

# Universality of transport and equilibrium thermodynamic properties of liquid mixtures in the critical phase-separation region

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Universal functions of the scale argument  $z = \tau/\Delta x^{1/\beta}$  for dynamic and static properties of binary phase-separating mixtures over a broad range of reduced temperatures  $\tau$  and concentrations  $\Delta x$  are obtained for the first time.

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The hypothesis of the universality of critical phenomena<sup>1-3</sup> generalizes the law of corresponding states and assumes that any physical quantity  $X(x, T)$ , whose asymptotic behavior near the critical point is determined by the critical index  $\varphi$ , is described in the hydrodynamic approximation by the following expression:

$$\frac{X(x, T)}{X_0 \Delta x^{\varphi/\beta} z_0^\varphi} = f_X\left(\frac{z + z_0}{z_0}\right), \quad (1)$$

where  $f_X(z)$  is a universal function of the scale argument  $z = \tau/\Delta x^{1/\beta}$ ,  $\beta$  is the critical index of the coexistence curve, and  $X_0$  is the critical amplitude. The curve  $z = -z_0$  is the coexistence curve.

Attempts to reveal experimentally the universal relations for the thermodynamic and kinetic properties were made in single-component systems.<sup>3,4</sup>

In this paper, we demonstrate for the first time that Eq. (1) can be used to describe the thermodynamic and diffusion properties of two, binary, phase-separating systems: nitrobenzene-heptane (I) and nitrobenzene-decane (II). A relationship between the universal functions  $f_S(z)$  and  $f_D(z)$ , which describe the behavior of the generalized susceptibility  $(\partial\mu_i/\partial x_i)_{p,T}$ , where  $\mu_i$  is the chemical potential of the  $i$ th component of the

mixture, and the coefficient of mutual diffusion  $D$ , respectively, is obtained in the Ornstein-Zernike approximation.

The diffusion coefficient was determined from the beat spectra of the scattered radiation using heterodyne detection.<sup>5</sup> Information on  $(\partial\mu_i/\partial x_i)_{p,T}$  was obtained from the measurements of the relative scattering intensity  $\mathcal{I}$ . The investigations were carried out in a single-phase region for seven concentrations of the systems I and II in the range  $10^{-4} \lesssim \tau \lesssim 10^{-1}$ , where  $\tau = (T - T_s)/T_c$ ,  $T_s$  is the phase-separation temperature,  $T_c$  is the critical temperature, and  $2 \times 10^{-4} \lesssim \Delta x \lesssim 0.5$ , where  $\Delta x = (x_1 - x_{1,s})/x_{1,s}$ . The critical concentrations of the systems  $x_{1,c}$  were determined previously<sup>6</sup> to within 0.01 mass %. The errors in the measurements of the diffusion coefficient and the relative scattering intensity did not exceed 3–5 and 10%, respectively.

For concentrations close to the critical value, it was found that the temperature dependences of the diffusion coefficient and scattering intensity have the form

$$D(\tau) = D_0 \tau^{\nu^*}, \quad \mathcal{I}^{-1} = \mathcal{I}_0^{-1} \tau^\gamma \quad (2)$$

with critical indices  $\gamma = 1.26 \pm 0.03$  and  $\nu^* = 0.63 \pm 0.02$ . The values  $\beta = 0.330 \pm 0.005$  and  $z_0 = 0.293 \pm 0.017$  were obtained for the coexistence curves.

It is evident from Fig. 1, in which the universal functions (1) are presented for  $\mathcal{I}^{-1} \sim (\partial\mu_i/\partial x_i)_{p,T}$ , that the experimental points lie on a single universal curve over a wide range of the argument  $(z + z_0)/z_0$ .

It may be assumed that the complex

$$\frac{D(x, T) \sqrt{x_1/x_{1,c}}}{D_0 \Delta x^{\nu^*/\beta} z_0^{\nu^*}},$$

which is comprised of the experimental data for the diffusion coefficient, is also a universal function.<sup>7</sup> This is confirmed by the graph in Fig. 2, where the experimental data on a dependence of the form (1) for  $D(x, T)$  lie on a universal curve. The empirical factor  $\sqrt{x_1/x_{1,c}}$  is introduced in order to exclude asymmetry in the measured quantities relative to the critical point.

