HYDROSTATIC EFFECT IN BINARY MIXTURES CLOSE TO THE CRITICAL STATE OF VAPORIZATION

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The effect of the external field on the structure of the liquid–vapor transition layer of a binary mixture in the critical state of vaporization is investigated.

The strong increase in the susceptibility of a binary mixture to external influences close to the critical state of vaporization is, as is well known, the reason for the considerable spatial nonuniformity of the properties of the system along the direction of the external field (e.g., the gravitational field). This phenomenon has been called the hydrostatic effect. Two forms of hydrostatic effect can be distinguished: 1) the macrohydrostatic effect and 2) the microhydrostatic effect. The macrohydrostatic effect produces nonuniformities of size greater than the correlation radius of the fluctuations of the characteristic order parameter (in this case fluctuations in the total density of the mixture), while the system is assumed to be uniform within the limits of the correlation radius. The microhydrostatic effect produces nonuniformities in regions comparable with the correlation radius [1]. It should be noted that the microhydrostatic effect is fairly noticeable in narrow regions close to the level with critical density and it affects those physical quantities which determine the properties (surface tension, density proile, etc.) of the transition layer between the liquid and vapor (the interface).

The macrohydrostatic effect in binary mixtures close to the critical state of vaporization has been considered in [2, 3] using the classical theory of phase transitions, and in [4, 5] using the scale equation of state [6]. The structure of the transition layer in binary mixtures has been investigated in [7] without taking into account the gravitational field. The microgravitational effect in binary solutions has been studied by statistical methods in [8].

In this paper we will consider the hydrostatic effects and the structure of the transition layer of a binary mixture close to the critical state using the Landau–Ginzburg Hamiltonian generalized to the case of a binary mixture, and the approximate theory of the renormalization group [9].

We will write the model Landau–Ginzburg Hamiltonian for a binary mixture with component densities ρ_i (i = 1, 2) close to the critical state of vaporization in an external field in the form [10]

$$H_{\text{eff}}\{\Delta\rho\} = \int d\mathbf{r}\,\{D(x)\,[\nabla\Delta\rho(\mathbf{r})]^2 + R(\tau,\ x)[\Delta\rho(\mathbf{r})]^2 + U(\tau,\ x)[\Delta\rho(\mathbf{r})]^4 - Z\Delta\rho(\mathbf{r})\}, \tag{1}$$

where $\Delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \langle\rho(\mathbf{r})\rangle$ is the local deviation of the total density of the binary mixture $\rho = \rho_1 + \rho_2$ from the mean value at the point $\mathbf{r}$, and $x = \rho_1/\rho$ is the concentration of the mixture. The quantities $R(\tau, x)$ and $U(\tau, x)$ are related to R_i and U_i of the pure components by means of expressions, explicit forms of which are given in [10]. The nonlocal properties of the system close to the critical state are described by the gradient term $D(x)[\nabla\Delta\rho(\mathbf{r})]^2$, where the parameter $D(x)$ is related to the radius of intermolecular interaction in the mixture. The term $Z\Delta\rho(\mathbf{r})$ defines the action of the external field on the system. Here $Z = \rho_c gh/P_c$ is the field variable, ρ_c and P_c are the critical values of the density and pressure of the mixture, h is the height measured from the critical level, $\tau = [T - T_c(x)]/T_c(x)$; T_c is the critical temperature.

We will consider the macrohydrostatic affect using Hamiltonian (1). It is well known that the nonlocal term $\sim [\nabla\Delta\rho(\mathbf{r})]^2$ is of the same order as the other terms of Hamiltonian (1) only in a small region comparable with the correlation radius R_c. When considering the macrohydrostatic effect, which is important outside this region, the term $D[\nabla\Delta\rho(\mathbf{r})]^2$ in (1) can be neglected. Then, from the condition

$$\partial H_{\text{eff}}/\partial\Delta\rho = 0 \tag{2}$$

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we obtain the following equation for the equilibrium value of the order parameter $\Delta\rho_0 = (\rho - \rho_c)/\rho_c$:

