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Comments on Universality of Critical Exponents for Fluid Systems

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Critical exponents (γ, ν, β, and μ) of one-component fluid systems from recent experiments show agreement with the universality concept and the critical exponent relations. Variations in the magnitude of exponents from different systems are well within the limits of error of present-day techniques. Thus, it is within reason to expect that observable deviations from universality could come from more complex fluid mixtures, where such a concept may break down, even though, based on published literature values, the prospects remain very small.

KEY WORDS: Critical phenomena; phase transitions; properties of fluids.

The scaling hypothesis, as first proposed by Widom,[1] has been very successful in summarizing the *asymptotic* formulation of the temperature dependence of thermodynamic properties near a critical point. For the critical exponents γ, ν, β, and μ, we have $K_T = f\epsilon^{-\gamma}$, $\xi = \xi_0\epsilon^{-\nu}$, $\Delta\rho = B\epsilon^{\beta}$, and $\sigma = \sigma_0\epsilon^{\mu}$, where K_T, ξ, and σ are the isothermal compressibility, the long-range correlation length, and the interfacial tension, respectively; $\Delta\rho = |\rho - \rho_c|/\rho_c$ and $\epsilon = |T - T_c|/T_c$; f, ξ_0, B, and σ_0 are the corresponding preexponential factors, being strongly coupled with the critical exponents. Various scaling relations exist among the four pairs of critical exponents[2] ($d\nu$, $\gamma + 2\beta$, $\mu + \nu$, and $2 - \alpha$) under consideration: $d\nu = \mu + \nu = \gamma + 2\beta = 2 - \alpha$,

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Table I. Experimental Values of Critical Exponents for Fluid Systems

System	Critical exponents γ	ν	β	μ
CO_2	1.24 ± 0.09[3]	<0.67[3]	0.350[4]	1.253[5]
	$1.26 \pm ?$[4]	--	—	—
	1.17 ± 0.02[6]	0.60 ± 0.03[12]	--	1.281[16]
	1.219 ± 0.01[7]	0.633 ± 0.01[7]	---	---
Xe	1.21 ± 0.03[8]	0.58 ± 0.05[8]	0.350[4]	1.287[17]
	$1.26 \pm ?$[4]	$0.60 \pm ?$[13]	—	—
SF_6	1.225 ± 0.02[9]	0.67 ± 0.07[9]	0.333[15]	1.30[18]
	1.235 ± 0.015[20]	$0.67 \pm ?$[14]	—	—
		0.61 ± 0.04[21]	—	—
Ar	1.20 ± 0.05[10]	0.61 ± 0.02[10]	0.35[10]	1.281[19]
$CClF_3$	1.275 ± 0.04[11]	—	—	1.320[16]
Estimated most probable value for fluid systems				
All fluid systems	1.22 ± 0.02	0.63 ± 0.02	0.34 ± 0.02	1.28 ± 0.06[2]

where d is the dimensionality of the system and α is the critical exponent representing the divergence in the constant-volume specific heat c_V.

Table I lists the experimentally determined values of critical exponents γ, ν, β, and μ for one-component fluid systems from recent studies.[2–21] The uncertainties, being dependent upon the methods of data analysis as well as the quality of the experimentalists, require further reevaluation.[22] Existing experimental data suggest that the most probable values of γ, ν, β, and μ are 1.22 ± 0.02, 0.63 ± 0.02, 0.34 ± 0.02, and 1.28 ± 0.06, respectively. These values were obtained purely on experimental considerations. For example, only good, trustworthy experiments were included. Furthermore, the estimates are consistent with the few reliable values of γ' determined along the coexistence curve, such as $\gamma'_{\text{low density}} = 1.244 \pm 0.17$ and $\gamma'_{\text{high density}} = 1.228 \pm 0.028$ for xenon.[23] Again, I have not taken the published error limits too seriously. Uncertainties on the most probable values represent the approximate bounds corresponding to the upper and lower limit of (what I believe to be) the true values which could differ from my estimates. For example, β could be 0.33 or even 5/16, while μ could be 1.26. On the basis of very general assumptions, Fisher[24] obtained the inequalities

$$\eta \geqslant 2 - d(\delta - 1)/(\delta + 1) \quad \text{and} \quad (2 - \eta)\,\nu \geqslant \gamma,$$

