Nature of Crossover between Ising-like and Mean-Field Critical Behavior in Fluids and Fluid Mixtures

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An analysis of experimental data for the susceptibility of fluids and of liquid mixtures in the critical region has been performed to elucidate the character of the nonasymptotic critical behavior. While fluids and fluid mixtures exhibit an ultimate crossover to Ising-like asymptotic behavior, the effective susceptibility exponent γ_{eff} approaches the universal value $\gamma \simeq 1.24$ either from *above* (*A*) or from *below* (*B*). We conclude that simple fluids belong to type *B*, whereas more complex systems may belong to type *A* and show a sharper nonmonotonic crossover from mean-field to Ising-like behavior.

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It has been well established that isotropic fluids belong to the three-dimensional (3D) anisotropic Ising model (equivalent to the 3D lattice gas) universality class. Specifically, the susceptibility χ (isothermal compressibility in one-component fluids and osmotic compressibility in liquid mixtures) in zero field in the one-phase region asymptotically close to the critical point behaves as

$$\chi = \Gamma_0 \tau^{-\gamma}(1 + \Gamma_1 \tau^{\Delta} + \Gamma_2 \tau^{2\Delta} + a_1 \tau + \cdots), \quad (1)$$

where $\tau = (T - T_c)/T$, T is the temperature, T_c the critical temperature, and γ and Δ are universal critical exponents, $\gamma = 1.239 \pm 0.002$, $\Delta = 0.52 \pm 0.03$ [1]; $\Gamma_0, \Gamma_1, \Gamma_2, a_1, \ldots$ are system-dependent amplitudes. Expansion (1) is called the Wegner series [2]. Since real fluids do not obey the symmetry of the lattice gas, the susceptibility χ also contains terms $\sim\tau^{-\alpha}(\alpha \simeq 0.11)$ [3] and $\sim\tau^{-\gamma+\Delta_a}$ ($\Delta_a \simeq 1.32$) [4] which are, however, weaker than the second Wegner correction term $\sim\tau^{-\gamma+2\Delta}$. In a wider region around the critical point the susceptibility of fluids may exhibit crossover from universal Ising-like behavior to mean-field (van der Waals–like) behavior [5–9]. If one defines an effective susceptibility exponent γ_{eff} as $\gamma_{\text{eff}} = -\tau\, d\ln\chi/d\tau$ [5], a positive value of Γ_1 means that γ_{eff} approaches the asymptotic value $\gamma \simeq 1.24$ from below providing a smooth crossover from the mean-field value $\gamma = 1$. However, there are several indications that such a simple monotonic crossover with positive Γ_1 is not universal. The possibility of negative corrections follows from field-theoretical renormalization-group approaches [10]. Liu and Fisher [11] concluded that for the nearest neighbor sc, bcc, and fcc 3D Ising lattices the first correction amplitudes for the susceptibility, correlation length, specific heat, and order parameter are *negative,* so that γ_{eff} asymptotically approaches $\gamma \simeq 1.24$ from *above.* Moreover, negative leading corrections have been reported for some aqueous solutions near the consolute critical point [12,13], whereas for other fluid systems [14,15] the corrections are positive. Recently, Narayanan and Pitzer have performed an extensive study of the near-critical turbidity of several nonaqueous ionic solutions [16,17]. They fitted the susceptibility and the correlation length, extracted from the turbidity data, by the Wegner expansion (1), and found that the character of the nonasymptotic behavior is strongly affected by the dielectric constant of a solvent. In particular, in their latest paper [17] they indicated possible negative Γ_1 at least for two of the systems investigated. With negative Γ_1 the crossover of γ_{eff} from $\gamma_1 = 1$ to $\gamma \simeq 1.24$, if such a crossover exists, would be nonmonotonic and sharper than usual.

The crossover between the asymptotic and regular regimes reflects a competition between universality caused by long-range fluctuations and nonuniversality associated with the microscopic structure of matter. Therefore, an important question arises: Does there exist any regularity in the character of the critical crossover behavior in fluids and fluid mixtures? One should note that extraction of the actual crossover from experimental data is a very delicate task. Specifically, the susceptibility of fluids is never measured directly. It can be extracted most accurately from light scattering or from turbidity experiments. The interpretation of such data requires reliable information on the correlation function which itself exhibits crossover behavior. Hence, the fit appears to be essentially nonlinear. Moreover, the actual crossover behavior may be masked by multiple scattering, gravity effects, and impurities close to the critical point and by noncritical (background) contributions away from the critical point. That is why, in spite of a large number of experimental studies, there are only a few with a precision sufficient to recover the actual nonasymptotic critical behavior. We note that as the convergence of the Wegner series is in doubt, a fit by the expansion (1) is dangerous, and an explicit crossover equation for the susceptibility is needed to determine the values of the correction amplitudes.