$$2R(\tau, x)\Delta\rho_0(Z) + 4U(\tau, x)[\Delta\rho_0(Z)]^3 - Z = 0. \tag{3}$$

The solution (3) has the form

$$\Delta\rho(Z, \tau, x) = \sqrt[3]{\frac{Z}{8U} + \sqrt{\left(\frac{R}{6U}\right)^3 + \left(\frac{Z}{8U}\right)^2}} + \sqrt[3]{\frac{Z}{8U} - \sqrt{\left(\frac{R}{6U}\right)^3 + \left(\frac{Z}{8U}\right)^2}}. \tag{4}$$

We recall that expression (4) only holds for regions $Z > Z_0$, where Z_0 is the thickness of the interface, whose dimensions will be determined below. From (4), taking into account the renormalization of the parameters R and U of the Hamiltonian, which follows from the approximate theory of the Wilson renormalization group [9, 10], at temperatures $T > T_c$ we have

$$\Delta\rho_0(Z, \tau, x) = Z / \left\{2\tau(x)^{1+\frac{\varepsilon}{3}\frac{1}{2-\varepsilon/3}}\left[1 + \frac{\varepsilon C(x)}{9\tau(x)^{-\nu\varepsilon}}\right]\right\} \tag{5}$$

for a direction isomorphous with the critical isochore which satisfies the condition $(R/6U) \gg (Z/8U)^3$,

$$\Delta\rho_0(Z, x) \sim Z^{1/(3+\varepsilon\nu/\beta)} \tag{6}$$

for the critical isotherm. Here $\varepsilon = 4 - d$, where d is the dimensionality of the space, $\nu \approx 0.6$; $\beta \approx 0.3$ are the critical indices, and C(x) is a parameter which depends on the concentration and is determined in [10]. Expressions (5) and (6) correctly describe the experimental results for the density profile in the critical binary mixtures in a gravitational field and differ considerably from the corresponding results of the classical theory of the macrohydrostatic effect [2].

Consider the structure of the liquid–vapor transition layer of a binary mixture in the region of the critical state of vaporization. We will first obtain an expression for the density profile in the interphase when there is no external field. To do this we will start from the Hamiltonian, which has form (1), in which we take as the expansion parameter the quantity $(\Delta\rho_i - \Delta\rho_0)$, which specifies the local variation in the order parameter of the mixture taking into account the effects of spatial dispersion ($\Delta\rho_i$ is the order parameter in the interface, and $\Delta\rho_0$ is the value of the order parameter outside the interface, i.e., $\sim [\nabla\Delta\rho_i]^2$) ignoring the term. The effective Hamiltonian (1) with this expansion parameter describes the total variation in the energy of the system with the "inclusion" of the nonlocality. The equilibrium value of $(\Delta\rho_i - \Delta\rho_0)$ is found from condition (2), which with (1) leads to the Euler equation, which has the form [11]

$$-D[\nabla\Delta\rho_i]^2 + R(\Delta\rho_i - \Delta\rho_0)^2 + U[\Delta\rho_i - \Delta\rho_0]^4 = \text{const}. \tag{7}$$

We will assume that the interface is concentrated in a plane-parallel layer situated perpendicular to the Z axis. The density distribution in the interface will depend only on Z and $\nabla\Delta\rho = d\Delta\rho/dZ$. As $Z \to \infty$ $\Delta\rho_i = \Delta\rho_0$, $\nabla\Delta\rho = 0$, whence we obtain the zero value for the integration constant in (7). Taking this into account we can rewrite (7) in the form

$$-D\left(\frac{d\Delta\rho_i}{dZ}\right)^2 + R[\Delta\rho_i - \Delta\rho_0]^2 + U[\Delta\rho_i - \Delta\rho_0]^4 = 0. \tag{8}$$

