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# Testing the Lorentz–Lorenz relation in the near-critical binary fluid mixture isobutyric acid and water

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The refractive index in each phase of the binary fluid mixture isobutyric acid and water was measured at temperatures below the system's upper consolute point. This data was combined with existing density data to test the Lorentz–Lorenz relation in a near-critical binary fluid mixture. The Lorentz–Lorenz relation is verified within experimental error (0.5%) when the volume change on mixing the components is taken into account. The density coexistence curve data is reanalyzed to determine the critical exponent  $\beta$  and amplitude  $B$ . By allowing the order parameter to be a definition of the volume fraction that includes volume loss on mixing, a very symmetric coexistence curve is obtained which can be described by simple scaling with  $\beta = 0.326 \pm 0.003$  and  $B = 1.565 \pm 0.021$ . This exponent agrees with theoretical predictions while the amplitude, when combined with existing turbidity data, confirms two-scale-factor universality. The amplitude obtained by analyzing the coexistence curve when the refractive index is the order parameter also combines with turbidity data to confirm two-scale-factor universality, but does not require knowledge of the volume loss on mixing or the composition dependence of the refractive index.

## I. INTRODUCTION

Substantial recent interest in critical phenomena in a multitude of physical systems has been built upon concepts of scaling and universality which developed from studying second order phase transitions in fluid systems. Wilson<sup>1</sup> provided a comprehensive framework in renormalization group theory that has been used by many others to predict relationships among exponents, the values exponents should have when they belong to different universality classes, and relationships among the amplitudes of thermodynamic phenomena.

The predictions for the exponents have been well verified in liquid–gas and in binary fluid mixtures, both of which belong to the same universality class (three dimensional Ising model). The amplitude predictions from two-scale-factor universality have been confirmed in a few systems, but violated in others. Several reviews<sup>2–5</sup> discuss the present status of experiments and theory.

The coexistence curve provides the location of the critical point and also determines the critical exponent  $\beta$  and amplitude  $B$ , since for simple scaling, the difference in a generalized order parameter  $x$  between the upper and lower phases goes as a power law in reduced temperature  $t \equiv (T_c - T)/T_c$ :

$$\Delta x \equiv x^u - x^l = B t^\beta. \quad (1)$$

The critical exponent  $\beta$  is predicted to be  $0.325 \pm 0.0015$  from renormalization group theory<sup>6</sup> and  $0.328 \pm 0.003$  from series expansion.<sup>7</sup> In liquid–gas systems the order parameter is density<sup>3,4</sup>; for binary fluid mixtures the proper order parameter is still uncertain, although many favor the volume fraction since this gives<sup>3,4,8</sup> a more symmetric, Ising-like coexistence curve.

By using the “static” properties of the system (dielectric constant, refractive index, density, turbidity, etc.) the behavior of such quantities as the correlation length, osmotic

compressibility, thermal expansion, and coexistence curve can be deduced.<sup>2–5</sup> In developing such quantities from the raw data, several assumptions are made. Two common assumptions that are utilized in analyzing coexistence curve data (obtained by measuring the refractive index) are the Lorentz–Lorenz relation and the additivity of volumes.<sup>9</sup>

The Lorentz–Lorenz relation has been used to analyze both liquid–gas and binary fluid coexistence curves. The Lorentz–Lorenz relation has been tested near a liquid–gas critical point and found<sup>10</sup> valid in xenon, where deviations are within the experimental error of 0.5%. Measurements made in argon, methane, and carbon tetrafluoride indicate a 1% decrease in the value of the Lorentz–Lorenz function when going from the liquid to the gas phase.<sup>11</sup> Beysens<sup>12</sup> investigated the density derivative of the refractive index for 15 liquids away from their critical points and found deviations from Lorentz–Lorenz as large as 10%. No one has yet performed a detailed test of the Lorentz–Lorenz relation in the two-phase region of a binary fluid mixture. However, Houessou *et al.*<sup>13</sup> have intercompared the amplitude of the coexistence curve obtained by assuming both the Lorentz–Lorenz relation and the additivity of volume with the amplitude obtained using the mass fraction as the order parameter in the system methanol–cyclohexane. They find the amplitudes to differ by 3%–4% as a result of these two assumptions.

The experimental study of binary liquid mixtures has several advantages over liquid–gas systems. Many binary liquid mixtures have a critical point at atmospheric pressure, a critical temperature close to room temperature, (usually) small gravity effects, and a coexistence curve that apparently can be described by simple scaling over a relatively large reduced temperature.<sup>3,4</sup> Since both liquid–gas and liquid–liquid systems belong to the same universality class, the information gained by studying one should be applicable to the other.

The additivity of volume assumption that is often made when analyzing binary fluid mixture data can lead to large uncertainties in important amplitudes. When two fluids are mixed, the volume is rarely a conserved quantity so that a positive or negative excess volume can result. The curvature of the excess volume isotherm at the critical composition goes to zero as  $T_c$  is approached.<sup>14,15</sup> Many systems exhibit a nonzero slope for the resulting linear dependence so that different excess volumes occur in the two phases. This can result in asymmetric coexistence curves depending upon the order parameter chosen.