To fit experimental susceptibility data we have used a crossover solution for the free energy based on

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renormalization-group matching [18] as implemented to fluids by Chen *et al.* [7]. For the inverse susceptibility χ^{-1} in zero field in the one-phase region in appropriate dimensionless units this crossover solution implies

$$\chi^{-1} = tY^{(\gamma-1)/\Delta}\Big(1 + \frac{u^*}{2\omega}\Big\{2\Big(\frac{\kappa}{\Lambda}\Big)^2\Big[1 + \Big(\frac{\Lambda}{\kappa}\Big)^2\Big] \times \Big[\frac{1}{\omega} + \frac{(1-\bar{u})Y}{1-(1-\bar{u})Y}\Big] - \frac{2-\nu^{-1}}{\omega}\Big\}^{-1}\Big). \quad (2)$$

The crossover function Y is defined by

$$1 - [1-\bar{u}]Y = \bar{u}\Big[1 + \Big(\frac{\Lambda}{\kappa}\Big)^2\Big]^{1/2} Y^{1/\omega},$$

$$\kappa^2 = tY^{(2\nu-1)/\Delta}, \qquad t = c_t\tau = c_t\frac{T-T_c}{T}, \quad (3)$$

where $\bar{u} = u/u^*\Lambda$ with u proportional to the coupling constant in the Landau-Ginzburg-Wilson Hamiltonian and u^* the fixed-point value of the coupling constant [6]. For 3D Ising-like systems $u^* \simeq 0.472$ [19]; $\nu \simeq 0.63$ and $\omega = \Delta/\nu \simeq 0.8$ are universal critical exponents, c_t is a system-dependent amplitude. In the mean-field approximation $\Lambda = c_t^{1/2} q_D \bar{\xi}_0$ [7] with q_D the actual cutoff wave number, characterizing a discrete structure of matter with spacing q_D^{-1}. Asymptotically close to the critical point ($\Lambda/\kappa \gg 1$) the crossover susceptibility (2) reduces to the Wegner expansion (1) with

$$\Gamma_1 = g_1 N_{\mathrm{Gi}}^{-\Delta}(1-\bar{u}), \quad (4)$$

where $g_1 \simeq 0.106$ is universal number. The crossover parameter

$$N_{\mathrm{Gi}} = \Big(\frac{\gamma - 1 - \nu u^*/2}{\Delta}\Big)^2 c_t^{-1}(\bar{u}\Lambda)^2 \simeq 0.0314 c_t^{-1}(\bar{u}\Lambda)^2 \simeq 0.141 c_t^{-1} u^2 \quad (5)$$

plays in this crossover solution, in the limit $\bar{u} \to 0 (\Lambda \to \infty)$, the same role of a *crossover scale* as the so-called Ginzburg number [20] in the ϵ-expansion solution obtained by Belyakov and Kiselev [8,9]. This is why we retain the name "Ginzburg number" for this parameter. It is important to note that N_{Gi} is always positive, whereas Γ_1 changes its sign with $\bar{u} > 1$. Far away from the critical point the susceptibility (2) approaches the mean-field limit ($\Lambda/\kappa \ll 1$) : $Y = 1$, $\chi^{-1} = t$. The behavior of the effective susceptibility exponent γ_{eff} according to the crossover model (2) is shown in Fig. 1. One can see that for $\bar{u} > 1$ ($u > u^*\Lambda$) the crossover is sharper and γ_{eff} approaches the asymptotic value $\gamma \simeq 1.24$ from above.

To analyze the crossover behavior of the susceptibility we have used the following experimental light-scattering data: (i) intensity data near the vapor-liquid critical point of xenon obtained by Güttinger and Cannell [15], (ii) intensity data for 3-methylpentane+nitroethane (3MPNE) near the critical consolute point obtained by Chang, Burstyn, and Sengers [14] and Shanks [13], (iii) intensity and turbidity data for isobutyric acid+water (IBAW) near the critical consolute point obtained by Shanks [13], (iv) turbidity data for five nonaqueous ionic solutions of tetra-*n*-butyl ammonium picrate (TBAP): TBAP+1-dodecanol (TPDD), TBAP+1-undecanol (TPUD), TBAP+1-tridecanol (TPTD), TBAP+1,2-propanediol (TPPD), TBAP+1,4-butanediol/1-dodecanol (0.75/0.25) (TPDB) near the critical consolute points obtained by Narayanan and Pitzer [16,17].

