RELAXATION TIMES OF NONHOMOGENEOUS LIQUIDS NEAR THE CRITICAL POINT IN A GRAVITATIONAL FIELD

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On the basis of the fluctuation theory of phase transitions and the gravitational effect theory, the dependences of the relaxation times of density and density gradient in nonhomogeneous liquids near the critical temperature on the altitude in a gravitational field have been calculated. The nonmonotonous dependences of the values concerned on the altitude for nonhomogeneous liquids in the critical state have been explained. The results obtained are confirmed by experimental data on the equilibration kinetics in nonhomogeneous systems near a critical point (CP).

Earlier, nonmonotonous dependences of the relaxation times for various optical and thermodynamic characteristics on both the temperature and altitude in a gravitational field have been revealed for nonhomogeneous liquids near a CP [1—3]. For example, it was shown in [2, 3] that, when approaching the altitude level $z = 0$ in liquids with critical density or concentration, the relaxation times of density, concentration, and compressibility decrease rather than increase, as was predicted in [4]. The results obtained found their theoretical substantiation in [5, 6] in the framework of the fluctuation theory of phase transitions [4] and the gravitational effect theory [7] for the case of the thermodynamic direction which is characterized by the inequality

$$\Delta\mu = \frac{\mu-\mu_c}{\mu_c} = h\frac{d\mu}{dh} \ll \theta^{\beta\delta}.$$

Here, $\theta = \frac{T-T_c}{T_c}$, $h = \frac{\rho_c g z}{p_c}$, μ_c, p_c, T_c, and ρ_c are the critical values for the chemical potential, pressure, temperature, and density of the system, respectively, g is a free fall acceleration, z is an altitude reckoned from the critical isochore level, and β and δ are critical indices [4].

In this work, the relaxation features of nonhomogeneous liquids in the gravitational field are investigated in the vicinity of the thermodynamic direction of the critical isotherm, where the inverse inequality is valid: $\Delta\mu \gg \theta^{\beta\delta}$.

The relaxation times of density, density gradient, and compressibility $\frac{d\rho}{d\mu} \sim \frac{d\rho}{dh}$ are calculated, as earlier [5, 6], on the basis of the relations

$$\delta\rho(z,t) = \rho(z,t) - \rho(z,t_{\mathrm{eq}}) = \delta\rho(z,t=0)\exp\left(-\Delta t/\tau_1\right), \tag{1}$$

$$\delta\frac{d\rho}{dh}(z,t) = \frac{d\rho}{dh}(z,t) - \frac{d\rho}{dh}(z,t_{\mathrm{eq}}) =$$

$$= \delta\frac{d\rho}{dh}(z,t=0)\exp\left(-\Delta t/\tau_2\right). \tag{2}$$

Here, t_{eq} is the equilibration time of the system. With these relations, the altitude and temporal dependences of the density $\Delta\rho(z,\Delta t) = \frac{dF_{\mathrm{fl}}}{d\mu}$ and the density gradient $\frac{d\rho}{d\mu} \sim \frac{d\rho}{dh} = \frac{d^2F_{\mathrm{fl}}}{d\mu^2}$ are determined with regard for the form of the fluctuation part of the thermodynamic potential $F_{\mathrm{fl}} = C_0R_c^{-3}$ [4]. In the case $\Delta\mu \gg \theta^{\beta\delta}$, the correlation length of the system is

$$R_c^{-1} = \Delta\mu^{\xi}\sum_{n=0}^{\infty} d_n z^{*n}. \tag{3}$$

Here, $z^* = \frac{\theta}{\Delta\mu^{1/\beta\delta}}$ is a scale variable, $\beta\delta = \frac{\nu}{\xi}$, and ν and ξ are the critical indices of the correlation length [4].

On the basis of Eqs. (1)—(3), let us consider the kinetics of establishing the equilibrium gravitational effect, provided that the equilibrium system is heated fast (during 10—15 min [1]) from the initial temperature $\theta_1 = 0$ to the final one $\theta_2 > 0$. As a result, a slow change of the altitude profile of the derivative $\frac{d\rho}{dz}(z,t)$ will begin to occur towards the equilibrium distribution $\frac{d\rho}{dz}(z,\theta_2)$. In so doing, the system will pass different states corresponding to temperatures θ within the interval from 0 to θ_2, at different times Δt's [1]. Earlier [1, 5], a relation between the equilibration time t_{eq} in a nonhomogeneous system, situated in the gravitational field, and the temperature was proposed in the form

$$\Delta t = t_{\mathrm{eq}}(\theta_2) - t_{\mathrm{eq}}(\theta_1 = 0) = k\theta_2^{\beta\delta-\nu} \approx k\theta_2. \tag{4}$$

Here, k is a constant and $\beta\delta - \nu \approx 1$ [4].