An example of the importance of the Lorentz-Lorenz relation occurred<sup>5</sup> in Beysens' test of two-scale-factor universality in the system isobutyric acid and water. An important constant is  $dn^2/d\phi$ , where  $n$  is the refractive index and  $\phi$  is the volume fraction. He calculated a value of 0.163 for  $dn^2/d\phi$  using Lorentz-Lorenz and the additivity of volume while he calculated a value of  $0.21 \pm 0.01$  from experimental measurements.<sup>5,16</sup> Such a large discrepancy had precluded a test of two-scale-factor universality in this system.

In order to resolve this discrepancy and to test the Lorentz-Lorenz relation in a binary fluid mixture near the critical point, we measured the refractive index as a function of temperature in the two-phase region of isobutyric acid and water. This system was chosen because of the existing,<sup>8</sup> very precise density data in the one- and two-phase region. Testing the Lorentz-Lorenz relation in the two-phase region near a binary fluid mixture's critical point allows an examination over a large range of densities with only small changes in temperature. We will not consider the refractive index anomaly in the one-phase region due to critical concentration fluctuations which have only been observed extremely close to the critical temperature and with a very small ( $<0.01\%$ ) amplitude.<sup>5,17,18</sup>

The expression for the Lorentz-Lorenz relation in a binary mixture will be developed, the excess volume will be defined, and the experimental techniques involved in our refractive index measurements will be presented. The refractive index data will be analyzed and used with Greer's density data to test the Lorentz-Lorenz relation. The necessity of including the excess volume will then be presented. The implications of using the volume fraction as the order parameter will be investigated, including discussion of the amplitude, exponent, and symmetry of the coexistence curve as well as two-scale-factor universality.

## II. LORENTZ-LORENZ RELATION

The Lorentz-Lorenz relation can be derived in a number of ways with correction terms appearing which depend on the assumptions and techniques.<sup>19</sup> In the limit where the mean polarizability approximates the average over all possible orientations of the molecule, the theories collapse to the Lorentz-Lorenz relation<sup>20</sup> stated here for a single component:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} \alpha \rho, \quad (2)$$

where  $n$  is the refractive index,  $\alpha$  is the mean polarizability, and  $\rho$  is the mass density of the material. When two or more

components are present, then the Lorentz-Lorenz relation becomes<sup>13,20,21</sup>

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} \left( \sum_i M_i \alpha_i / V \right), \quad (3)$$

where the sum is over all the components of mass  $M_i$  and polarizability  $\alpha_i$ . This can be rewritten for the case of two components using the density  $\rho_i = M_i/V_i$  as

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} (\alpha_2 \rho + (\Delta\alpha) \rho_1 \phi_1), \quad (4)$$

where  $\phi_i = V_i/V$ ,  $V$  is the total volume occupied by the fluids,  $\rho$  is the density of the mixture, and  $\Delta\alpha = \alpha_1 - \alpha_2$ .

No assumption has been made about the additivity of volumes. In fact, for most fluid mixtures the  $\Sigma\phi_i \neq 1$ . The fraction of the total volume lost (or gained) upon mixing the two components can be written as

$$\phi_E = \left( \sum_i \phi_i - 1 \right) / \sum_i \phi_i = -\tilde{V}_E / (x_1 \tilde{V}_1 + x_2 \tilde{V}_2). \quad (5)$$

The quantity  $\phi_E$  will be referred to as the volume loss (since volume is lost in the system studied here) and is easily related to the excess molar volume  $\tilde{V}_E$  others<sup>9,14,15</sup> have used. We choose to use  $\phi_E$  in this paper because, as will be discussed later, the temperature dependence of  $\phi_E$  is very small.

In order to test the Lorentz-Lorenz relation [Eq. (4)] in a binary fluid mixture, the refractive index and density of the mixture must be known as well as the polarizabilities  $\alpha_1$  and  $\alpha_2$  of the pure components. The volume fraction of component one  $\phi_1$  is related to the densities and to the volume loss  $\phi_E$  by

$$\phi_1 = [\rho - \rho_2 / (1 - \phi_E)] / (\rho_1 - \rho_2). \quad (6)$$

Equations (4)–(6) should hold in each phase so that the coexistence curve expressed in the order parameter  $\phi$  is related to density through a temperature and composition dependent expression:

$$\Delta\phi \equiv \phi_1^u - \phi_1^L = \left\{ \Delta\rho - \rho_2 \left[ \frac{\phi_E^u - \phi_E^L}{(1 - \phi_E^u)(1 - \phi_E^L)} \right] \right\} / (\rho_1 - \rho_2). \quad (7)$$

Since  $\phi_E$  varies linearly with composition near the critical point,<sup>14</sup> the difference between  $\phi_E^u$  and  $\phi_E^L$  can be large enough for the second term on the right-hand side of Eq. (7) to become significant when compared to  $\Delta\rho \equiv \rho^u - \rho^L$ .

The importance of the volume loss will become apparent as the coexistence curve and Lorentz-Lorenz relation are analyzed in this investigation of isobutyric acid and water.

## III. EXPERIMENTAL-REFRACTIVE INDEX

### A. Fluids

A sample of isobutyric acid and water at the critical composition of 38.90% by mass isobutyric acid was provided by Greer at the University of Maryland. The isobutyric acid was Purissima Grade and purchased from Fluka Chemical Company. The acid was purified by a common technique<sup>22,23</sup>; the acid was shaken with KOH then distilled under a vacuum with the middle fraction used. The water was ultrapure and boiled to remove dissolved  $\text{CO}_2$ .

