Revised scaling analysis of Xe coexisting densities†

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Analysis of dielectric data along the coexistence curve in Xe shows that neither revised scaling nor corrections to scaling has a significant effect on the value of the critical exponent β. The data are best represented by a single β value ($\beta = 0.356$) over the entire range $2\times10^{-5} < |t| < 3\times10^{-2}$, but they are also compatible with a variation in β from 0.356 at large $|t|$ to 0.340 at small $|t|$. However, these data are incompatible with the Ising β value even when correction terms are included. Revised scaling effects are small, and available ρ_d values are compatible with either a $|t|$ or a $|t|^{1-\alpha}$ variation.

A current dilemma for the theory of ordinary critical points is the disparity between the experimental exponents obtained for pure fluids and the Ising values obtained for lattice-gas models. The hope has been expressed that an analysis based on revised scaling might resolve this problem.[1] A reanalysis of our Xe coexisting-density data[2] shows that neither revised scaling nor "corrections to scaling" will change the best value (0.356 ± 0.002) for β. This value is typical of the value in many other fluids[3] and is significantly different than $\beta_I = 0.3125$. Thus we believe that decorated lattice-gas models[4] belong to a different universality class than real fluids. Another possibility is that fluids have forces of sufficiently long range to cause the critical exponents to depend on some potential parameter.

A second apparent disparity can be resolved more easily. Revised scaling predicts that the rectilinear diameter $\rho_d \equiv \frac{1}{2}(\rho_L + \rho_V)$ should be curved, with a divergent slope $\dot{\rho}_d = d\rho_d/dT \sim -|t|^{-\alpha}$.[5] With the possible exception of SF_6,[6] nonpolar fluids all seem to have $\dot{\rho}_d = -$ const. We shall show that the magnitude of the leading singular term in $\dot{\rho}_d$ is very small for Xe, and existing data are compatible with either ordinary or revised scaling theory.

Revised scaling[1,5] involves the use of a primary scaling axis $\tilde{h} = h - rt$ and a thermal scaling axis $\tilde{t} = t + qh$, where for fluids $t \equiv (T - T_c)/T_c$, $h = (\mu - \mu_c)/kT_c$, $r = \lim \dot{\mu}/k$, and $q = k \lim (\dot{\rho}_d/\dot{s}_d)$, with $\dot{\mu}$ being the temperature derivative of the chemical potential along the coexistence curve and $\dot{s}_d$ being that of the average entropy density. The quantities r and q are nonuniversal, and in ordinary scaling one sets $q = 0$, but the value $q = -\frac{1}{2}$ for the Widom-Rowlinson model[7] suggests that there may be an important difference between $\tilde{t}$ and t. If we *assume* the Widom-Rowlinson form for $\dot{\rho}_d$ (i.e., $\dot{\rho}_d = -b\rho_c C_V$) and evaluate the effective value of b from the Xe density data (see below), we find that $q = -0.044$ for Xe.[8] Thus the effect of a nonzero q will be quite small for Xe.

The use of revised scaling axes produces two sorts of change in the expression for $(\rho - \rho_c)/\rho_c$. The leading term will be $B|\tilde{t}|^{\beta}$, and there will be a singular correction term $C|t|^{1-\alpha}$. Taking the $(\mu - \mu_c)$ values along the coexistence curve from Ref. 2, we find that a $\Delta\rho$ analysis based on using $|\tilde{t}|$ rather than $|t|$ will cause a negligible *increase* in β. Even when we artificially let $-q/(1+|qr|) = \frac{1}{2}$, which makes the effect more than ten times too large, the β value obtained from a fit over the range $t = 10^{-5}$–10^{-2} is only 0.0005 greater than that obtained with $q = 0$. Let us now look at the role of the various correction terms in $(\rho - \rho_c)/\rho_c$:

$$(\rho_\pm - \rho_c)/\rho_c = \pm B|t|^{\beta} + C_\pm|t|^{1-\alpha} + D_\pm|t|^{\Delta_2+\beta} + R_\pm|t|, \tag{1}$$

where plus is used to indicate the high-density (liquid) and minus the low-density (gas) phase. It is assumed, as usual, that the leading term is symmetric along the coexistence curve. The correction term $C_\pm|t|^{1-\alpha}$ arises from revised scaling,[5] $D_\pm|t|^{\Delta_2+\beta}$ comes from "corrections to asymptotic scaling,"[5,9] and $R_\pm|t|$ comes from the regular "background" part of μ which is analytic in T_c.[10] This last term could also include higher-order contributions from the singular part of μ.