Then, making use of (1)—(4), one can obtain the following relations which determine the relaxation times for the density, compressibility, and density gradient of a nonhomogeneous liquid in the gravitational field to the relevant equilibrium values:

$$\tau(\rho(z)) = \Delta t \left[1 + \frac{A_2}{A_1}(\theta_2 - \theta)h^{-\beta\delta}\right], \tag{5}$$

$$\tau\left(\frac{d\rho}{d\mu} \sim \frac{d\rho}{dh}\right) = \Delta t \left[1 + \frac{B_2}{B_1}(\theta_2 - \theta)h^{-\beta\delta}\right]. \tag{6}$$

Here, $A_1 = 3C(3\xi - 1/\beta\delta)d_1 d_0^2$, $A_2 = 3C(3\xi - 2/\beta\delta)d_2 d_0^2$, $B_1 = 3C\xi(3\xi - 1/\beta\delta)(3\xi - 1/\beta\delta - 1)d_1 d_0^2$, $B_2 = 3C\xi(3\xi - 2/\beta\delta)(3\xi - 2/\beta\delta - 1)d_2 d_0^2$; C_0, d_0, d_1, d_2, and ξ are parameters of relation (3).

As is seen from (5) and (6), the relaxation times of those characteristics of a nonhomogeneous liquid are functions of both the temperature θ and altitude h. Eqs. (5) and (6) lead to an important conclusion that the relaxation times in nonhomogeneous systems in the gravitational field do not decrease with moving off from the critical temperature ($\Delta t \sim \theta$) [4], but, on the contrary, increase. This conclusion was experimentally confirmed in [1] and other papers.

To analyze the dependences of τ on the altitude [Eqs. (5) and (6)], it is necessary to know the signs of the coefficients A_n and B_n. Therefore, one should consider experimental data on the altitude and temperature dependences of the scattered light intensity $I(z,\theta) \sim \frac{d\rho}{d\mu}(z,\theta)$ [7], correlation length [8], and substance density [9] near the CP. An analysis of those data for the altitudes z, where the inequality $\Delta\mu \gg \theta^{\beta\delta}$ is valid, makes it possible to find the coefficient signs: $A_1 < 0$, $A_2 < 0$, $B_1 > 0$, $B_2 > 0$ ($A_1 A_2 > 0$, and $B_1 B_2 > 0$). Then it follows from (5) and (6) that the relaxation time decreases with moving away from the critical isochore level. This conclusion is also confirmed by experimental data in [2, 3] for altitudes far from the critical isochore level.

But for altitudes close to $z = 0$, i.e. if $\Delta\mu \ll \theta^{\beta\delta}$, the relaxation times were shown, both experimentally [2, 3] and theoretically [5, 6], to increase rather than decrease, with moving off from the critical isochore level. Therefore, our results together with the results of [5, 6] evidence for that the extrema of the relaxation times of the density and compressibility of a nonhomogeneous liquid in a gravitational field have to occur in the range of the altitudes z, where the condition $\Delta\mu = h\frac{d\mu}{dh} \sim \theta^{\beta\delta}$ is fulfilled. In other words, those calculations show the nonmonotonous dependences for the relaxation times of the density, density gradient, and compressibility of a nonhomogeneous liquid in a gravitational field near the CP.

Earlier [3, 10], it was shown that the altitudes z_0, where the nonequilibrium isotherms $\frac{d\rho}{d\mu} \sim \frac{d\rho}{dh}(z,t)$ cross one another, when the system approaches the equilibrium state, correspond to that level of extrema of the relaxation times $\tau(z)$. The substance properties at those points of extremal relaxation times [3, 10] combine simultaneously the substance properties along three critical directions: critical isochore, critical isotherm, and phase interface.

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ЧАСИ РЕЛАКСАЦІЇ НЕОДНОРІДНИХ РІДИН В ГРАВІТАЦІЙНОМУ ПОЛІ ПОБЛИЗУ КРИТИЧНОЇ ТЕМПЕРАТУРИ

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Резюме

На основі флуктуаційної теорії фазових переходів і теорії гравітаційного ефекту проведено розрахунки висотної залежності часів релаксації густини і градієнта густини до своїх рівноважних значень у неоднорідній речовині в гравітаційному полі поблизу критичної температури. Обгрунтовано немонотонну висотну залежність вказаних характеристик неоднорідної рідини в критичному стані. Одержані результати підтверджуються експериментальними даними з кінетики встановлення рівноваги в неоднорідних системах поблизу критичної точки (КТ).