The densities of the pure components have been studied by others. The density of water has been reported by Kell<sup>24</sup>; isobutyric acid has been measured less precisely (errors of parts in  $10^4$ ) by several investigators.<sup>16,23,25</sup> The density of isobutyric acid as a function of the temperature  $T$  in  $^{\circ}\text{C}$  was fit by us to a straight line:  $\rho_{\text{IBA}} = 0.968\,66 - 1.03 \times 10^{-3} T$ . The refractive indices of pure isobutyric acid and pure water were measured in our laboratory at 632.8 nm by a technique described below. Using our measured values of  $n$  and published values for  $\rho$ , the polarizabilities of water and isobutyric acid in the temperature region 23–29  $^{\circ}\text{C}$  were determined to be  $\alpha_2 = 0.048\,935 \pm 0.000\,007$  and  $\alpha_1 = 0.060\,010 \pm 0.000\,007\text{ cm}^3/\text{g}$ , respectively. The error is the statistical fluctuation in calculated polarizabilities; the accuracy in  $\alpha$  as determined from the errors in the densities and refractive index measurements is  $\pm 2.1 \times 10^{-5}$  and  $\pm 2.5 \times 10^{-5}\text{ cm}^3/\text{g}$  for water and isobutyric acid, respectively. Thus the Lorentz-Lorenz relation [Eq. (2)] provided consistent polarizabilities for these two components over the restricted region in temperature where the coexistence data would be taken.

The critical mixture was heated several degrees above the critical temperature before being syringed into the cell used to measure the refractive index. The transfer was completed and the cell sealed before the mixture became two-phase. A 1  $\text{cm}^3$  air bubble was sealed over the 6  $\text{cm}^3$  sample to prevent pressure fluctuations during the experiment.

## B. Cell, thermostat, and spectrometer

An aluminum, prism-shaped cell<sup>26</sup> was used to seal the sample and allow the refractive index to be measured in each phase. The fluids were sealed with a Teflon plug and Kalrez *o* rings. The cell was electroplated with copper and then with gold to prevent the isobutyric acid from reacting with the aluminum cell. It is well known that impurities can drastically affect the critical temperature, but will have little effect on the exponent or amplitude of the coexistence curve.<sup>27</sup>

The cell's temperature was controlled with an AC bridge using a ratio transformer and lock-in amplifier. A temperature controlled thermostat surrounded the cell as described previously.<sup>26,27</sup> The temperature of the cell was monitored with a Leeds & Northrup potentiometer sensing a Thermometrics ultra-stable thermistor which was calibrated on the International Practical Temperature Scale of 1968 to 0.01 K. Temperature resolution was  $\pm 0.2\text{ mK}$  with control of  $\pm 1\text{ mK}$  over 24 h.

The refractive index was determined from measurements of the minimum deviated angle of the 632.8 nm He-Ne laser light bending through each phase of the prism-shaped sample of fluid. The undeviated angle and the prism angle were also measured. Angles were read with a Gaertner spectrometer to a precision of 20 s of arc which provided a resolution in refractive index of  $\pm 0.0001_5$ .

## C. Procedure

The procedure for taking a data point and calculating the refractive index is the same as reported previously.<sup>21,26</sup> No gravity effects<sup>3</sup> were observed in this system. Some wetting<sup>28</sup> in the upper, isobutyric-acid rich phase was observed

as it has been by others.<sup>8</sup> One other effect was observed which needs further comment.

As the two-phase refractive index data as a function of temperature was taken, it became clear that the critical temperature was drifting steadily in time. This was determined by (1) the phase separation temperature increasing at an average rate of 8.7 mK/day. And by (2) the properties of the coexistence curve which can be used to determine the drift rate. A particular difference between the refractive indices of the upper and lower phases will only occur at a fixed temperature relative to  $T_c$ . By monitoring the temperature where the difference in refractive index was 0.0071 as a function of time, the critical temperature was found to drift at a rate of 9.1 mK/day. The drift was linear and could be attributed to small cracks in the gold plating which allowed the isobutyric acid to react with the copper underneath. This was confirmed upon dismantling the cell and noting small green cracks around the *o* ring grooves.

## IV. RESULTS-REFRACTIVE INDEX

The two-phase refractive index was measured over a four week period at 22 temperatures in the region  $6 \times 10^{-5} < t < 2 \times 10^{-2}$ . These temperatures correspond to the region in reduced temperature  $t = (T_c - T)/T_c$ , where Greer<sup>8</sup> took density data in a near critical mixture of isobutyric acid-water. The refractive index of the mixture at the critical point was  $1.3620 \pm 0.0002$  as determined by extrapolating the (linear) diameter to the critical temperature.<sup>21</sup>

The critical temperature was determined for each point as follows. As discussed above, the linear drift rate of the critical temperature was a constant  $8.9 \pm 0.2\text{ mK/day}$  which must be multiplied by the number of days from the observation of the phase transition temperature which occurred in the middle of the data run. The temperatures close to critical ( $t < 6 \times 10^{-4}$ ) were obtained one week before and after the phase transition was observed. Since the uncertainty in  $T_c$  is typically 2 mK, then the uncertainty in the drift rate did not significantly increase the error in  $t$  when  $t$  was small. For larger  $t$ , the uncertainty in the drift rate becomes a much smaller percentage and has little effect on the amplitude or exponent of the coexistence curve.<sup>29</sup>

The critical temperature adjustment must be added to a constant that represents  $T_c$  at the origin of time which was taken as the observation of the phase transition in the middle of the run. A value of  $t = (T_c - T)/T_c$  was then determined for each two-phase data point. Unless the system is precisely at the critical composition, the phase transition temperature is lower than the critical temperature so that  $T_c$  must be determined in the fits.

