SCALED EQUATION OF STATE FOR FREON-113 NEAR THE PHASE SEPARATION BOUNDARY

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The equation of state of Freon-113 near the phase separation boundary and the behavior of a nonisotropic medium in a gravitational field near the critical point are studied using data on the scattered light intensity.

In recent years, significant progress in theoretical investigations of phase transitions of the second kind and of critical phenomena [1-3] has stimulated deeper and more detailed experimental investigations of different properties of matter in near-critical conditions.

The progress achieved in this direction mainly involves the study of temperature behavior of substances near the critical point. The study of field dependences of thermodynamic properties of matter, which are no less important than the temperature dependences, are performed much less often. The basic information is provided by methods using the gravitational effects [4, 5], with the help of which the asymptotic form of the scaled equation of state near the critical isotherm and critical isochore was checked experimentally in [6].

According to the similarity theory [1-3], all thermodynamic properties of a substance near the critical point are determined by the fluctuation part of the free energy of the system

$$f_0 = \Delta F\ (k_B T)^{-1} = CV_0 R_c^{-3}. \tag{1}$$

Here C is a constant quantity; V_0 and R_c are the volume and correlation radius of an isotropic system.

Starting with this relation, in order to determine the equation of state of a substance near the critical point, experimental data are necessary on the field and temperature dependences of the correlation radius R_c.

Basic information concerning the correlation properties of a substance can be obtained by the method of molecular light scattering. This method was used in the present work. The object of our investigation was the single substance Freon-113 ($C_2F_3Cl_3$ — trifluorotrichloroethane). The experimental technique, which allowed studying the intensity of light scattering at an angle of 90° as a function of the height of the system, and the method for processing the experimental data are described in detail in [5]. The overall error in determining the intensity of single scattering varies from 2 to 6% depending on the temperature $t = (T_{cr} - T)T_{cr}^{-1}$. The critical temperature of Freon-113 was chosen as $T_{cr} = 487.1$°K, at which the phase separation boundary vanished, while the scattered light intensity at a height where the critical density of the substance is realized attained its highest value. The precision with which T_{cr} is determined in this manner is 0.01°. Near the critical temperature, the substance was thermostatically controlled with a precision of 0.005° for a period of 10-12 h.

We studied the height dependences of the scattered light intensity I(h, t) in the region of subcritical temperatures t from $1.4 \cdot 10^{-4}$ to $5 \cdot 10^{-3}$ and the field variable $h = \rho_{cr} g H_0 P_{cr}^{-1}$ from 0 to $2 \cdot 10^{-5}$, as well as at the critical temperature. Here, H_0 is the height measured from the center of the layer of the scattering volume of height $\Delta H = 5 \cdot 10^{-4}$ m to the phase separation boundary, ρ_{cr} and P_{cr} are the critical density and pressure. The data obtained on I(h, t) were used for studying the correlation properties of Freon-113 near the phase separation boundary.

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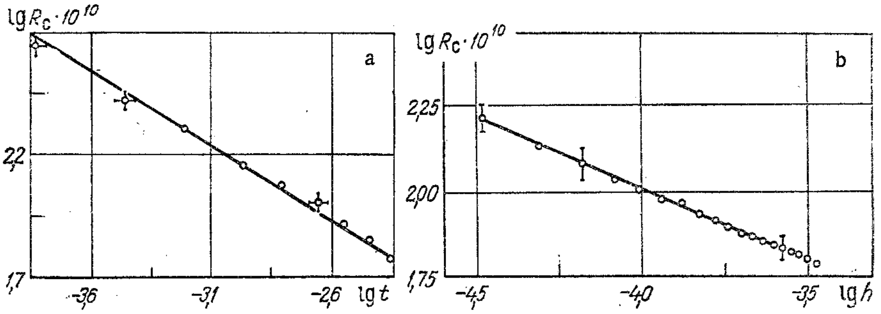

Fig. 1. Behavior of the correlation radius along the phase separation boundary $h = 0$ (a) and along the critical isotherm $t = 0$ (b). R_c, m.