For $\Delta\rho \equiv \rho_L - \rho_V$, we obtain

$$\Delta\rho/\rho_c = 2B|t|^{\beta} + \Delta C|t|^{1-\alpha} + \Delta D|t|^{\Delta_2+\beta} + \Delta R|t|, \tag{2}$$

where $\Delta C = C_+ - C_-$, etc. If all these correction terms are actually present, it will be very difficult to distinguish them experimentally since $1-\alpha \simeq 0.9$ for fluids ($1-\alpha_I = 0.875$) and $\Delta_2+\beta$ is

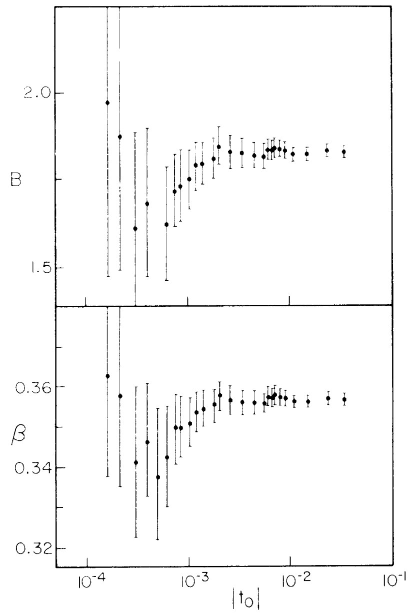

FIG. 1. Effect of range shrinking on the coefficient B and the critical exponent β. Points at a given $|t_0|$ value indicate the B and β value obtained from a least-squares fit of all $\Delta\rho$ data with $|t| \leq |t_0|$. The error bars represent ±1 standard deviation.

close to unity ($\Delta_2 + \beta = 0.95$ for an Ising lattice[9]). We have analyzed the $\Delta\rho$ data for Xe three different ways in a search for the possible effects of correction terms.

(i) Using only the leading term in Eq. (2), we have tested the effect of progressively shrinking the range from 36 data points with $|t| < 3.4\times10^{-2}$ to seven points with $|t| < 1.6\times10^{-4}$. Figure 1 shows the resulting values of β and B. All the β values are compatible with a single "best" value of 0.356,[11] and the corresponding "best" B value is 1.83. Note also that the B values are closely correlated to the β values (i.e., increasing the β value used in fitting a set of data will cause B to increase). Thus, the choice of a single β value for the entire range implies a constant B value. If a smaller β value is chosen to represent the data close to T_c, it will be necessary to use a smaller B value in that range also. The weighting of the experimental data points and the resulting error bars on β and B values were based on generous estimates of the uncertainties in the temperature ($\sigma_T = 0.001$ °C) and the observed dielectric constant ($\sigma_\epsilon = 0.0004$). On the basis of these error bars, our data obtained for $|t| < 10^{-3}$ are also compatible with $\beta = 0.340$ and $B = 1.61$; but significantly lower values of β are not consistent with the eight data points in the range 2×10^{-5}–2×10^{-4}. The results shown in Fig. 1 were obtained with the fixed value 16.6445 °C chosen for T_c. There is very little change in the pattern of the β and B values when T_c is varied over a narrow range. In Ref. 2, we used $T_c = 16.643$ °C for a fit to data with $|t| < 9.1\times10^{-3}$ and obtained $\beta = 0.357 \pm 0.002$. A three-parameter least-squares fitting procedure, with T_c as an adjustable parameter, gave results very similar to those shown in Fig. 1, and all the T_c values obtained from different fits were in the range 16.642–16.645 °C.

(ii) Representing the three correction terms in Eq. (2) by a single correction term $B_2|t|^{\beta_2}$, we carried out a four-parameter least-squares fit. The result was a rejection of this correction term: B and β did not change as a result of including this term, the ratio $B_2|t|^{\beta_2}/2B|t|^{\beta}$ varied from 3×10^{-5} to 3×10^{-3} as a function of t, and the sign of B_2 changed on range shrinking while β_2 stayed roughly constant at ~1.3.

(iii) We also tested this $2B|t|^{\beta} + B_2|t|^{\beta_2}$ form using a three-parameter fit with β fixed at 0.3125. The result was very poor ($\chi_\nu^2 = 91$ and strong systematic deviations), again indicating that our Xe data are incompatible with the Ising β value even when correction terms are taken into account.

