, the center of mass of the substance is shifted vertically by the distance ΔZ_0, so that the work $A_1 = VQ\Delta Z_0$ is expended. Here, Q is the resistance force of the medium per unit volume of the substance, when the system goes to the equilibrium state.

Owing to the altitude-induced variation of the specific energy of fluctuations $f = C_0 R_0^{-3}$ in the equilibrium state, the fluctuation part of the chemical potential $\Delta\mu_f(h) = df/d\rho$ also varies, which brings about the modification $\Delta U(h) = \Delta\mu(h)$ of the internal field in the system. The work of formation of this inhomogeneous field can be expressed in the form [10]

$$A_2 = S\varepsilon\int\limits_L \frac{df}{dh}dz = S\varepsilon\int\limits_L \frac{df}{d\rho}\frac{d\rho}{dh}dz = S\varepsilon\int\limits_L \Delta\mu(h)\frac{d\rho}{dh}dz, \quad (3)$$

where ε is the constant.

As the system changes to the equilibrium state, the variation of the fluctuation part of the system free energy $\Delta F_{\mathrm{F}} = F_{\mathrm{FI}} - F_{\mathrm{FH}}$ is expended on doing the work A_1 to displace the center of mass of the substance, as well as the work A_2 to form the internal inhomogeneous field $\Delta U(h)$, i.e.

$$\Delta F_{\mathrm{F}} = F_{\mathrm{FI}} - F_{\mathrm{FH}} = A_1 + A_2 =$$

$$= VQ\Delta z_0 + S\varepsilon\int\limits_L \Delta U(h)\frac{d\rho}{dh}dz. \quad (4)$$

Let us determine this work at various densities of system filling: $\overline{\rho_1} = \rho_c$, $\overline{\rho_2} > \rho_c$, and $\overline{\rho_3} < \rho_c$. Earlier, in work [10], the quantities ΔF_F, A_1, A_2, and Δz_0 were calculated in the case $\overline{\rho_1} = \rho_c$:

$$\Delta F_{\mathrm{F}}(\overline{\rho_1} = \rho_c) = \frac{Vk_2}{3\xi}\left(\frac{d\mu}{dh}\right)\left(\frac{L}{2}\right)^{3\xi}, \quad A_1 = VQ\Delta z_0^*,$$

$$A_2 = \Delta F_{\mathrm{F}}\varepsilon(1+3\varepsilon)\left(\frac{L^*}{2}\right)^{-1},$$

$$\Delta z_0 = k\left(\frac{L^*}{2}\right)^{3\xi}, \quad k = \frac{3\xi}{1+3\xi}C_0 d_0\left(\frac{d\mu}{dn}\right)^{3\xi-1}. \quad (5)$$

In the other cases ($\overline{\rho_2} > \rho_c$ or $\overline{\rho_3} < \rho_c$), analogously to Eq. (5) [10], we obtain

$$\Delta F_{\mathrm{F}}(\overline{\rho_2} > \rho_c) = \Delta F_{\mathrm{F}}(\overline{\rho_3} < \rho_c) =$$

$$VC_0 d_0^3\left(\frac{d\mu}{dh}L^*\right)^{3\xi}\left[\frac{1}{3\xi+1} - \frac{1}{3\xi^{3\xi/3\xi-1}}\right] =$$

$$= 0.118VC_0 d_0^3\left(\frac{d\mu}{dh}\right)^{3\xi}L^{3\xi}; \quad (6)$$

$$\Delta z_0(\overline{\rho_2} > \rho_c) = \Delta z_0(\overline{\rho_3} < \rho) =$$

$$= \frac{1}{2}\left(\frac{3\xi-1}{3\xi+1}\right)C_0 d_0^3\left(\frac{d\mu}{dh}\right)^{3\xi-1}L^{*3\xi},$$

$$A_1(\overline{\rho_2} > \rho_{\text{к}}) = VQ(\overline{\rho_2} > \rho_{\text{к}})\Delta z_0(\overline{\rho_2} > \rho_{\text{к}}),$$

$$A_1(\overline{\rho_3} < \rho_c) = VQ(\overline{\rho_3} < \rho_c)\Delta z_0(\overline{\rho_3} < \rho_c,)$$

$$A_2(\overline{\rho_2} > \rho_c) = A_2(\overline{\rho_3} < \rho_c) = V\varepsilon C_0 d_0^3\left(\frac{d\mu}{dh}\right)^{3\xi}L^{*3\xi-1}.$$