If simple scaling holds, then a log-log plot of  $\Delta n = n_u - n_l$  vs  $t$  should be a straight line of slope  $\beta$ . Figure 1 illustrates our refractive index data on such a plot. The parameters  $B_n$ ,  $\beta$ , and  $T_c$  were allowed to vary using a properly weighted fit<sup>30</sup> of simple scaling to our data. The best fit gave  $B_n = 0.096 \pm 0.006$  and  $\beta = 0.334 \pm 0.012$  (error bars are three standard deviations) with a reduced  $\chi^2$  of 0.25, where the error in  $\Delta n$  was taken as  $\pm 0.0003$  and the error in  $t$  was  $\pm 6 \times 10^{-6}$  ( $\pm 2\text{ mK}$  in  $T_c - T$ ). This fit is not improved when extended scaling terms<sup>3,4</sup> are included.

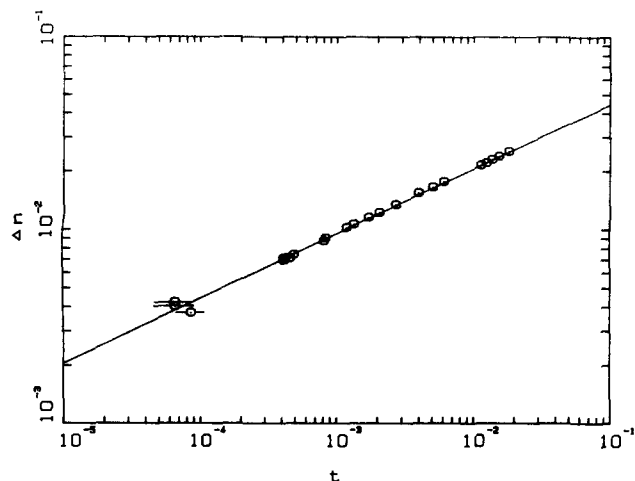


FIG. 1. The difference in refractive index  $\Delta n$  between the upper and lower phases exhibits a simple scaling, power law dependence on the reduced temperature  $t$ . The slope of this plot is the critical exponent  $\beta = 0.334 \pm 0.012$ , while the intercept is related to the amplitude  $B_n = 0.096 \pm 0.006$  of the coexistence curve. The errors quoted in the parameters are three standard deviations.

This is shown in Table I, fits 1 and 2, and also compared to  $\Delta\rho$  fits<sup>8</sup> (fits 3 and 4). A variety of values for  $\beta$  have been obtained. The fit to the  $\Delta n$  data gave a  $\beta$  consistent with the theoretical renormalization group theory value<sup>6</sup> of 0.328 or the series expansion value<sup>7</sup> of 0.325 and with Greer's<sup>8</sup> extended scaling value of  $\beta = 0.333 \pm 0.01$ . This system provided a higher  $\beta$  than others<sup>5,21,26,27,31</sup> investigated by refractive index techniques although the difference is small. Greer<sup>8</sup> found  $\beta$  to become closer to the theoretical values (0.325–0.328) when using the volume fraction (fit 5 in Table I) as the order parameter. This approach is also tested here in a later section.

## V. TESTING LORENTZ-LORENZ

The refractive index data taken on the isobutyric acid–water system can be combined with previous measurements<sup>8</sup>

of the density to test the Lorentz–Lorenz relation. Both experiments explore the two-phase region within 4 °C of the critical temperature. Although this is a narrow temperature range, the compositions of the phases vary from 0.21 to 0.61 mass fraction isobutyric acid. In the two-phase region, the composition of each phase depends upon  $(T_c - T)$  and not on the composition of the one-phase sample above  $T_c$ .<sup>3,4</sup> Thus, we can compare our refractive index data with Greer's density data in the two-phase region even though the samples were prepared with slightly different compositions. Thus, a wide range of compositions can be investigated to determine if the Lorentz–Lorenz relation is valid near the critical point of a binary fluid mixture.

In testing Eq. (4), the Lorentz–Lorenz relation for binary mixtures, the subscript 1 refers to isobutyric acid and the 2 to water. Since the refractive index comes in squared, its error should dominate. Thus, we did not use any fit to determine the refractive index, but rather used the raw refractive index of each phase at a given  $t$  and calculated the corresponding density from Greer's fits<sup>8</sup> to the 120 density data points. Since the mixture's density has a linear temperature dependence, a small correction is used to account for the difference between our critical temperature (27.9 °C) and Greer's (26.00 °C). The volume fraction  $\phi_1$  in Eq. (4) is calculated from Eq. (6). The left- and right-hand sides of Eq. (4) can thus be determined from independent experiments and evaluated at several reduced temperatures  $t$ . The difference of the left- from the right-hand sides divided by the left-hand side will give a fractional deviation (hereafter called the deviation of the Lorentz–Lorenz relation). The propagated error resulting from the random error in  $n$ ,  $\rho$ ,  $t$ ,  $\rho_1$ ,  $\rho_2$ ,  $\alpha_1$ ,  $\alpha_2$ , and  $\phi_E$  places our resolution in the fractional deviation at  $\pm 0.0014$ .

