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Scaling Equation of State for a Nonequilibrium Solution Under Gravity Close to Phase Interface

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Experimental investigations of equilibration kinetics for a methanol-hexane binary solution under gravity have been carried out at temperatures T below the critical consolute temperature, $T < T_c$, by using a refractometry technique. As a result of the experiment, both equilibrium $n_z(z, t_e)$ and nonequilibrium $n_z(z, t)$ height dependences of the refractive index gradient n_z at different times t after the beginning of thermal equilibration have been obtained. Analysis of the data shows that the relaxation properties of the system at different fixed heights are determined not by a single relaxation time $\tau(z)$, but by a spectrum of relaxation times $\Sigma\tau_i(z_j, t)$. On the basis of the experimental data, the height dependence of the relaxation times has been analyzed for the studied solution in the course of its transition to equilibrium. The average relaxation time $\overline{\tau(z)}$ has been shown to decrease when nearing the phase interface ($z = 0$). The relaxation time $\tau(z, t)$ at a certain height z has been shown to also decrease when the system approaches an equilibrium state. A dynamic nonequilibrium equation of state has been proposed on the basis of the fluctuation theory of phase transitions for a substance under gravity close to the phase interface of a binary solution. It is based on the assumption that for small solution concentrations, $(c - c_c)/c_c \ll 1$, every nonequilibrium height distribution $n_z(z, t)$ corresponds to an equilibrium distribution $n_z(z, \Delta T)$ at a certain temperature $\Delta T = T - T_c$. Here, c_c is the critical concentration of the solution.

KEY WORDS: critical point; equation of state; inhomogeneous solution; nonequilibrium state; phase interface; refractive index gradient.

1. INTRODUCTION

According to the fluctuation theory of phase transitions in liquid systems [1, 2], the equilibration time t_e, which is proportional to the relaxation

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time $t_e \sim \tau \sim R_c$, must increase infinitely in the vicinity of a critical point due to infinite growth of the correlation length R_c. The relaxation properties of fluid systems near critical points were studied recently [3, 4]. It should be noted that results for spatially homogeneous systems concerning the significant growth of the relaxation times τ and the equilibration time t_e turned out to be incorrect for spatially inhomogeneous systems under gravity close to the critical point [5, 6]. For example, it can be seen [7] that even the microgravity effect considerably decreases the equilibration times to $t_e \leqslant 24$ h for weakly inhomogeneous systems near the critical consolute temperature. The equilibration time for essentially real inhomogeneous systems under gravity is much smaller. Such systems have been systematically investigated at Kyiv National Taras Shevchenko University [8, 9].

Our experimental studies of equilibration kinetics in such inhomogeneous systems [5, 6, 10–15] near the critical temperature have revealed a whole spectrum of peculiarities in the behavior of inhomogeneous liquids, which are not observed for homogeneous systems. A nonmonotonic temperature dependence at temperatures $T > T_c$ has been detected for the first time for the equilibration time $t_e(\Delta T)$ of an inhomogeneous substance under gravity [5, 6]. The longest time $t_e = \max$ corresponds not to the critical temperature T_c, but to a temperature $\Delta T = T - T_c > 0$ above the critical value. It was proved for the first time that the time t_e depends not only on the diffusion coefficient $D(\rho_c)$ or the relaxation time $t_e \sim \tau(\rho_c) \sim D^{-1}(\rho_c) \sim \Delta T^{-\nu}$, but also on the thickness of the liquid layer $\Delta z(\Delta T)$ with a critical density ρ_c. It increases with temperature as $\Delta z \sim \Delta T^{\beta\delta}$ [1, 16]. That is, $t_e \sim \tau\, \Delta z \sim \Delta T^{\beta\delta - \nu}$. So, when moving away from the critical temperature, the equilibration time does not decrease, but increases. Only after the moment when the thickness of the layer Δz will be equal to the entire height L of the cell with a substance ($\Delta z \approx L = \text{const}$), the equilibration time in the system $t_e \sim \Delta T^{-\nu}$ decreases when moving away from the critical temperature. A nonmonotonic height dependence of the relaxation time $\tau(z)$ has also been obtained at temperatures $T > T_c$ for an inhomogeneous liquid under gravity [10–14]. Maximum values of the relaxation time of density gradient ρ_z or concentration gradient c_z correspond not to the level of the critical isochore ($z = 0$) but to the heights $\Delta z \sim \Delta T^{\beta\delta}$. Nonequilibrium isotherms of the refractive index gradient (RIG) n_z intersect at these heights when the system goes to the equilibrium state [10, 11]. It has also been detected for the first time [10, 11] that the relaxation properties of the inhomogeneous liquid at a certain height z are determined not by a single relaxation time, but by the spectrum of these times $\Sigma\tau_i(z_j)$, which characterizes the entire inhomogeneous system under gravity.