Solving the differential equation (8) for $T < T_c$ and the boundary condition $\Delta\rho_i(0) = 0$, we obtain the following expression for the density profile in the interface when there is no gravitational field:

$$\Delta\rho_i(Z) = \Delta\rho_0\left\{1 - \sqrt{1 - \text{th}^2\sqrt{-\frac{R}{D}}Z}\right\}, \tag{9}$$

where $\Delta\rho_0 = \sqrt{R/U}$. It follows from (9) that when $Z = 0$, $\Delta\rho_i = 0$, and as $Z \to \infty$ $\Delta\rho_i = \Delta\rho_0$. The equation obtained differs from the expression for the interface profile

$$\Delta\rho = \Delta\rho_0 \,\text{th}\sqrt{-\frac{R}{D}}Z, \tag{10}$$

obtained in [7, 11]. The difference is due to the fact that when calculating the structure of the transition layer in [7, 11] the approximate equation $\Delta\rho_i^4 - \Delta\rho_0^4 \approx [\Delta\rho_i^2 - \Delta\rho_0^2]^2$ was used. It is obvious that the density distribution in the interface of the mixture close to the critical state of vaporization as described by Eq. (9) is the same as in the case of a pure material.

We will now consider the structure of the interface in the region of the critical state of vaporization taking the gravitational field into account. In this case the equation for the equilibrium value of $\Delta\rho_i$ has the form

$$D\frac{d^2(\Delta\rho_i-\Delta\rho_0)}{dZ^2}-R(\Delta\rho_i-\Delta\rho_0)-U(\Delta\rho_i-\Delta\rho_0)^3=-Z, \tag{11}$$

where $\Delta\rho_0(Z)$ is the value of the order parameter in the gravitational field outside the interface. We will obtain a solution of this second-order nonlinear nonuniform differential equation for a number of limiting directions. In the neighborhood of the critical isochore $[R \gg U(\Delta\rho_i-\Delta\rho_0)^2]$ the cubic term in (11) can be neglected, after which, for $T > T_c$, the solution of Eq. (11) takes the form

$$\Delta\rho_i-\Delta\rho_0=C_1\exp[\sqrt{R/D}Z]+C_2\exp[-\sqrt{R/D}Z]+\frac{Z}{R}-\frac{1}{R\sqrt{R/D}}\,\mathrm{sh}\sqrt{R/D}Z. \tag{12}$$

The constants C_1 and C_2 are found from the condition that when $Z = 0$, $\Delta\rho_i = 0$. Taking into account the fact that outside the interface $\Delta\rho_0 = Z/R$, we can rewrite (12) in the form

$$\Delta\rho_i=\frac{2Z}{R}-\frac{1}{R\sqrt{R/D}}\,\mathrm{sh}\sqrt{R/D}\,Z+2C_1\,\mathrm{sh}\sqrt{R/D}\,Z. \tag{13}$$

To obtain the thickness of the interface Z_0 and the constant C_1, we will use the following conditions, which were used previously in [12] to calculate the thickness of the interface of a single-component liquid at the critical point:

$$\Delta\rho_i\big|_{Z_0-0}=\Delta\rho_0\big|_{Z_0+0}, \tag{14}$$

$$\left.\frac{d\Delta\rho_i}{dZ}\right|_{Z_0-0}=\left.\frac{d\Delta\rho_0}{dZ}\right|_{Z_0+0}, \tag{15}$$

$$\left.\frac{d^2\Delta\rho_i}{dZ^2}\right|_{Z_0-0}=\left.\frac{d^2\Delta\rho_0}{dZ^2}\right|_{Z_0+0}. \tag{16}$$