As a first attempt, the volume loss on mixing was assumed negligible ( $\phi_E = 0$ ) and the deviation of the Lorentz–Lorenz relation was calculated. The resulting values are plotted in Fig. 2 as a function of  $t$ . The large (6%) and very systematic error exhibited in this figure indicates an error in our assumptions.

TABLE I. Fits of coexistence curve data in the system IBA–H<sub>2</sub>O using different order parameters. Fits 1 and 2 are on our data; the remaining fits were done on data reported by Greer (Ref. 8). The equations tested are a difference in order parameter between the two phases as a function of the reduced temperature  $t$ . Errors on the parameters are three times the standard deviations given by the fits.  $\rho$  is the density,  $n$  is the refractive index,  $\phi'$  is the volume fraction assuming additivity of volume, and  $\phi$  is the volume fraction including the volume loss on mixing.

Fit #	Equation	$B$	$\beta$	$B_1$	$\chi^2/N$
1	$\Delta n = Bt^\beta$	$0.096 \pm 0.006$	$0.334 \pm 0.012$	...	0.25
2	$\Delta n = Bt^\beta + B_1t^{\beta+1/2}$	$0.11 \pm 0.04$	$0.35 \pm 0.06$	$-0.04 \pm 0.15$	0.24
3 <sup>a</sup>	$\Delta\rho = Bt^\beta$	$0.053 \pm 0.001$	$0.309 \pm 0.004$	...	2.8
4 <sup>a</sup>	$\Delta\rho = Bt^\beta + B_1t^{\beta+1/2}$	$0.063 \pm 0.005$	$0.333 \pm 0.01$	$-0.048 \pm 0.023$	1.6
5 <sup>a</sup>	$\Delta\phi' = Bt^\beta$	$1.071 \pm 0.023$	$0.328 \pm 0.004$	...	0.70
6	$\Delta\phi' = Bt^\beta$	$1.079 \pm 0.012$	$0.326 \pm 0.002$	...	1.2
7	$\Delta\phi = Bt^\beta$	$1.565 \pm 0.021$	$0.326 \pm 0.003$	...	0.94
8 <sup>b</sup>	$\Delta\phi = Bt^\beta + B_1t^{\beta+1/2}$	$1.547 \pm 0.009$	0.325	$0.10 \pm 0.05$	0.92
9	$\Delta\phi = Bt^\beta + B_1t^{\beta+1/2}$	$1.52 \pm 0.09$	$0.323 \pm 0.006$	$0.22 \pm 0.39$	0.92

<sup>a</sup> As reported in Ref. 8.

<sup>b</sup> Exponent  $\beta$  is fixed.

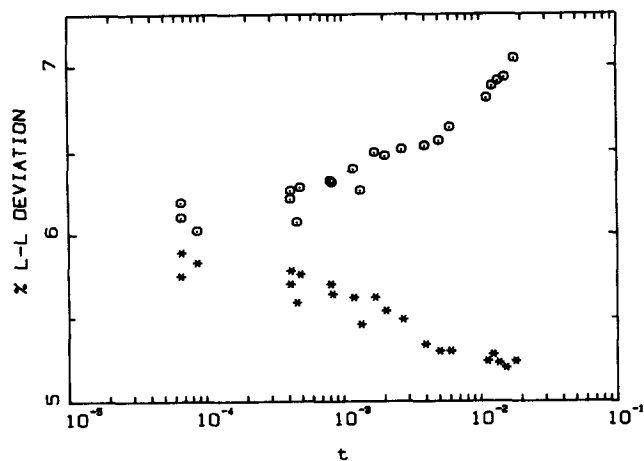


FIG. 2. The percent deviation of the Lorentz-Lorenz relation Eq. (4) shows a large and systematic error when the volume loss on mixing is neglected ( $\phi_E = 0$ ), which depends on  $t$  and the phase ( $\circ$  = upper,  $*$  = lower).

The volume loss of mixing can be calculated from the density as a function of mass fraction  $f \equiv M_1/(M_1 + M_2)$ , which has been measured by several investigators<sup>16,23,25</sup> on mixtures of isobutyric acid-water. The relation is

$$\phi_E = 1 - \left\{ f \left[ \frac{\rho}{\rho_1} + \left( \frac{1}{f} - 1 \right) \frac{\rho}{\rho_2} \right] \right\}^{-1}, \quad (8)$$

where  $\rho_1$  and  $\rho_2$  are the densities of the pure components isobutyric acid and water. The values of  $\phi_E$  at 26.3 °C as a function of the composition are shown in Fig. 3. The values of  $\phi_E$  do not change within experimental error over the temperature region 22–26.3 °C. A least squares fit<sup>30</sup> of the 26 data points in the region  $0.2 < f < 0.6$  provided the relationship:  $\phi_E = 7.6 \times 10^{-3} + 0.0405f - 0.0294f^2$ . The mass