where the exponent η is a small positive number whose magnitude indicates deviations from the Ornstein–Zernike and Debye theory, and δ is the pressure-density exponent. With $\delta \leqslant 4.6$, the first inequality gives $\eta \geqslant 0.071$. If we take 1.22, 0.63, and 0.071 for γ, ν, and η, the second inequality is invalid. Thus, the value of ν could have been underestimated, even though I believe that in general the d-dependent exponent relations are on a distinctly different and less certain footing.[25] However, such discrepancies are within reason, as critical exponents have been obtained using formulas which are often first approximations in the singular part of the thermodynamic properties and the exponent η has invariably been neglected in the determination of ν. The important point is that there seems to exist a set of critical exponents which is valid for all fluid systems. It is interesting to note that careful experiments have almost always tended to strengthen rather than weaken this universality assumption.

If we substitute the most probable values of critical exponents into the scaling equalities, we get $\gamma + \beta = 1.90$, $\mu + \nu = 1.91$, and $3\nu = 1.89$, which yield $\alpha = 0.09$–0.11, in good agreement with $\alpha = (1/8) \pm 0.01$ for CO_2.[26] The scaling equalities are satisfied exactly if $\gamma = 1.23$, $\nu = 0.63$, $\beta = 0.33$, and $\mu = 1.26$. Indeed, the best experiments have either 1/3 or 5/16 for β and about 1.26 for μ.[5] On the other hand, with the Fisher inequalities, we get $\eta \leqslant 0.0476$ and $\delta \geqslant 4.73$, which is again too high for δ according to current experimental evidence. Nevertheless, the values are so close to the numerical results of the 3-D Ising model that we should certainly keep in mind the possibility of having the critical exponents of the 3-D Ising model as those for fluid systems.[28] In any case, we should not be too anxious to state a breakdown of the universality concept or the scaling relations even though we consider them to be approximations of real fluid systems.

Theoretical models have predicted a breakdown of the universality assumption.[29] Yet, experimental evidence has so far shown that deviations from true values, or perturbations of the universality concept, are likely to be very small for fluid systems. This implies that routine measurements of more one-component fluid systems are less attractive. Instead, we need to pay more attention in our methods of analysis and measurement, and to ask much more difficult questions, such as background corrections and the influence of η on ν.

The situation in binary critical mixtures is somewhat different. A cursory examination of the values of critical exponents of two-component fluid systems, as listed in Table II, shows comparable experimental uncertainties when compared with those in Table I. However, a detailed analysis of data shows otherwise. For example, the best data for CO_2[3,7] xenon,[8] and SF_6[9] lead us toward a value of 1.22 for γ, while the best data for critical mixtures show $\gamma = 1.22$–1.23 with an *exception* for the carbon tetrachloride–perfluoromethyl cyclohexane system. Similarly, the large differences in ν (0.54 and 0.63) for two-component systems are difficult to reconcile.

Table II. Experimental Values of Critical Exponents for Two-Component Fluid Mixtures

System	Critical exponents			
	γ	ν	β	μ
Isobutytic acid–H_2O	<1.24[30]	0.62 ± 0.03[30]	1/3[30]	—
Aniline–C_6H_{12}	1.22 ± 0.01[31]	0.63 ± 0.01[31]	0.34[32]	1.29–1.31[33]
Phenol–H_2O	1.32 ± 0.03[34]	0.58 ± 0.1[34]	—	—
CCl_4–$CF_3C_6F_{11}$	$>1.15 \pm 0.04$[35]	($>0.54 \pm 0.04$[35])	0.333[27]	—
			0.359[36]	1.28[36]
3-Methylpentane–nitroethane	1.231 ± 0.008[37]	0.616 ± 0.003[37]	0.34[32]	1.34[38]

However, we believe that a value of 0.54 for ν from linewidth measurements is much too low. The error could come from the utilization of the Fixman–Botch equation in the nonlocal hydrodynamic region where the viscosity is assumed to be independent of $K\xi$, with K being the magnitude of the momentum transfer vector. In fact, there is strong evidence that the high-frequency shear viscosity of Kawasaki depends upon $K\xi$. It is within reason to expect that deviations from universality, if they occur, could probably be detected using binary fluid systems instead of one-component fluids where such small differences, if they exist, are beyond reach with present-day techniques, even though the possibility remains small.

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