

## COEXISTENCE CURVE OF A BINARY MIXTURE\*

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We report precise measurements of the refractive index as a function of temperature in the one- and two-phase region near the consolute point in the binary mixture methanol–cyclohexane. By measuring forty-four data points over four decades in  $\epsilon = (T_c - T)/T_c$ ,  $6 \times 10^{-6} < \epsilon < 6 \times 10^{-2}$ , we were able to determine the coexistence curve and found the critical exponent  $\beta$  to be  $0.326 \pm 0.003$  by using a properly weighted least squares fit to the data. The uncertainty is three times the standard deviation. Our data is consistent with other refractive index data of the same binary fluids although a different value for the critical exponent was found. We do not find a need for the Wegner type correction terms reported by others recently, nor do we see an anomaly in the rectilinear diameter.

### 1. Introduction

It has recently become important to investigate the coexistence curve of a binary fluid mixture in order to determine whether binary mixtures belong to the same universality class [1] (have the same critical exponents) as pure fluids and the Ising model, whether the rectilinear diameter of the coexistence curve has an anomaly, and if corrections to scaling as proposed by Wegner [2] are needed. We have determined the coexistence curve of methanol–cyclohexane by using a prism cell to measure the bulk value of the refractive index for the 6328 Å He–Ne laser line. That one can use the refractive index to measure the coexistence curve is now well accepted [3].

The coexistence curve of methanol–cyclohexane was first studied by Lecat [4] and then by Jones and Amstell [5] and Eckfeldt and Lucasse [6] where the effect of impurities was considered. The only recent studies have been done by Gilmer et al. [7] and Campbell and Kartzmark [8], both of which involved use of a refractive index technique. However, these

works were not extensive enough to answer the questions posed above and so the experiment described here was undertaken.

For some time a disparity has existed between the critical exponent  $\beta$  describing the coexistence curve of pure fluids [3,9] ( $\beta = 0.355 \pm 0.007$ ) and of binary mixtures [10] ( $\beta = 0.34 \pm 0.01$ ) and that from the series expansion result for the Ising (lattice-gas) model [11] ( $\beta = 0.313$ ). However, recent measurements on pure fluids [12,13] and binary mixtures [14,15] show that by taking gravity effects [16] and a correct form for extended scaling [17] into account, the values of  $\beta$  for pure fluids [12,13] ( $\beta = 0.321 - 0.329$ ) and binary mixtures [14,15] ( $\beta = 0.316 - 0.328$ ) agree with recent renormalization group calculations [18,19] for the Ising model ( $\beta = 0.322 \pm 0.002$ ) and are much closer to the old series expansion value. We point out that for our system, which is virtually free of gravity effects [20], a value of  $\beta = 0.326 \pm 0.003$  is determined with only simple scaling needed to fit our data for  $\epsilon < 0.06$ .

The experimental methods used in this work are discussed in section 2. The data collection and analysis techniques we used are treated in section 3, and section 4 consists of a short concluding discussion. We choose to present and fit the refractive index data taken rather than convert to volume fraction or other

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order parameters. The volume fraction would seem to be the preferred order parameter since it gives a coexistence curve [9,15,21] which approaches the completely symmetric curve predicted by the Ising model [22]. We show in an Appendix that, to good approximation, the change in volume fraction is proportional to the change in refractive index between the two phases. Others [7,12–14] who have used refractive index techniques to measure the coexistence curve have used equivalent presentations.

## 2. Experimental methods

### 2.1. Sample cell and fluids

The sample cell (shown in fig. 1) is a piece of aluminum carefully shaped to be an equilateral triangle. The cell is anodized in order to prevent reaction with the fluids which are contained in a one inch hole bored parallel to the base. The fluids are captured by two optically flat ( $\lambda/20$ ) pieces of glass sealed with teflon. The cell is heated by means of three heaters located symmetrically inside it and the temperature is monitored with a thermistor. The fluids are Fisher "Spectranalyzed" methanol (99.95% pure) and cyclohexane (99.98% pure). The major impurity in each one is water. Before filling, the cell was baked overnight in an oven at  $110^{\circ}\text{C}$  and then cooled in a dry-box with a dry nitrogen atmosphere and dessicant.