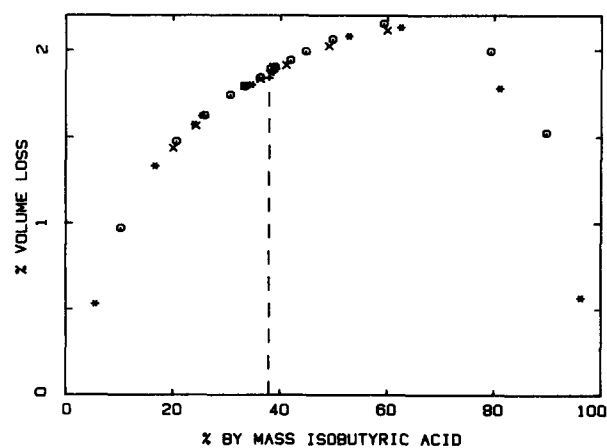


FIG. 3. The volume loss on mixing  $\phi_E$  expressed as a percentage is a function of the composition of isobutyric acid in mixtures with water. The critical composition is indicated by the vertical dashed line. The range of compositions investigated in this experiment are from 20% to 60% by mass isobutyric acid. The volume loss in the vicinity of the critical point is roughly linear; a quadratic function is used in the text to describe the data in the range of compositions investigated. These data are for 26.3 °C, but the volume loss does not vary outside the experimental error in the temperature region of interest to our experiment (22–26 °C).  $\times$  from Ref. 16;  $*$  from Ref. 23;  $\circ$  from Ref. 25;  $+$  from Ref. 8.

fraction can be calculated from the density of the mixture, the densities of the components, and the volume loss  $\phi_E$  using Eq. (8). Using Greer's density data, where the mass fraction in each phase is unknown, to determine the volume loss  $\phi_E$  requires an iterative solution using Eq. (8) and the fit of  $\phi_E$  vs  $f$ . This technique was tested on the data represented in Fig. 3 and produced  $\phi_E$  values within experimental error.

By including the volume loss  $\phi_E$  in determining the  $\phi_1$  used in Eq. (4), the deviation of the Lorentz-Lorenz relation could again be calculated. The result is illustrated in Fig. 4.

## VI. DISCUSSION

### A. Lorentz-Lorenz

The fractional deviation between the left- and right-hand sides of Eq. (4) as shown in Fig. 4 averages ( $0.28 \pm 0.2$ )% which is only slightly larger than the estimated error of 0.14% as determined from the random errors in the experiments. The accuracy of each experiment is unknown, but one can estimate a systematic error at least comparable to the random error. The slight systematic dependence in Fig. 4 on the phase and reduced temperature  $t$  could easily be due to the uncertainty in the values of  $\phi_E$ ; the volume loss  $\phi_E$  has a much larger effect on the Lorentz-Lorenz variation (see Fig. 2) than one would expect.

We conclude that the Lorentz-Lorenz relation is valid within 0.5% in this binary mixture when the volume loss on mixing  $\phi_E$  is taken into account. The Lorentz-Lorenz relation could hold to a better resolution; however, more accurate density measurements are needed on various mass fractions so that  $\phi_E$  can be better determined.

### B. Coexistence curve symmetry and shape

The volume loss on mixing for this system is sufficiently large to produce significant errors (see Fig. 2) should it be neglected. It is natural to consider the effect  $\phi_E$  might have on the symmetry and shape of the coexistence curve as a result of the order parameter utilized.

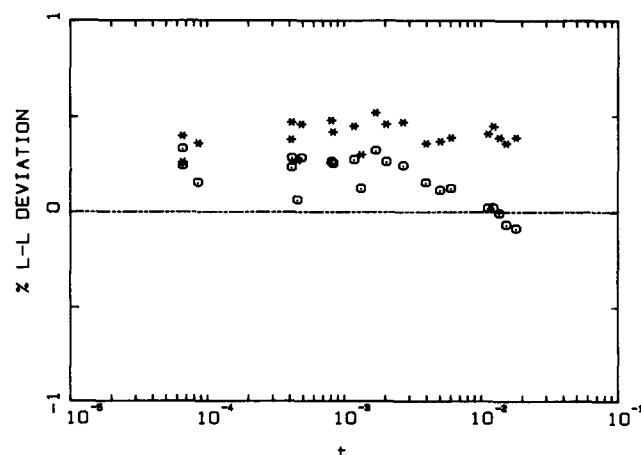


FIG. 4. The deviation of the Lorentz-Lorenz relation, Eq. (4) when the volume loss on mixing is taken into account.  $t$  is the reduced temperature; the upper phase is indicated by an  $\circ$  while an  $*$  denotes the lower phase.