Starting from the form of the correlation function given by Fisher [7] $G(r) = \frac{A}{r^{1+\eta}}\exp(R_c^{-1}r)$, the relation between the scattered light intensity and the correlation radius near the critical point can be represented in the form [8]

$$R_c = \frac{1}{k}\left[\frac{1}{k^2}\left(\frac{D}{I\lambda^4}\right)^{1+\eta/2} - 1\right]^{-0.5}. \qquad (2)$$

Here $k = (4\pi/\lambda)\sin(\theta/2)$; D is a constant quantity, which was determined from the experimental data on the scattered light intensity for two wavelengths of the exciting light $\lambda_1 = 5.461 \cdot 10^{-7}$ m and $\lambda_2 = 4.358 \cdot 10^{-7}$ m; and the critical index of the correlation function is $\eta = 0.06$ [7].

The functions $R_c(h, t)$ computed from formula (2) are shown in Figs. 1a, b and Fig. 2. In calculating R_c, we used the symmetrized values of the scattered light intensity $I = 0.5[I(h < 0) + I(h > 0)]$. The values $I(h > 0)$ and $I(h < 0)$ were chosen at heights that are symmetrical relative to the height $H = 0$, where the phase separation boundary is realized.

According to the similarity theory [1], the scaled equation for the correlation radius can be represented as

$$R_c^{-1} = t^{1/\Delta_t}\psi(Z), \qquad (3)$$

where $\psi(Z)$ and $Z = ht^{-\Delta_h/\Delta_t}$ are the scaled function and variable in the theory of similarity [1]; Δ_h and Δ_t are the scales for the field and temperature variables ($R_c^{-1}(t = 0) \sim h^{1/\Delta_h}$, $R_c^{-1}(h = 0) \sim t^{1/\Delta_t}$).

The values computed according to least squares based on the values of the correlation radius given along the line $h = 0$ (see Fig. 1a) and $t = 0$ (Fig. 1b) are $1/\Delta_t = 0.618 \pm 0.017$ and $1/\Delta_h = 0.408 \pm 0.008$. The form of the scale function $\psi(Z) = (R_c t^{1/\Delta_t})^{-1}$ for Freon-113 in the region $Z \approx 10^{-1} \ll 1$ is shown in Fig. 3. The experimental points are described by the following scaling function:

$$\psi(Z) = \sum_{n=0}^{\infty} a_n Z^n \approx a_0 + a_1 Z + a_2 Z^2, \qquad (4)$$

where $a_0 = (0.446 \pm 0.004) \cdot 10^{10}$ m^{-1}; $a_1 = (1.47 \pm 0.07) \cdot 10^{10}$ m^{-1}, and $a_2 = (0.93 \pm 0.05) \cdot 10^{10}$ m^{-1}.

Substituting (4) into the equation for the free energy (1) and differentiating with respect to the variables h and t, it is possible to study various thermodynamic properties of the substance near the critical point.

Function (4) confirms the form of the scaled equation of state near a phase separation boundary, proposed in [3], and permits analyzing some of the behavior of thermodynamic properties of a substance in a gravitational field near the critical point.

It is known that the theory of similarity [1-3] is applicable only in equilibrium and isotropic systems. However, under the actual experimental conditions, the system being studied is not of this kind. Near the critical state, due to the unbounded increase in compressibility of the substance under the action of the gravitational field, the system becomes nonuniform with respect to height. This nonuniformity can be eliminated by mixing