Condition (16) is necessary in order to find the value of the displacement of the density Δm from the zero value obtained when extrapolating solution (5) from the region outside the interface at the critical level $Z = 0$. Solving the system of equations obtained from (13) and (14)-(16) for C_1, Δm, and Z_0, we obtain

$$\Delta\rho_i=\frac{2Z}{R}-\frac{1-R^2}{R\sqrt{R/D}}\,\mathrm{sh}\sqrt{R/D}Z, \tag{17}$$

$$\Delta m=\frac{Z_0}{R}-\frac{1-R^2}{R\sqrt{R/D}}\,\mathrm{sh}\sqrt{R/D}Z_0, \tag{18}$$

$$Z_0=\sqrt{R/D}\,\mathrm{arch}\left[\frac{1}{1-R^2}\right]. \tag{19}$$

Since $R \sim \tau(x)^\gamma$, where $\gamma = 1.25$, it follows from an analysis of Eq. (19), which holds in the region $R \gg U(\Delta\rho_i-\Delta\rho_0)^2$, that as one approaches the critical state of vaporization of the binary mixture the thickness of the interface approaches infinity, as in [7], i.e., in the neighborhood of the critical isochore the effect of the external field on the thickness of the interface is negligible. But comparison of Eqs. (9) and (17) shows that a gravitational field leads to a considerable change in the density profile of a binary mixture in the interface.

In the neighborhood of the critical isotherm $[R \gg U(\Delta\rho_i-\Delta\rho_0)^2]$ we have for $\Delta\rho_i$ a nonlinear differential equation which is difficult to solve. But in this case the difference between the densities of the liquid and gas phases is small, while the thickness of the transition layer is fairly large, so that we can assume that $(\Delta\rho_i-\Delta\rho_0)$ in the interface is a smooth function. We then have the approximate equation $d(\Delta\rho_i-\Delta\rho_0)/dZ \approx (\Delta\rho_i-\Delta\rho_0)/L$. As a result, Eq. (11) for the critical isotherm can be rewritten in the form

$$D\frac{(\Delta\rho_i-\Delta\rho_0)}{L^2}+U(\Delta\rho_i-\Delta\rho_0)^3=Z. \tag{20}$$

Here $\Delta\rho_0 = (Z/U)^{1/3}$ is the value of the order parameter outside the interface, while L has the same order of magnitude as the thickness of the interface Z_0. Solving (20) we obtain

$$\Delta\rho_i=\left(\frac{Z}{U}\right)^{1/3}+\sqrt[3]{\frac{Z}{2U}+\sqrt{\left(\frac{Z}{2U}\right)^2+\left(\frac{D}{3UL^2}\right)^3}}+\sqrt[3]{\frac{Z}{2U}-\sqrt{\left(\frac{Z}{2U}\right)^2+\left(\frac{D}{3UL^2}\right)^3}}. \tag{21}$$

We will use the following approximation to obtain the thickness of the interface. As one moves away from the critical layer, the role of the gradient term in (20) becomes less, as a result of which, in the region of the interface boundary, the following relation holds:

$$U(\Delta\rho_i - \Delta\rho_0)^3 \gg \frac{D(\Delta\rho_i - \Delta\rho_0)}{L^2}.$$

The value of the density at the interface boundary can then be obtained from (20) by the method of successive approximations, which gives

$$\Delta\rho_i = \left(\frac{Z}{U}\right)^{1/3}\left[2 + \frac{D}{3L^2U(Z/U)^{2/3}}\right]. \tag{22}$$

Taking $L = Z_0$, we use condition (14) and obtain the following expression for the thickness of the interface:

$$Z_0 = 2\left(\frac{D}{3U^{1/3}}\right)^{3/8}. \tag{23}$$

Assuming that $D \approx 10^{-16}$ cm^2, $\rho_c g/P_c \approx 10^{-5}$ cm^{-1}, and $U \approx 1$, we obtain from (23) that the thickness of the interface has the value $Z_0 \approx 10^{-(1-2)}$ cm.