The proper order parameter for a binary liquid mixture is still uncertain.<sup>3,4</sup> In the analysis of the isobutyric acid–water density data, Greer<sup>8</sup> used another order parameter to analyze the coexistence curve. This order parameter, also called volume fraction, is the same as our volume fraction when the volume loss on mixing is zero ( $\phi_E = 0$ ). Reeder *et al.*<sup>9</sup> had previously shown that the critical exponent  $\beta$  did not depend on the choice of order parameter (mole fraction, volume fraction with  $\phi_E = 0$ , and volume fraction with  $\phi_E \neq 0$ ) in studying the system nitroethane + 3-methylpentane; they did not report on the amplitude  $B$ . Greer<sup>8</sup> used Eq. (6) (with  $\phi_E = 0$ ) to calculate  $\phi_1$  from the measured  $\rho$  and from a quadratic fit to unpublished isobutyric acid density measurements. The result of fitting Eq. (1) to this  $\phi_1$  data is shown in Table I, fit 5: the critical exponent  $\beta = 0.328 \pm 0.004$  and  $B = 1.071 \pm 0.023$ .<sup>8</sup> This value of  $\beta$  was much closer to the theoretical predictions and fit the data without correction-to-scaling terms. The volume fraction thus appeared to be preferred over density as the order parameter. Others have found the volume fraction to give more symmetric coexistence curves than other order parameter such as mole fraction.<sup>3–5</sup>

We wanted to determine if using the excess volume in the volume fraction definition would affect these conclusions. As pointed out above, the excess volume near the critical point has a (roughly) linear dependence on the mass fraction so that the calculated difference in the volume fraction between the phases can be significantly affected. Equation (7) shows this dependence and Fig. 3 illustrates the difference between  $\phi_E$  in an isobutyric acid rich phase vs that in an isobutyric acid deficient phase. For example, in the isobutyric acid–water mixture at  $t = 4.7 \times 10^{-3}$ , the density difference between the phase is  $\Delta\rho = 0.010$  and  $\phi_E^u - \phi_E^l = 0.0046$ , which results in a 46% correction to the calculated volume fraction  $\Delta\phi_1$  from Eq. (7).

A linear fit to the density of pure isobutyric acid and the fit provided by Kell<sup>2</sup> for water were used to determine  $\Delta\phi_1$  in Eq. (7). The quadratic fit of  $\phi_E$  as a function of mass fraction  $f$  discussed in the Lorentz–Lorenz section was also used. The resulting  $\Delta\phi_1$  data as a function of  $t$  could be fit<sup>30</sup> by the simple scaling relation  $\Delta\phi_1 = Bt^\beta$ . As a check, we forced  $\phi_E = 0$  (fit 6 in Table I) and duplicated Greer's<sup>8</sup> fit (fit 5). The remaining fits (7–9) in Table I are with  $\phi_E \neq 0$ . The exponent  $\beta$  does not change as  $\phi_E$  is introduced, but the amplitude does. The best fit is fit 7, where  $\beta = 0.326 \pm 0.003$  and  $B = 1.565 \pm 0.021$ . Correction-to-scaling terms do not improve the fit as shown by the last two fits in Table I. The larger value of  $B$  resulting from our operational definition of volume fraction becomes important when testing two-scale-factor universality relations between amplitudes.

It is important to recognize that the error in  $\Delta\phi_1$  is dominated by the uncertainty in the measurements leading to  $\phi_E$ . Because this system has a large volume loss on mixing, the description of the coexistence curve is limited by the precision in  $\phi_E$  as was the Lorentz–Lorenz relation.

The symmetry of the coexistence curve involves more than finding the exponent  $\beta$  with the “proper” value and for which simple scaling fits the data. The Ising model used in

the theoretical models<sup>6,7</sup> has a two-phase diameter which is independent of temperature. Real systems have diameters which depend linearly on temperature with a slope that is related to the order parameter chosen.

The volume fraction calculated from Eq. (6) ( $\phi_E \neq 0$ ) was used to determine the diameter in the isobutyric acid–water system. Using Greer's<sup>8</sup> density measurements in the two-phase region, the diameter was calculated to be a constant  $\bar{\phi} = 0.422$  within the experimental error of  $\pm 0.003$ . The point furthest from  $T_c$  ( $T_c - T = 3.57^\circ\text{C}$ ) is the only exception; its diameter is higher by 0.009. The variation in this order parameter's diameter is much less than that obtained by either density or refractive index which have diameters that vary linearly<sup>8,26,27</sup> with temperature. As a measure of the constancy of the diameters obtained by using either volume fraction, density or refractive index as the order parameter, the maximum variation  $\delta\bar{x}$  in the diameter is divided by the maximum width of the coexistence curve in that parameter,  $\Delta x = |x_u - x_l|$ . This gives  $\delta\bar{\phi}/\Delta\phi = 0.010$ ,  $\delta\bar{\rho}/\Delta\rho = 0.037$ , and  $\delta\bar{n}/\Delta n = 0.034$ . Thus the volume fraction provides a more symmetric coexistence curve.

It should be noted that this highly symmetric coexistence curve was obtained using an order parameter, volume fraction, which was determined solely from experimental measurements. Others<sup>32,33</sup> have tried to achieve symmetrical coexistence curves by introducing adjustable parameters into a calculated order parameter. This procedure results in more symmetric coexistence curves than obtainable by using the mole fraction alone, but still has diameters that vary linearly with the temperature. One<sup>32</sup> such definition assumes additivity of volumes and results in “nonuniversal” values for  $\beta$  (0.28 to 0.39). At least in the system studied here, such extensions were not necessary to produce a symmetric coexistence curve, an Ising exponent  $\beta$ , and an amplitude consistent with two-scale-factor universality as will now be discussed.