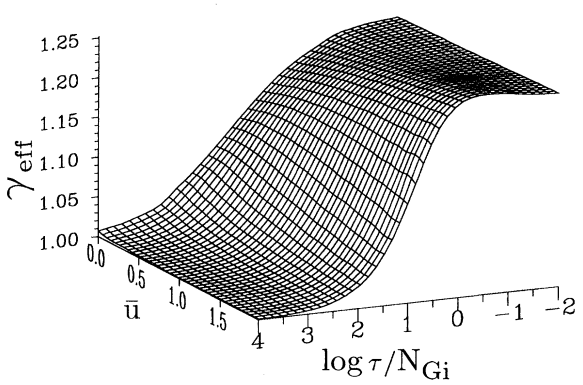

FIG. 1. Effective susceptibility exponent according to Eq. (2).

The expressions for the light scattering intensity I and turbidity τ_c have the forms

$$I = I_0 R_1(t) R_2(t) \chi(t) g(q\xi) + I^b,$$

$$\tau_c = \tau_0(T) f(y) \chi(t) + \tau_c^b,$$

where I_0 is a reference amplitude, $R_1(t)$ and $R_2(t)$ are functions accounting for turbidity and double-scattering corrections, $g(q\xi)$ is the correlation function taken in the Ornstein-Zernike approximation, $g(q\xi) = [1 + (q\xi)^2]^{-1}$ with the wave number of the scattered light (for 90°) $q = 2\sqrt{2}\,\pi n/\lambda_0$ (λ_0 is the wavelength in vacuum, n the refraction index). The function $f(y)$ is given by $f(y) = (2y^2 + 2y + 1)y^{-3}\ln(1+2y) - 2(1+y)y^{-2}$ [21] with

$$y = y_0\Big(\frac{\chi}{\Gamma_0}\Big)^{2\nu/\gamma}, \qquad y_0 = 2(2\pi n \xi_0/\lambda_0)^2,$$

$$\tau_0 = \frac{\pi^3 v_0}{\lambda_0^4 N_A}\Big(\frac{\partial n^2}{\partial x}\Big)^2.$$

ξ_0 is the amplitude of the power law $\xi_0\tau^{-\nu}$ for the correlation length ($\xi_0 \leq \bar{\xi}_0$ [9]), x the mole fraction, N_A Avogadro's number, I^b and τ_c^b are background contributions to the intensity and turbidity, respectively. I^b, τ_c^b, and ξ_0, as well as the two crossover parameters, $\bar{u}$ and $\Lambda/c_t^{1/2}$, were found by fitting, while T_c was recovered

within the accuracy of its experimental determination; Γ_1 and N_{Gi} were calculated with Eqs. (4) and (5). Since the turbidity and intensity data for the mixture of isobutyric acid and water have a comparable accuracy in the range $\tau < 7 \times 10^{-3}$, both the intensity and turbidity data were fitted jointly. To reduce effects of background contributions the range of fitting was generally restricted to $\tau < 2 \times 10^{-2}$. The range of temperatures close to the critical point was restricted to $\tau > 5 \times 10^{-6}$ for IBAW, $\tau > 10^{-5}$ for 3MPNE, and $\tau > 10^{-4}$ for xenon and nonaqueous ionic solutions.

The results are presented in Table I. The most striking result is a negative Wegner correction amplitude Γ_1 (correspondingly $\bar{u} > 1$) for the isobutyric acid+water mixture (already noticed by Shanks [13]) and for three nonaqueous ionic solutions. For 3MPNE and for two ionic systems, TPUD and TPPD, the amplitudes Γ_1 are small and difficult to be determined. We also tried to fit the experimental data with different versions of the crossover solutions. Xenon and 3MPNE can be fitted equally well with the crossover function proposed by Belyakov and Kiselev as a phenomenological generalization of the ϵ expansion [8,9] with a very similar crossover scale. In all cases a random distribution of deviations in addition to the χ^2_ν criterion served as a test of a good fit. It should be noted that we never could obtain an adequate fit for IBAW, TPDB, TPDD, and TPTD with $\bar{u} < 1$ for any crossover model.

In Fig. 2 the effective exponent γ_{eff} is presented for the four systems studied. It is clearly seen that the character of the crossover is obviously different for the systems with $\bar{u} < 1$ (simple monotonic crossover with γ_{eff} approaching $\gamma \simeq 1.24$ from below) and for the systems with $\bar{u} > 1$ (much sharper crossover with γ_{eff} approaching $\gamma \simeq 1.24$ from above). All fluids studied can be divided into two types of crossover behavior, A and B (Fig. 3). For type A γ_{eff} approaches the universal number $\gamma \simeq 1.24$ from above (negative Γ_1) and for type B from below (positive Γ_1). These two types are separated by the effective fixed point of the renormalization group theory for which $\bar{u} = 1 (u\Lambda^{-1} = u^*)$ and $\Gamma_1 = 0$ [11]. A question arises: What features of the microscopic structure drive the systems along the universal line in Fig. 3(b)?