Analysis of expression (23) shows that in the neighborhood of the critical isotherm the thickness of the interface is mainly determined by the gravitational field of the earth and takes the finite value $Z_0 \approx 10^{-(1-2)}$ cm. This result differs radically from the conclusions arrived at in [7], in which calculations of the transition-layer thickness ignoring the external field led to the result $Z_0 \to \infty$ when $T = T_c$. Hence, for a binary mixture situated in an external field in the temperature region $R \gg U(\Delta\rho_i - \Delta\rho_0)^2$, when $T \to T_c$, the thickness of the liquid–vapor transition layer increases, but, beginning at a certain temperature, which satisfies the inequality $R \ll U(\Delta\rho_i - \Delta\rho_0)^2$, the rate of increase of the interface decreases, and at a critical point Z_0 takes a finite value which depends only on the gravitational field and the concentration of the mixture. This is due to the fact that in the temperature region $R \ll U(\Delta\rho_i - \Delta\rho_0)^2$ the gravitational field begins to have a considerable effect on the properties of the interface, and at the critical point itself all the properties of the transition layer are due to the gravitational field.

NOTATION

H_{eff}	is the effective Landau–Ginzburg Hamiltonian;
ρ_i	is the density,
i	is the component;
ρ	is the total density of the binary mixture;
x	is the concentration of the mixture;
$\Delta\rho$	is the fluctuation in the total density of the mixture;
D, R, U	are the parameters of the Hamiltonian H_{eff};
Z	is the dimensionless field variable;
τ	is the dimensionless temperature variable;
h	is the height measured from the critical level;
ρ_c	is the critical density;
P_c	is the critical pressure;
$\Delta\rho_0$	is the order parameter outside the interface;
$\Delta\rho_i$	is the order parameter inside the interphase;
Z_0	is the thickness of the interface;
ε	is the departure of the dimensionality of the space from 4;
d	is the dimensionality of space; and ν, β, γ are the critical indices.

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HEAT EXCHANGE IN THE FLOW OF A GAS SUSPENSION IN A LONG HORIZONTAL PIPE

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The results of an experimental investigation of the heat exchange of a gas-suspension stream in different lengths of horizontal pipes are presented.

It is known [1] that two-phase streams of the gas–solid-particle type are distinguished by a number of high qualities as the heat-transfer agent and working substance in power engineering. The inadequate degree of study and the complexity of the mechanism of heat-exchange processes in the flow of such streams result in the necessity of the systematic accumulation of test data.

The results of an investigation of heat exchange in the motion of a gas suspension in a horizontal pipe are presented in the report being offered. Air served as the carrier medium of the stream, while particles of white marble 110-220 μm in size were used as the solid phase.

The investigation* was carried out on an experimental installation for which a schematic diagram and the measurement procedure was described in [2]. But in contrast to [2], the start-up and heated sections were made of one common pipe without joints or connections. The inner diameter of the pipe was 14 mm. The heating was accomplished with radiative electric furnaces in sections on a pipe length of 4 m.

The separate determination of the transferred heat flux for the sections from the difference in the power supplied and lost through the thermal insulation of the furnaces made it possible to find in each test the characteristics of the heat exchange for different pipe lengths $x = 1$, 2, 3, and 4 m.

In order to study the influence of the dynamic conditions of entrance of the stream on the heat exchange we provided for the delivery of solid particles to the carrying air at distances of 0.07, 0.3, 0.75, and 1.37 m from the heated section. The start-up section had special fitting in its upper part for this. A calculated estimate of the velocity of the solid particles at the entrance to the heated section, made on the basis of a one-dimensional flow model, showed that with such start-up lengths under the conditions of the experiments the particle velocity was about 0.2-0.85 of the velocity of the transporting gas.

The investigation was carried out at flow-rate concentrations of the solid phase of from 0.17 to 8 kg per 1 kg of air. The Reynolds number of the gas was varied in the interval of $\mathrm{Re}_{w;d} = 1950$-18,000. In this case the transportation of the particles was stable with a stable drop of stream pressure over the pipe length in each test. The stream temperature at the entrance to the heated section was in the range of $t_0 = 10$-60°C. The wall temperature along the length of the pipe was kept nearly constant and was varied from 130 to 690°C from test to test. Measurements in the cross sections $x/d = 35.7$ and 207 showed that it also hardly varied over the perimeter of the pipe in each test.

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*Engineer V. I. Rednikov took part in conducting the tests.

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