### C. Two-scale-factor universality

Sengers and Moldover<sup>34</sup> showed that the amplitude of the coexistence curve could be used to test two-scale-factor universality. Two-scale-factor universality uses two scale factors in a renormalization group setting to universally relate the amplitudes of different phenomena in the same system.<sup>35</sup> The coexistence curve amplitude  $B$  is related to the correlation length amplitude  $\xi_0$  and osmotic compressibility amplitude  $\chi_0$  by<sup>34</sup>

$$R = \xi_0 [B^2 / (4k_B T_0 \chi_0)]^{1/3}, \quad (9)$$

The predicted values of  $R$  are 0.65 (series expansion) and 0.67 (renormalization group expansion).<sup>34</sup>

The amplitudes  $\xi_0$  and  $\chi_0$  can be determined from measurements of the turbidity  $\tau$  near the critical point<sup>5,36</sup>:

$$\tau = \tau_0 (1 + t)^{-\gamma} F(k_0 \xi), \quad (10)$$

where  $k_c$  is  $2\pi n/\lambda_0$ ,  $\xi$  is the correlation length,  $\tau_0$  is a constant determined in the analysis and related to  $\chi_0$  by

$$\tau_0 = \frac{2\pi^3}{\lambda_0^4} \left( \frac{\partial n^2}{\partial \phi} \right)^2 k_B T \chi_0, \quad (11)$$



and  $F(x)$  is a function described elsewhere.<sup>36,37</sup> Thus, the two-scale-factor prediction becomes

$$R = \xi_0 \left[ \frac{B^2 \pi^3}{2\tau_0 \lambda_0^4} \left( \frac{\partial n^2}{\partial \phi} \right)^2 \right]^{1/3} \quad (12)$$

Beysens *et al.*<sup>5,36</sup> measured the turbidity in isobutyric acid-water and found  $\xi_0 = (3.63 \pm 0.07) \text{ \AA}$  and  $\tau_0 = (1.08 \pm 0.02) \times 10^{-5} \text{ cm}^{-1}$  using He-Ne laser light ( $\lambda_0 = 632.8 \text{ nm}$ ). The discrepancy in  $(\partial n^2/\partial \phi)$  when data obtained by Freedlander<sup>16</sup> is compared to a value calculated by the Lorentz-Lorenz relation was noted by Beysens<sup>5</sup> and discussed in our Introduction. When calculated by Lorentz-Lorenz, the quantity  $(\partial n^2/\partial \phi)$  does not depend on  $\phi_E$  so that our value  $(0.159 \pm 0.003)$  agrees with Beysens's<sup>5</sup> (0.163). Freedlander's compositions are mass fractions which can be converted to a volume fraction by taking the volume loss  $\phi_E$  into account. Freedlander's<sup>16</sup> data for the sodium  $D$  line thus give  $(\partial n^2/\partial \phi) = 0.178 \pm 0.02$ . This value and that calculated by the Lorentz-Lorenz relation are in agreement.

The universal amplitude ratio  $R$  in Eq. (12) can be calculated using  $\partial n^2/\partial \phi = 0.159 \pm 0.003$  and  $B = 1.565 \pm 0.02$  from fit 7 in Table I. Combined with Beysens' values<sup>5,36</sup> of  $\xi_0$ ,  $\tau_0$ , and  $\lambda_0$ , the value of  $R$  is  $0.65 \pm 0.02$ . This value agrees well with the predicted values of 0.65–0.67.

The amplitude ratio  $R$  can also be written<sup>37</sup> in terms of the coexistence curve amplitude  $B_n$ :

$$R = \xi_0 \left[ \frac{2B_n^2 n_c^2 \pi^3}{\tau_0 \lambda_0^4} \right]^{1/3} \quad (13)$$

where the constant  $(\partial n^2/\partial \phi)$  cancels out since  $B_n = B (\partial n/\partial \phi)$ . Using the value of  $B_n = 0.096 \pm 0.006$  from fit 1 in Table I,  $n_c = 1.362$ , and the values of  $\xi_0$ ,  $\tau_0$ , and  $\lambda_0$  from Beysens,<sup>5,36</sup>  $R$  is calculated to be  $0.66 \pm 0.03$  which agrees with both the theoretical values 0.65–0.67 and the value ( $R = 0.65 \pm 0.02$ ) determined above using the volume fraction as the order parameter when analyzing Greer's<sup>8</sup> density data.

## VIII. CONCLUSION

Precise refractive index measurements in the two-phase region of the binary fluid mixture isobutyric acid and water were combined with independent density measurements<sup>8</sup> of the same system to verify the Lorentz-Lorenz relation within experimental error (0.5%). The volume loss on mixing was large in this system and had to be included in the analysis to verify the Lorentz-Lorenz relation.

The shape of the coexistence curve was analyzed to obtain the critical exponent  $\beta$  and amplitude  $B$  when using different order parameters. A definition of volume fraction that included the volume loss on mixing provided the most symmetric coexistence curve and produced an amplitude  $B = 1.565 \pm 0.021$  that confirmed two-scale-factor universality predictions  $R = 0.65 \pm 0.02$ . Use of this order parameter allowed Greer's data to be described by simple scaling and produced an exponent  $\beta = 0.326 \pm 0.003$  that agreed with theoretical predictions. The refractive index coexistence curve produced an amplitude which could be combined with turbidity data to also verify two-scale-factor uni-

versality,  $R = 0.66 \pm 0.03$  without determining the volume loss on mixing or the quantity  $\partial n/\partial \phi$ .

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