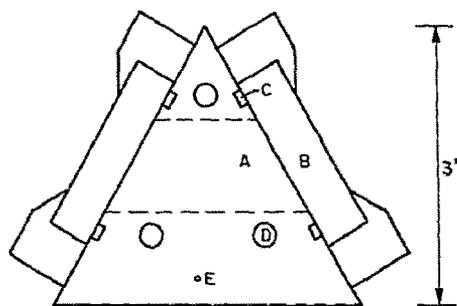


Fig. 1. The prism cell used in this experiment is made of anodized aluminum with a one-inch bore (A) for the fluids which are captured by two optically flat pieces of glass (B) and sealed with teflon (C). The cell is heated by three symmetric internal heaters (D) and the temperature is monitored with a thermistor (E).

The fluids were then separately syringed into the cell while in the dry box and the cell was sealed and massed after each component was added. The methanol concentration in the cell was 28.94% by weight, which is very close to the quoted value of 29.0% [7,23,24].

### 2.2. Refractive index measurement

The prism angle,  $\theta$ , of the cell was determined by autocollimation to 10 sec of arc and was found to be  $60.156^{\circ}$ . The undeviated angle,  $\psi_0$ , was then measured and checked occasionally. The cell was placed on the spectrometer table at a position which compensated for the shift of the light due to the half-inch thick windows. (A shift does not alter the measured deviated angle since the glass surfaces are flat and parallel.) A spectrometer with an  $11\frac{1}{2}$  inch base was used allowing a resolution of 10 sec of arc in the deviated angle. We measured the minimum deviation angle,  $\psi$ , for each line several times with a precision of less than 10 sec of arc. We estimate the error in refractive index due to the uncertainties in measurement to be  $\pm 0.0001$ . The refractive index is related to the angles we measure by the well known relation

$$n = \sin[(\psi - \psi_0 + \theta)/2] / \sin(\theta/2).$$

The accuracy of our measurements was checked by measuring the refractive index of our pure cyclohexane for the sodium D line at  $25^{\circ}\text{C}$  giving a value of 1.4232 which agrees with the latest value given by Timmermans [25] of 1.4233.

### 2.3. Temperature control

The cell was thermally isolated from the outside environment by being placed on nylon posts inside a half-inch thick aluminum heat shield which was then attached to a surrounding vacuum envelope by means of an additional set of nylon posts. The temperature was controlled by means of a two-stage thermostat utilizing dc bridges which were capable of controlling to  $\pm 0.5$  mK over 24 hours as tested in a well-stirred oil bath. The dc bridge is basically a Wheatstone bridge with the error signal being amplified by an op-amp and fed back by way of a power amplifier to the heater [26]. The thermistors we used were "aged" YSI 44004 thermistors, one of which was calibrated with respect to a standard platinum resistance element

that had been calibrated at the National Bureau of Standards. With this calibration, absolute temperatures were known to  $\pm 0.015$  K. However, we were able to measure all of our temperatures relative to the critical temperature to an accuracy of about  $\pm 3$  mK. The precision with which we were able to measure any given temperature was about  $\pm 2.5$  mK. The heat shield was heated to about 40 mK below the cell temperature and controlled to  $\pm 10$  mK over 12 hours allowing the cell to be controlled to  $\pm 2.5$  mK over the same period. The temperature gradients were measured and determined to be less than 2.5 mK across the cell. Also, we were able to determine from visual observation of the fluids whether significant temperature gradients were present. None were observed.

#### 2.4. Sources of systematic error

Impurity effects in binary liquid mixtures seem to be confined to causing a shift in the critical temperature but to have little effect on the critical exponents [13,24,27]. The critical temperature of our system, methanol and cyclohexane, is more sensitive to water impurities [6] but small amounts of water do not seem to affect the shape of the coexistence curve [5], or equivalently, the value of  $\beta$ . Others have also found no effect on the critical exponents until very large amounts of impurities [27] are added. This agrees with theoretical predictions [28].