The purpose of the present work is to continue the experimental studies of the peculiarities in equilibration kinetics for the spatially inhomogeneous liquid systems in the vicinity of critical points. In particular, the goal is to understand the time-dependent equation of state for such systems under gravity for temperatures $T < T_c$.

2. MEASUREMENTS

The well-known Toepler method [17] was used as an experimental technique for the RIG n_z measurement. It has been described in detail previously [8, 18]. The methanol-hexane binary solution with a critical methanol mass fraction $c_c = 0.31$ was poured into a thermally isolated parallel optical cell. The solution mass was such that the vapor phase was preserved above the studied liquid at all temperatures. First, the solution was heated from the two-phase region at room temperature $T = 293$ K to the consolute critical temperature $T_c = 307.1$ K. Then it was carefully thermostatted for almost a day at this constant temperature (better than 0.01 K uncertainty) until the RIG at all heights of the inhomogeneous solution remained unchanged. The critical temperature was associated with the point of the phase interface disappearance. Shortly after, this inhomogeneous but equilibrium system was cooled rapidly from the critical temperature to a selected temperature $T_i < T_c$. The system was kept at this temperature long enough to achieve another equilibrium state at temperature T_i. The equilibration time t_e was defined as the interval elapsing from the initiation of the quench until the RIG values $n_z(z)$ would essentially remained changed. In the course of thermal equilibration at this temperature, the height and time dependences of the RIG $n_z(z, t)$ for the solution were investigated by a well-known technique, as described elsewhere [8, 17, 18]. Such investigations were carried out for the series of temperatures $T_i < T_c$. The error in the RIG $n_z(z, t)$ measurement is (1 to 3)% for the heights $z = 0$ to 1 cm.

3. RESULTS

3.1. Equilibration Kinetics

Figure 1 shows the kinetics of change of the symmetrized values of the RIG $n_z(z, t) = 1/2\ \{n_z(z > 0, t) + n_z(z < 0, t)\}$ at different heights z in the cell containing the inhomogeneous methanol-hexane solution for the system approaching equilibrium at a temperature $\Delta T = T - T_c = -1.55$ K.