Then, on the basis of relationships (4)—(6), we find the values of the internal field gradient $dU/dh = d\mu/dh$ in inhomogeneous systems for three various filling densities, namely:

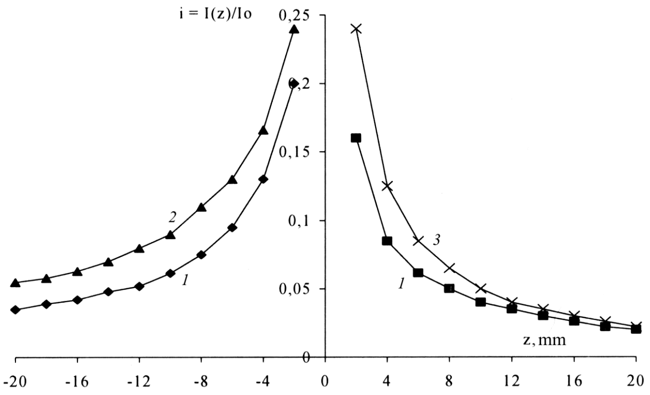
1) for $\overline{\rho_1} = \rho_c$,

$$\frac{d\mu}{dh}(\overline{\rho_1} = \rho_c) = \frac{1.2Q}{1 - 4.4\varepsilon L^{*-1}}; \quad (7)$$

2) for $\overline{\rho_2} > \rho_c$ or $\overline{\rho_3} < \rho_c$,

$$\frac{d\mu}{dh}(\overline{\rho_2} > \rho_c, \overline{\rho_3} < \rho_c) = \frac{0.41Q}{1 - 8.4\varepsilon L^{*-1}}. \quad (8)$$

The obtained results, (7) and (8), testify that if the level of the system filling with the substance is critical



Dependences of the scattered light (λ = 546 nm) intensity on the altitude at the critical temperature of freon-113 and various densities of system filling: $\overline{\rho_1} = \rho_c$ (*1*), $\overline{\rho_2} > \rho_c$ (*2*), and $\overline{\rho_3} < \rho_c$ (*3*)

($\overline{\rho_1} = \rho_c$), the gradient of the internal field $\frac{d\mu}{dh}\left(\overline{\rho_1} = \rho_c\right)$ exceeds the gradient $\frac{d\mu}{dh}\left(\overline{\rho_2} > \rho_c, \overline{\rho_3} < \rho_c\right)$, because $\left|\frac{d\mu}{dh}\right|\left(\overline{\rho_1} = \rho_c\right) \approx 3\left|\frac{d\mu}{dh}\right|\left(\overline{\rho_{2,3}} \neq \rho_c\right)$. To check this conclusion, the experimental researches of the dependence $I(z)$ of the scattered light intensity on the altitude were carried out at the critical temperature of inhomogeneous freon-113 (trifluorotrichloroethane $C_2Cl_3F_3$) and various densities of system filling: $\overline{\rho_1} = \rho_c = 0.576$ g/cm^3, $\overline{\rho_2} = 0.71$ g/cm$^3 > \rho_c$, and $\overline{\rho_3} = 0.47$ g/cm$^3 < \rho_c$. Under those conditions, the phase interface disappears at the half-height of the system $L/2$, in the top and in the bottom part of the chamber, respectively. The obtained dependences $I\left(z, \overline{\rho_1}, \overline{\rho_2}, \overline{\rho_3}\right)$ are shown in the figure.