The function  $D(x, T)$  can be approximated by a sum of power-law functions

$$D(x, T) \sqrt{\frac{x_1}{x_{1,c}}} = D_0 \tau^{\nu^*} + D_1 \Delta x^{\nu^*/\beta}, \quad (3)$$

where  $D_0$  and  $D_1$  are the critical amplitudes. After incorporating (1) and (3), the function  $f_D(z)$  takes the form

$$f_D\left(\frac{z + z_0}{z_0}\right) = \frac{D_1}{z_0^{\nu^*} D_0} + \left(\frac{z + z_0}{z_0}\right)^{\nu^*}, \quad (4)$$

where  $D_1/z_0^{\nu^*} = D'_0$  characterizes the temperature behavior of the diffusion coefficient along the coexistence curve at  $T < T_c$ . The theory does not predict the magnitude of the ratio of critical amplitudes  $D'_0/D_0$ , but its universality follows from the universality of  $f_D(z)$ . For the systems investigated, it was found that  $D'_0/D_0 = 2.1 \pm 0.4$ .

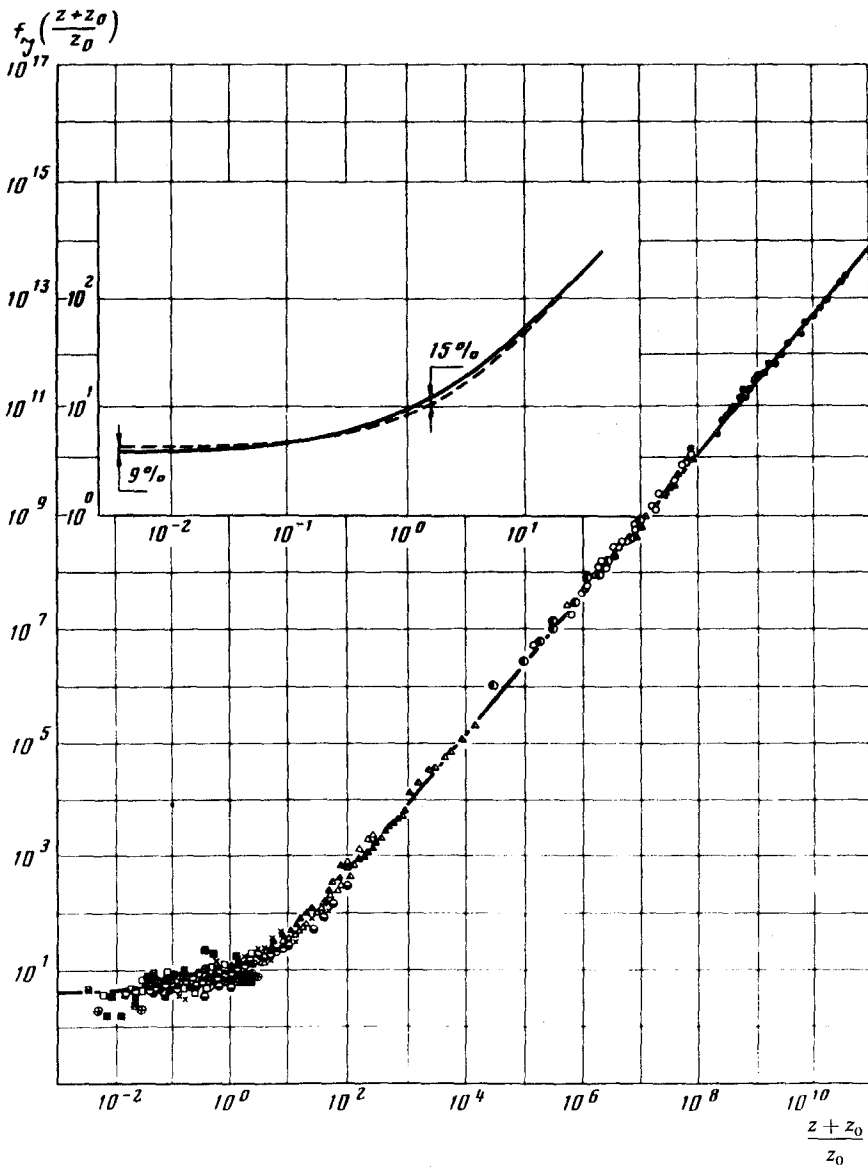


FIG. 1. The scale function  $f_T(z)$  for  $(\partial\mu_i/\partial x_i)_{p,T}$  for the following concentrations of system I: ●—52.11; ○—52.02; ●—52.24; ●—44.58; ●—36.05; ●—60.25; ⊕—78.25; and, for system II: ▲—53.71; △—50.92; ▲—55.72; X—43.96; □—71.96; ▲—60.13; ⊞—33.07, expressed in wt. % of nitrobenzene.

The fluctuation nature of the processes occurring near the critical point accounts for the fact that the static and dynamic properties depend only on the correlation radius  $r_c$ .<sup>1</sup> In the vicinity of the critical point,<sup>8</sup>