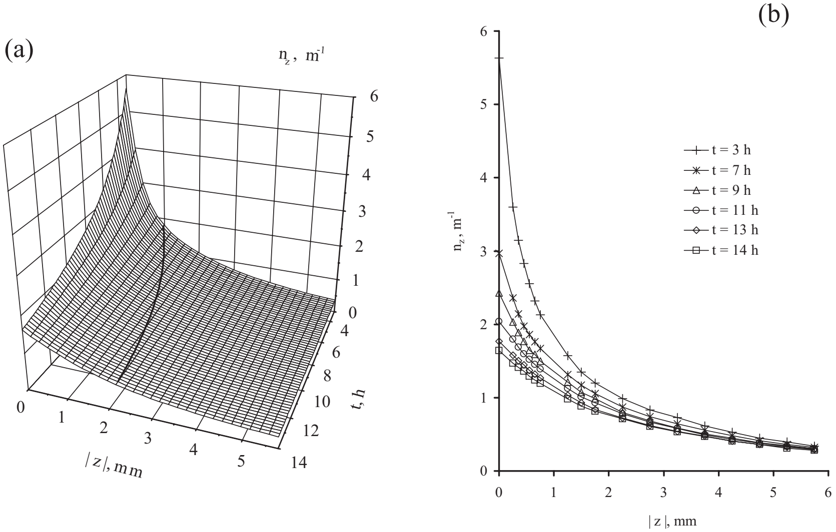

Fig. 1. (a) Three-dimensional surface of $n_z(z,t)$ for the inhomogeneous methanol-hexane solution at temperature $\Delta T = -1.55$ K below the critical consolute temperature. (b) Time projections of kinetics of the refractive index gradient n_z for different times t after quenching (bottom curve corresponds to the equilibrium values of $n_z(z,t_e) \equiv n_z(z,\theta_e)$).

Values of n_z are determined at heights symmetric around the phase interface $z = 0$. The equilibrium state of the substance at this temperature was achieved in 14 h after system cooling ($t_e = 14$ h). Equilibration is characterized by the height dependence $n_z(z,t_e)$ corresponding to the bottom curve in Fig. 1b. It is obvious that for a transition to equilibrium, the values of n_z change the most at the level of the phase interface $z=0$. At heights $|z| \geqslant 0.3$ cm, the derivative $n_z(z)$ changes with time much more slowly. For other studied temperatures ΔT the kinetics of change of n_z is qualitatively preserved.

Using the data represented in Fig. 1 and the following relation,

$$\Delta n_z(z,t) = \underline{n}_z(z,t) - n_z(z,t_e) = \Delta n_z(z,t=0)\exp(-t/\tau), \qquad (1)$$

the relaxation times $\tau(z)$ have been calculated for $n_z(z,t)$ at different heights in the studied system. The results of these calculations are shown in Fig. 2. It is obvious that dependences $\ln(\Delta n_z(t))$ are not linear functions of time. Consequently, at a selected height in the inhomogeneous system, the equilibration kinetics is characterized not by a single relaxation time $\tau(z)$, but by a spectrum of relaxation times $\tau_i(z_j)$. This is due to the fact that during transition of a system to its equilibrium state, the relaxation properties of any individual substance layer certainly depend on the solution density and concentration at this height. Both of these substance characteristics are changing continuously with time while the system approaches equilibrium. It should be also noted that equilibration kinetics at a certain height z_i is likewise dependent on the relaxation properties of the rest of liquid layers involved in mass transport, while system goes to its equilibrium state.

As can be also seen from Fig. 2, the average relaxation times $\overline{\tau(z)} = [\ln(n_z(z, t_1)) - \ln(n_z(z, t_2))]/[t_2 - t_1]$ at all heights z decrease monotonically when nearing the phase interface $z \to 0$. Here $t_1 = 3$ h, and $t_2 = 14$ h.

It is obvious (Fig. 2) that the curvature of the dependences of $\ln(\Delta n_z(z, t))$ becomes more pronounced with time. This is evidence of a decrease of the RIG relaxation time (determined by the slope of the tangent to the curve $\ln(\Delta n_z(z, t))$) in the course of the transition to the equilibrium

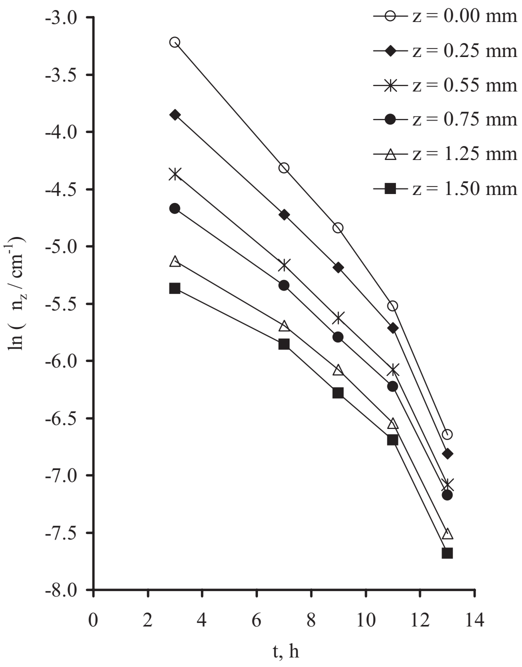

Fig. 2. Equilibration kinetics of n_z for the inhomogeneous methanol–hexane solution at different heights at a temperature below the critical temperature $[\Delta T = -1.55\ \mathrm{K}]$.