Thus the correction terms in Eq. (2) do not play an important role in fitting our coexisting-density data for Xe. These data can be represented over the range $2\times10^{-5} < |t| < 5\times10^{-2}$ by only the leading term $2B|t|^{\beta}$ with $\beta = 0.356$ and $B = 1.83$. Although small variations in β with the fitting range cannot be ruled out, Fig. 1 does not indicate that β will go to β_I at small $|t|$, and we conclude that β for Xe must be significantly larger than β_I. The deviation plot given in Fig. 2 is another way to show that our Xe data do not indicate systematic deviations from the simple power law $\Delta\rho/\rho_c = 3.66|t|^{0.356}$.

We can also compare our results with recent optical measurements of the coexistence curve in Xe. The $\Delta\rho/\rho_c$ data of Estler *et al.*[12] over the range $|t| > 10^{-3}$ are well represented by $3.66|t|^{0.353}$, which is in excellent agreement with our power-law fit. However, systematic deviations are reported, with the β value being lower when only data at small $|t|$ are used. These deviations are indicated by the solid line in Fig. 2, and one can see that the magnitude of such systematic deviations is comparable to the standard deviation due to random errors in our own experiment. However, even if such systematic deviations are real (and not due to systematic errors in the experiment), one would still not conclude that β_I is a good limiting value for β. Estler *et al.* reported $\beta = 0.337$ and $2B = 3.30$ for a simple power-law fit over the range $10^{-5} < |t| < 10^{-3}$. They also reported that the form $2B|t|^{\beta} + B_2|t|^{\beta_2}$ gave a quite good fit to all their data over the range $10^{-5} < |t| < 5\times10^{-2}$. The resulting parameters were $2B = 3.042$,

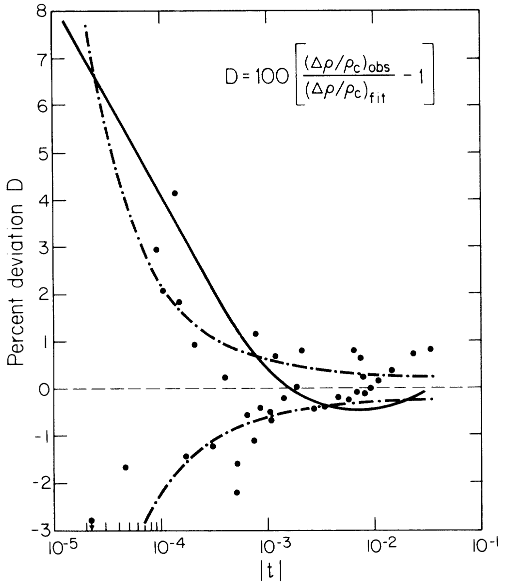

FIG. 2. Deviation plot representing the percent deviation of observed $\Delta\rho/\rho_c$ data from a simple power-law fit with $2B|t|^{\beta}$. For our data points, $(\Delta\rho/\rho_c)_{\rm fit} = 3.66|t|^{0.356}$ has been used and the broken lines represent ±1 standard deviation in D due to experimental uncertainties. The solid line indicates the deviations of the data reported in Ref. 12 from $3.66|t|^{0.353}$ (see text).

$\beta = 0.332$, $B_2 = 0.93$, and $\beta_2 = 0.61$. This β_2 value is not consistent with any of the theoretically expected correction exponents, and furthermore the inclusion of such a correction term has still not reduced the experimental β value to β_I. A further complication is the fact that Estler *et al.* obtain a β value of 0.352–0.358 from their scaled equation-of-state fit to the Fraunhofer interference pattern along near-critical isotherms.

On the basis of the above discussion, we conclude that a revised-scaling analysis will not bring presently available experimental data on Xe into agreement with the Ising exponents predicted by current lattice-gas models. New experimental work of very high quality will be required to establish β values with suitably small error bars when $|t| < 10^{-4}$. However, it can already be seen that including the correction terms in Eq. (2) has not made the reliable data at larger $|t|$ (where such corrections would have their greatest effect) consistent with $\beta = \beta_I$, and new theoretical efforts are also needed.