The experimental data in the figure are normalized to the amplitude of the scattered light intensity at the critical isochore level. These data demonstrate that, at the same altitude $|z|$,

$$I\left(z, \overline{\rho_{2,3}} \neq \rho_c\right) \sim \Delta\mu_{2,3}^{\frac{1-\delta}{\delta}} > I\left(z, \overline{\rho_1} = \rho_c\right) \sim \Delta\mu_1^{\frac{1-\delta}{\delta}}.$$

Whence, it follows that the altitude-induced variation of the chemical potential $\Delta\mu_1\left(z, \overline{\rho_1} = \rho_c\right)$ exceeds the variations $\Delta\mu_{2,3}\left(z, \overline{\rho_{2,3}} \neq \rho_c\right)$. Therefore, the following inequality is valid for the gradients of the internal field:

$$\frac{d\mu_1\left(\overline{\rho_1} = \rho_c\right)}{dh} > \frac{d\mu_{2,3}\left(\overline{\rho_{2,3}} \neq \rho_c\right)}{dh}.$$

The obtained experimental result confirms the calculations made by formulas (7) and (8). Thus, the experimental and theoretical studies enable us to draw a conclusion that the internal field gradient induced by the gravitational field of the Earth in the inhomogeneous substance that is in the critical state depends on the density of the system filling, with the maximal value of the derivative $d\mu/dh$ corresponding to the critical filling of the system $\overline{\rho_1} = \rho_c$.

1. *Patashinski A.Z., Pokrovski V.L.* Fluctuation Theory of Phase Transitions. — Oxford: Pergamon Press, 1982.
2. *Anisimov M.A.* Critical Phenomena in Liquids and Liquid Crystals. — Philadelphia: Gordon and Breach, 1991.
3. *Van der Waals J.D., Constamm Ph.* Lehrbuch der Thermostatik. — Leipzig: Verlag von Johann Ambrosius Barth, 1927.
4. *Golik A.Z., Shimanskii Yu.I. et al.* // The Equation of State for Gases and Liquids (to the Centenary of the Van der Waals Equation). — Moscow: Nauka, 1975. — P. 189—217 (in Russian).
5. *Artyukhovskaya L.M., Shimanskaya E.T., Shimanskii Yu.I.* // Zh. Eksp. Teor. Fiz. — 1973. — **64**, N 5. — P. 1679.
6. *Bulavin L.A., Ostanevich Yu.I., Simkina A.P.* // Ukr. Fiz. Zh. — 1971. — **15**, N 1. — P. 91—99.
7. *Bulavin L.A.* Properties of Liquids in the Critical Range. — Kyiv: Kyiv Univ. Publ. House, 2002 (in Russian).
8. *Alekhin A.D.* // Ukr. Fiz. Zh. — 1983. — **28**, N 8. — P. 1261.
9. *Alekhin A.D., Bulavin L.A., Rudnikov E.G.* // Ibid. — 1996. — **41**, N 11—12. — P. 1059—1061.
10. *Alekhin A.D.* Liquid—Vapor Critical Phenomena in the Gravitational Field. Thesis for Dr. Sci. degree in physics and mathematics. — Kyiv, 1994 (in Russian).

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ГРАДІЄНТ ВНУТРІШНЬОГО ПОЛЯ В НЕОДНОРІДНИХ СИСТЕМАХ В КРИТИЧНОМУ СТАНІ ПРИ РІЗНИХ ГУСТИНАХ ЇХ ЗАПОВНЕННЯ

О.Д. Альохін

Р е з ю м е

На основі флуктуаційної теорії фазових переходів і теорії гравітаційного ефекту показано, що градієнт внутрішнього поля неоднорідної системи поблизу критичної точки залежить від густини її заповнення. Одержані результати підтверджуються експериментальними дослідженнями висотної залежності інтенсивності розсіяного світла в таких системах.