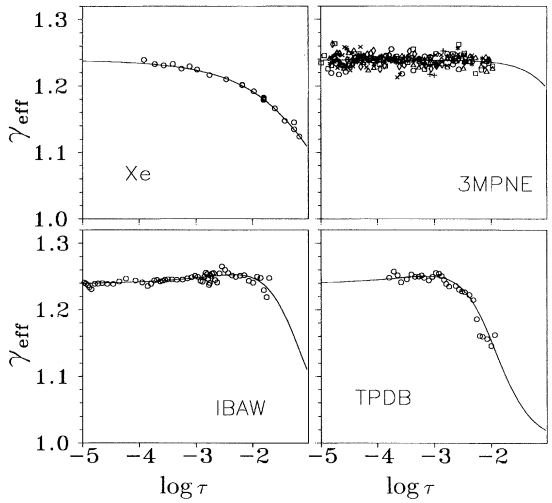

FIG. 2. Effective susceptibility exponent according to Eq. (2): xenon [15]; 3MPNE mixture: run 1 (∘), run 2 (□), run 3 (△), run 4 (∗), run 5 (◇), run 6 (×) [14], and [13] (+); isobutyric acid-water [13]; TPDB [17]. The points indicated the values deduced from the experiments with 2-point (xenon) and 5-point averaging procedure.

The crossover solution, used in this work, was successfully applied earlier to a number of simple fluids to represent thermodynamic properties in a broad region around of the critical point [7]. For all these fluids $\bar{u} < 1$, the crossover is monotonic, and the crossover temperature scale is represented by a single crossover parameter, namely, $N_{Gi}(1 - \bar{u})^{1/\Delta}$ [9]. It has not been demonstrated theoretically that the crossover function (3) is also valid for $\bar{u} > 1$ which implies $\Gamma_1 < 0$. Nevertheless, we see from Fig. 2 that the crossover function does give a good account of γ_{eff} even when $\Gamma_1 < 0$. If we adopt this solution, we may speculate that in complex fluids the crossover parameter $\Lambda/c_t^{1/2}$, which is not necessarily identified with the actual cutoff wave number q_D, may be related to the additional microscopic scale $\xi_D \sim \bar{\xi}_0 c_t^{1/2}/\Lambda$. For simple fluids $c_t^{1/2}/\Lambda \simeq 1$ and $\xi_D \simeq \bar{\xi}_0$. When $c_t^{1/2}/\Lambda \gg 1$, $\xi_D \gg \bar{\xi}_0$. The latter case is relevant to the discussion of criticality in ionic systems [22]. Nonaqueous ionic

TABLE I. Crossover parameters for different systems.

	Adjustable			Calculated	
	$\sqrt{c_t}/\Lambda$	$\bar{u}$	ξ_0 (nm)	Γ_1	N_{Gi} ($\times 10^3$)
Xenon	1.5	0.48	0.184	1.08	3.0
3MPNE	1.25	0.97	0.215	0.02	13.2
IBAW	3.2	1.50	0.361	−0.68	6.7
TPDB	7.6	1.44	0.353	−1.5	1.1
TPTD	6.6	1.09	0.360	−0.35	0.86
TPDD	6.4	1.11	0.364	−0.42	0.94

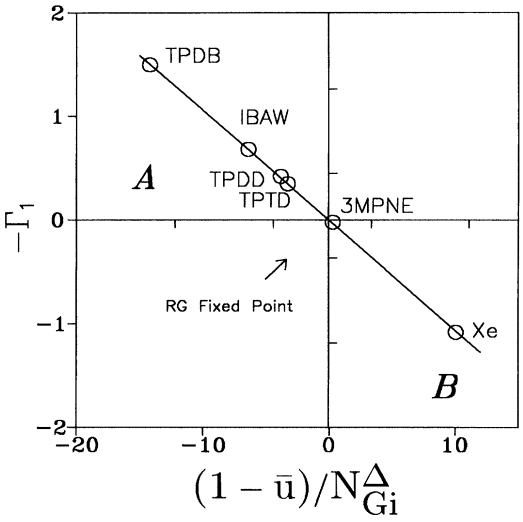

FIG. 3. The first correction amplitude of the susceptibility plotted on a universal scale in accordance with Eq. (4).

solutions are characterized by a small value of the Ginzburg number [23]. The inequality $u/u^*\Lambda > 1$ may, however, be satisfied provided that Λ is very small and ξ_D is very big. The physical origin of this scale depends on the particular microscopic structure and might reflect either supramolecular association or an additional interaction of a longer range, or both. To elucidate the connection of the additional scale with the physical properties of fluids one requires more systematic information on the crossover behavior in different classes of fluids and fluid mixtures, as well as new experiments specially designed to recover details of the crossover behavior. Ionic fluids, in particular, metal-ammonia solutions in which a sharp crossover and mesoscopic-range order [24] have been reported, and polymer systems [25] are promising candidates for such a study.

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