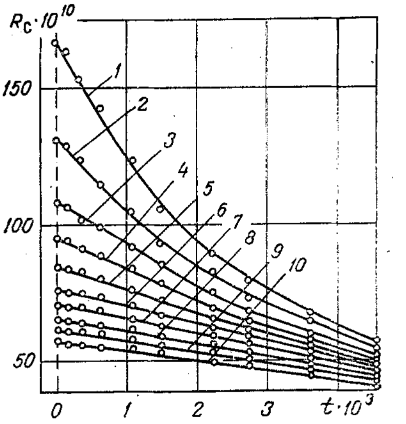

Fig. 2

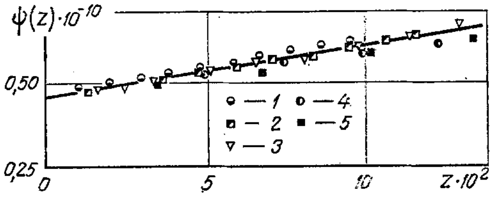

Fig. 3

Fig. 2. Temperature dependence of the correlation radius as a function of the different fixed heights H near the critical point: 1) $H = 2 \cdot 10^{-3}$ m; 2) $4 \cdot 10^{-3}$ m; 3) $6 \cdot 10^{-3}$ m; 4) $8 \cdot 10^{-3}$ m; 5) 10^{-2} m; 6) $1.2 \cdot 10^{-2}$ m; 7) $1.4 \cdot 10^{-2}$ m; 8) $1.6 \cdot 10^{-2}$ m; 9) $1.8 \cdot 10^{-2}$ m; 10) $2 \cdot 10^{-2}$ m.

Fig. 3. Form of the scale function $\psi(Z) = (R_c t^{1/\Delta t})^{-1}$ near the phase separation boundary: 1) $t = 5.2 \cdot 10^{-3}$; 2) $4.5 \cdot 10^{-3}$; 3) $3.65 \cdot 10^{-3}$; 4) $2.77 \cdot 10^{-3}$; 5) $2.25 \cdot 10^{-3}$. $\psi(Z)$, m.

the substance. But, such a mixed isotropic system will already be in a nonequilibrium state and after some time will again pass into an equilibrium state, but one which is nonisotropic with respect to height. In our opinion, in order to study the thermodynamic properties of a substance near the critical point it is useful to study this particular nonuniform, but equilibrium, state of the system. A mixed nonequilibrium system can serve as an object of study of the kinetic properties of a substance.

The nonuniformity of the system with the height of the specimen is created by the gravitational field. However, the thermal fluctuation motion of the molecules strives to destroy this nonuniformity. For a system with large linear dimensions, the gravitational effect predominates over fluctuation processes. However, in small systems, density fluctuations (especially near the critical point) completely destroy the gravitational change in density within the linear dimensions of the specimen being studied. On the basis of available experimental data, it is possible to calculate the linear parameters of such an isotropic system in a gravitational field for which the theory of scale transformations will be directly applicable. For this it is necessary that within the limits of the linear dimensions L_0 of the specimen, the gravitational change in density does not exceed the magnitude of the density fluctuations in the substance $[<(\Delta\rho/\rho_{cr})_f^2]^{1/2} \geq (\Delta\rho/\rho_{cr})_{gr}$, i.e.,

$$\left(\frac{k_B T}{V_0} \rho_{cr} \beta_T \right)^{1/2} \geqslant \rho_{cr} \frac{\partial \rho}{\partial H} L_0. \tag{5}$$

Here, $V_0 = L_0^3$, and β_T is the compressibility of the substance.

According to experimental data on the gravitational effect [4], light scattering [5, 9], and P, V, T measurements [10], near the phase separation boundary $\rho_{cr}^{-1} \cdot \partial\rho/\partial h \approx 10^{-4} t^{-\gamma}$; $P_{cr}\beta_T \approx 10^{-2} t^{-\gamma}$. Then, on the basis of (5), we find that $L_0 \leq (10^{-5} t^{\gamma/5})$ m.

The analysis made above shows that, near the phase separation boundary in the temperature range $t \geq 10^{-5}$, a system in a gravitational field with linear dimensions $L_0 \gg R_c$ is completely isotropic. The correlation radius of such a system in a gravitational field and the correlation function G(r) are spherically symmetrical. Scaling laws [1-3] can be applied with complete justification to such systems.