Finally let us consider the rectilinear diameter. From Eq. (1) we obtain

$$\rho_d/\rho_c = 1 + \overline{C}\,|t|^{1-\alpha} + \overline{D}\,|t|^{\Delta_2+\beta} + \overline{R}\,|t|\,, \qquad (3)$$

where $\overline{C} = \frac{1}{2}(C_+ + C_-)$, etc. Taking the Ising value[9] 0.64 as the best estimate for Δ_2 and combining it with the experimental β indicates that the "corrections-to-scaling" term $\overline{D}\,|t|^{\Delta_2+\beta}$ may be indistinguishable from the linear term. The question is: How important is the revised scaling term $\overline{C}\,|t|^{1-\alpha}$? Figure 3 indicates that the experimental ρ_d values in Xe do not show obvious curvature close to T_c. Indeed, our data down to 7 °C are well represented by $\rho_d/\rho_c = 1 + a|t|$ with $a = 0.691$ and are consistent with the linear variation in ρ_d observed from −67 to +15 °C.[13]

In order to exaggerate the effect of the revised scaling term, we can set $\overline{D} = \overline{R} = 0$ and determine an effective value for $\overline{C}$ by fitting our ρ_d line at 14.6 °C. The result is $\rho_d/\rho_c = 1 + 0.465|t|^{0.92}$, where we have used $\alpha = 0.08$.[2,14] Another almost equivalent representation is to assume the form $\rho_d/\rho_c = 1 + b(E_c - E)$, which will give the Widom-Rowlinson expression $d(\rho_d/\rho_c)/dT = -bC_V$. The values of $E_c - E$ can be obtained from integrating the specific-heat data,[14] and $bT_c = 5.3\times10^{-3}\ {\rm J}^{-1}$ mole deg represents the best empirical choice of b [in contrast to $bT_c = (2R)^{-1} = 60\times10^{-3}\ {\rm J}^{-1}$ mole deg for the penetrable-sphere model[7]]. The ρ_d/ρ_c values calculated in this way are essentially identical to those calculated from $1 + 0.465|t|^{0.92}$. The remarkable feature of these calculated values is the very small apparent curvature (which is related to the small overall slope[4]) in spite of the fact that formally $\dot{\rho}_d \sim -|t|^{-\alpha}$. Indeed, it is not possible to display clearly the difference between the curve $1 + 0.465|t|^{0.92}$ and the straight line $1 + 0.691|t|$ on the direct ρ_d/ρ_c plot in Fig. 2. Thus we have also included a difference plot which compares the deviations from the best straight line of the data points and the curve $1 + 0.465|t|^{0.92}$.

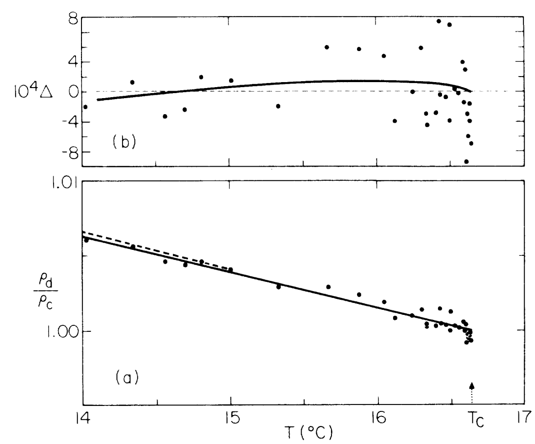

FIG. 3. (a) Variation in the rectilinear diameter for Xe. The solid line represents the best linear fit to the data points and corresponds to $a = 0.691$. The dashed line, corresponding to $a = 0.726$, represents extensive visual data below 15 °C (see Ref. 12). (b) Deviations Δ of the data points and the curve $1 + 0.465|t|^{0.92}$ from the straight line shown in part (a).

Although the ρ_d/ρ_c data are compatible with the existence of a revised-scaling term $0.465|t|^{0.92}$, it should be stressed that the magnitude of this term would diminish markedly if a nonzero value were assigned to $\bar{R}$. Any significant test of revised scaling for ρ_d in Xe will require an experimental precision better than 10 ppm and a better theoretical understanding of the magnitude of $\bar{R}|t|$ in Eq. (3). Our conclusion that revised-scaling effects are very small in Xe is also supported by the observed $(\partial\rho/\partial\mu)_T$ values along the coexistence curve for $10^{-4}<|t|<10^{-2}$.[15]

As a final remark, we should point out that our analysis is based on the assumed validity of the Clausius-Mosotti relation $(\epsilon-1)/(\epsilon+2)=K_1\rho$ with K_1 constant over the temperature and density range of interest.[2] This assumption is fully consistent with the best available experimental information for xenon.[16] It is estimated that any small variations in K_1 which may exist will change β by less than ± 0.002.

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