state. That is, the equilibration process is accelerated when the system approaches an equilibrium state. Such behavior of $\tau(z, t)$ is caused by the fact that the solution concentration and density depart from their critical values at all heights z at temperatures $T < T_c$ when the system approaches an equilibrium state.

3.2. Nonequilibrium Scaling Function

The experimental data $n_z(z, t)$ of equilibration kinetics of the solution were used to develop a dynamic scaling equation of state for a substance under gravity close to the critical point. Analysis of the height and time dependences of the RIG or concentration gradient $n_z \sim c_z(z, t)$ has allowed the assumption that the equilibrium properties of a substance for different temperatures $\theta = |T - T_c|/T_c$ correspond to these nonequilibrium characteristics of the solution at different times t.

This suggestion follows qualitatively from the same time behavior of nonequilibrium values of $n_z(z, t) \sim c_z \sim \rho_z$ (Fig. 1), and temperature dependences of equilibrium values $n_z(z, \theta)$ and scattered light intensity $I(z, \theta) \sim \rho_\mu(z, \theta)$ [19, 20]. An analysis of the data has showed that a value $n_z(z, t)$ at the level $z = 0$ decreases by a power relation $n_z(z = 0, t) \sim t^{-x}$ with time t (Here $x = 0.8$.). Far from this height, ($z \geqslant 0.3$ cm), the value n_z changes much more weakly with time t. The temperature dependences of the equilibrium values of the derivatives $n_z(\theta) \sim \rho_z(\theta) \sim \theta^{-\gamma}$ and scattered light intensity $I \sim \rho_\mu(z = 0, \theta) \sim \theta^{-\gamma}$ [19, 20] are qualitatively the same as the time behavior of nonequilibrium values n_z (Here $\gamma \approx 5/4$ [1].).

Proceeding from these observations for the case $n_z(z, t_i) = n_z(z, \theta_i)$, it is possible to propose the following relation between the temperature of equilibrium $n_z(z, \theta_i)$ and the time t_i of nonequilibrium $n_z(z, t_i)$:

$$\frac{n_z(z=0, t_i)}{n_z(z=0, t_e)} = \left(\frac{t_i}{t_e}\right)^{-x} = \frac{n_z(z=0, \theta_i)}{n_z(z=0, \theta_e)} = \left(\frac{\theta_i}{\theta_e}\right)^{-\gamma}. \tag{2}$$

Here $n_z(z = 0, t_e) \equiv n_z(z = 0, \theta_e)$ is the experimentally measured equilibrium value of the RIG at the temperature $\Delta T = -1.55$ K ($\theta_e = \Delta T/T_c = 5.05 \times 10^{-3}$), for which the equilibration time is $t_e = 14$ h. From Eq. (2) the relation between t_i and θ_i follows:

$$\theta_i(t_i) = \frac{\theta_e}{t_e^{x/y}} t_i^{x/y}. \tag{3}$$

From the data shown it follows that with $\gamma \approx 5/4$ [1], the exponent $n = x/\gamma \approx 0.6 \approx 1/(\beta\delta)$ (since $\beta \approx 1/3$ and $\delta = 1 + \gamma/\beta \approx 4.75$ [1]). Thus, the relation between time t_i and equilibrium temperature θ_i can be written as follows: $t_i \sim \theta_i^{\beta\delta}$.