However, it is necessary to note that under actual experimental conditions the linear dimensions L of the specimens being studied significantly exceed the parameter L_0. In such systems, the action of the gravitational field leads to density nonuniformities with respect to the height of the specimen. Then, the fluctuating part of the free energy of such a nonuniform system in a gravitational field must be represented in the form

$$f_{\mathrm{gr}} = \int\limits_{V \gg V_0} f_0 V_0^{-1} dV = S \int\limits_0^H C V_0^{-1} t^{3/\Delta_t} [\psi(Z)]^3 \, dH, \tag{6}$$

where $V_0 = L_0^3$ is the volume within which the substance is completely isotropic; S is the cross-sectional area of the specimen. Substituting the series (4) into relation (6), and integrating with respect to the volume $V \gg V_0$, the center of which is located at a height H/2, we obtain

$$f_{\mathrm{gr}} = CVt^{3/\Delta_t} \sum_{n=0}^{\infty} b_n \frac{Z^n}{n+1}. \tag{7}$$

Here, $b_0 = a_0^3$, $b_1 = 3a_1 a_0^2$, and $b_2 = 3a_2 a_0^2$.

Taking into account only the first two terms of the series (7), we can conclude that the free energy of the nonisotropic system near the phase separation boundary $(0 < Z \ll 1)$ in a gravitational field equals the free energy of an isotropic medium in the same volume V, each point of which is characterized by the field variable $\Delta\mu = (\mu - \mu_0)\mu_0^{-1} = -h/2$ (μ_0 is the value of the chemical potential μ on the phase separation boundary itself).

The fluctuating parts of the free energy of the system in a gravitational field near a critical isotherm and isochore were studied previously in [11].

The gravitational density change of the substance near the critical temperature has an important effect on the experimental measurement of the boundary curve $\rho(t)$. Usually, in such investigations, the densities of the existing phases are equated to the average density $\bar{\rho} = M/V$ of the specimen.

On the basis of the equality $\partial f/\partial H = (\rho - \rho_{\mathrm{cr}})/\rho_{\mathrm{cr}})$, the average density of the specimen in the gravitational field can be represented as

$$\bar{\rho} = \rho_{\mathrm{cr}}\left[1 + H^{-1} \int\limits_0^H \frac{\partial f}{\partial H} \, dH \right]. \tag{8}$$

Near the phase separation boundary, according to (4), the derivative $df/dH = 3Ca_1 a_0^2 t^{\beta}(1 + \frac{a_2}{a_1} Z)$, while the critical index is $\beta = 3/\Delta_t + \Delta_h/\Delta_t$. On the basis of the measured values of Δ_h and Δ_t, the magnitude of the index is $\beta = 0.34$. Substituting the derivative df/dH in (8) and assuming that the density of the existing phases is determined by the relation $\rho_c = \rho_{\mathrm{cr}} \cdot (1 + Bt^{\beta})$, where $B = 3Ca_1 a_0^2$, after integrating we have

$$(\bar{\rho} - \rho_c)\rho_{\mathrm{cr}}^{-1} = \pm Bt^{\beta} \frac{a_2}{a_1} \frac{Z}{2}. \tag{9}$$

Under actual experimental conditions, when $H \approx 10^{-2}$ m, the case $Z \leq 10^{-1} \ll 1$ occurs only for $t \geq 10^{-3}$. Under these conditions on the basis of (9) the difference between $\bar{\rho}$ and ρ_c is 0.2%. In order that this distance not increase for $t \ll 10^{-3}$, it is necessary to decrease significantly the linear dimensions of the specimen being studied. For $t \leq 10^{-5}$ and $H \approx 10^{-3}$ m, when $\rho_c \approx \rho_{\mathrm{cr}}$, while $Z \gg 1$, the effect of the gravitational field will lead to the fact that $(\bar{\rho} - \rho_c)\rho_{\mathrm{cr}}^{-1}$ will attain a magnitude $\gtrsim 3 \cdot 10^{-2}$.

The calculations performed above lead to the conclusion that in measuring the boundary curve $\rho(t)$ near T_{cr} the equality $\bar{\rho} = \rho_c$ cannot be used. In order to study the density of existing phases $(h = 0)$ near the critical temperature correctly, careful measurements of the entire density profile are necessary for small field deviations from the phase separation boundary. Such experiments are possible only with methods using the gravitational effect phenomenon [4].

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