$$D \sim r_c^{-1} . \quad (5)$$

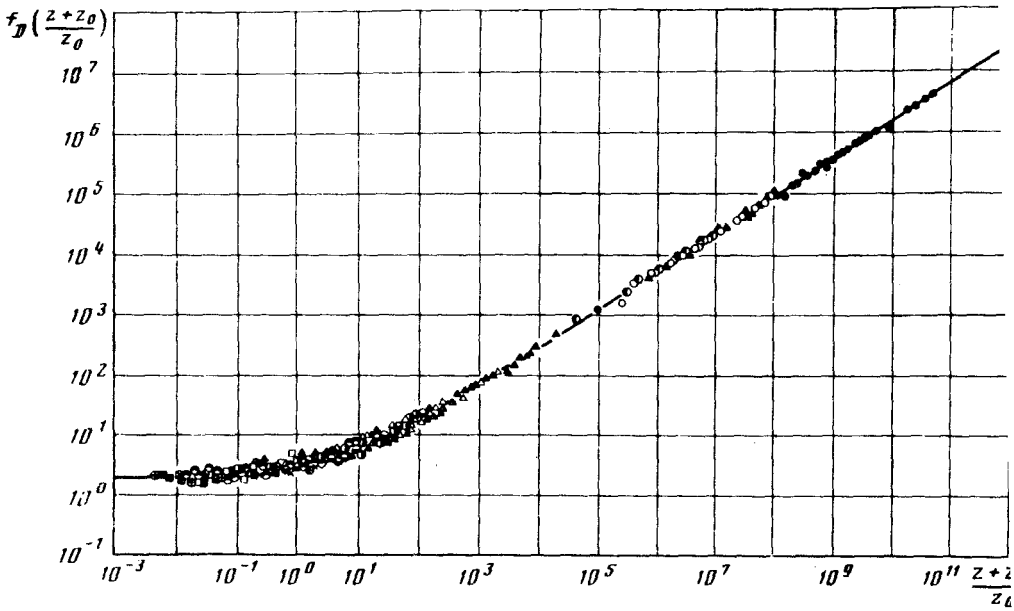


FIG. 2. The scale function  $f_D(z)$  for the diffusion coefficient  $D$ . The concentrations of the systems are indicated in the caption to Fig. 1.

In the Ornstein-Zernike approximation for separating systems,<sup>9</sup> we have

$$\left( \frac{\partial \mu_i}{\partial x_i} \right)_{p, T} \sim r_c^{-2}. \quad (6)$$

It follows from this expression that  $\nu^* = \nu = \gamma/2$ , where  $\nu$  is the critical exponent for the correlation radius. This relation is satisfied for the values of  $\nu^*$  and  $\gamma$  obtained by us. Assuming that expressions (5) and (6) are valid at some distance from the critical point of phase separation and keeping in mind (4), we obtain

$$f_D(z) = f_D^2(z) = \left[ 2,1 + \left( \frac{z + z_0}{z_0} \right)^{\nu^*} \right]^2. \quad (7)$$

This dependence is represented in Fig. 1 by the solid curve. This curve satisfactorily agrees with the experimental points over the entire temperature range presented. The inset in Fig. 1 shows that dependence (7) (solid curve) is in satisfactory agreement with the calculations based on the linear model of the equation of state (dashed curve).<sup>3</sup>

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