Given this, on the basis of the observed data (Fig. 1) a dynamic equation of state was studied for the inhomogeneous liquid near the phase interface at temperatures $T < T_c$. The dynamic equation of state for the supercritical region of temperatures $T > T_c$ was studied earlier [15]. Proceeding from Refs. 1 and 9, it can be written as follows:

$$n_z \sim c_z = \theta^{-\gamma} f_1\left(\frac{z}{\theta^{\beta\delta}}\right) = t^{*\ \ -\gamma/\beta\delta} f_2\left(\frac{z}{t^*}\right). \tag{4}$$

Here f_1 and f_2 are scaling functions of the scaling arguments $z_1^* = z/\theta^{\beta\delta}$ and $z_2^* = z/t^*$, respectively; $t^* = \frac{t}{t_e}$. This scaling function $f_2(z/t^*)$ is shown in Fig. 3. It is determined by using the data for $n_z(z, t) \sim c_z(z, t)$ (Fig. 1) in the range of heights $z \approx 0$ to 0.2 cm. This range of heights was used, because it is at these small heights that the concentration of the solution $\Delta c = (c - c_c)/c_c$ is much less than 1 (i.e., $\Delta c = 0$ to 0.3). It is for such small concentrations that the Ginzburg criterion [21] is valid. Calculations of concentrations were made using the Lorentz–Lorenz formula for binary solutions, as in other studies [8, 15]. Thus, for such small concentrations

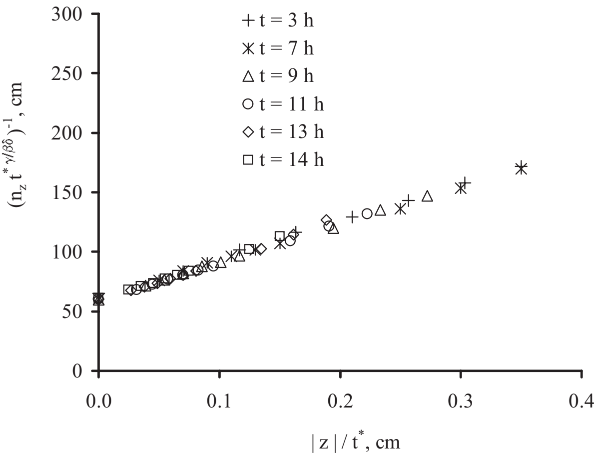

Fig. 3. Scaling function close to the phase interface of the inhomogeneous nonequilibrium methanol–hexane solution under gravity in the concentration range $\Delta c \ll 1$.

of the methanol-hexane solution, the three-dimensional surface $n_z(z, t) \sim c_z(z, t)$ (Fig. 1a) shrinks to a single line $f_2(z_2^*)$ (Fig. 3) of the scaling argument z_2^*:

$$f_2^{-1}(z_2^*) = \sum_{n=0}^{\infty} A_n z_2^{*n} = \mathrm{A}_0 + \mathrm{A}_1 \, z/t^* + \cdots \tag{5}$$

Here $A_0 = (58 \pm 3)$ cm; $A_1 = (310 \pm 20)$. The valid region for this scaling equation is marked by a line in Fig. 1a, which limits the concentrations to $\Delta c \leqslant 0.3$. Beyond these boundaries, where $\Delta c > (0.4 \text{ to } 0.8) \approx 1$, the order parameter is no longer small, and the Ginsburg criterion [21] can be violated. In this case, the inhomogeneous system is not within the fluctuation range and cannot be described by the scaling Eq. (4) of the fluctuation theory of phase transitions [1].

4. CONCLUSIONS

An analysis of the experimental investigations carried out here shows that the relaxation properties of a system at different fixed heights z are determined not by a single relaxation time $\tau(z)$, but by a spectrum of relaxation times $\sum \tau_i(z_j, t)$. The average relaxation time $\overline{\tau(z)}$ decreases when nearing the phase interface ($z \to 0$). The relaxation time $\tau(z, t)$ at any height z decreases as the system approaches an equilibrium state.

It has been shown that the equilibration process in an inhomogeneous nonequilibrium system under gravity for small concentrations $\Delta c = 0$ to 0.3 can be described by a dynamic scaling equation of state $c_z = t^{* \, -\gamma/\beta\delta} f_2 \left(\frac{z}{t^*}\right)$. This conclusion is confirmed by analogous results in another study [15].

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