In order to insure accurate temperature intervals, we calibrated an auxiliary thermistor with respect to the calibrated platinum resistance element mentioned earlier. The critical temperature was measured to be  $318.624 \pm 0.015$  K ( $45.474 \pm 0.015^\circ\text{C}$ ) which differs from other reported values [6,23,24] of  $318.29 \pm 0.01$  K ( $45.14 \pm 0.01^\circ\text{C}$ ) by an amount consistent with the water impurity content of our fluids of 0.03% by weight.

Because of the recent observations [29,30] of density gradients due to gravity in binary fluids, we started our experiment by looking for such gravity effects, although they are predicted to be very small [20] for our system due to the closely matched densities ( $|\rho_{\text{CH}_4\text{O}} - \rho_{\text{C}_6\text{H}_{12}}|/\bar{\rho} = 0.016$ ). After our system had been at room temperature for some time with the source slit images ("lines") straight, we raised the temperature a few degrees and noticed some curving of the lines near the meniscus for many hours

after the new temperature had been reached. We discovered that this was due to concentration gradients in the cell caused by the slow diffusion across the meniscus and not a density gradient that others [29] have reported using a similar technique. The meniscus was also observed to persist well above the critical temperature. We found no curving of the lines even very close to the critical temperature ( $T - T_c < 5$  mK) if the cell was shaken after temperature equilibrium had been reached. Shaking the cell did not affect the deviated angle of the line within our precision of measurement. We have also looked for gravity effects in these fluids using a Fabry–Perot interferometer in the wedge mode, but have been unable to detect any suggestion of the characteristic sigmoid shape [29] in the fringes above or below the critical point even after waiting several days.

### 3. Data collection and analysis

#### 3.1. Data collection

For each data point, the minimum deviated angle was measured several times after which the temperature was changed and allowed to come to equilibrium before shaking the cell. The time span between shaking and taking the next set of measurements depended on the proximity of  $T_c$ , but typically the wait was from 4–12 hours. The critical point was defined as the temperature at which the meniscus would just appear or disappear after shaking the cell and allowing it to stand for several hours. Although strong opalescence was encountered near the critical point, we were still able to take reproducible measurements within 5 mK of the critical temperature. After about twenty-five points were taken, some pump oil condensed on the outer surfaces of the cell and shield. To remove this contaminant, the sealed cell was placed in a vapor degreaser for a few seconds; however, this caused a shift of 110 mK in the readings of the controlling thermistor relative to the critical point. An auxiliary thermistor imbedded deep in the cell body showed no change in the critical temperature, so the fluids were not contaminated. Since all of the data agrees whether taken before or after this occurrence or while raising or lowering the temperature, we make no distinction in presenting it in table 1 in order of increasing ( $T_c - T$ ).

Table 1

Coexistence curve data for methanol + cyclohexane.  $T_c - T$  is the temperature below critical in kelvin,  $n_1$  and  $n_2$  are the refractive indices of the upper and lower phases, respectively

$(T_c - T)$ (K)	$n_1$	$n_2$	$n_1 - n_2$	$(n_1 + n_2)/2$
0.0026	1.38155	1.3785	0.00305	1.38002
0.0074	1.38222	1.3774	0.00482	1.37981
0.0094	1.38218	1.37743	0.00475	1.3798
0.012	1.38233	1.37692	0.00541	1.37962
0.0124	1.38239	1.37677	0.00562	1.37958
0.0294	1.38292	1.3765	0.00642	1.37971
0.036	1.38307	1.37562	0.00745	1.37934
0.0484	1.38354	1.37575	0.00779	1.37964
0.0654	1.38406	1.37536	0.0087	1.37971
0.084	1.38429	1.3744	0.00989	1.37934
0.0864	1.38473	1.37484	0.00989	1.37978
0.094	1.38442	1.37411	0.01031	1.37926
0.1104	1.38494	1.37431	0.01063	1.37962
0.171	1.38557	1.37327	0.0123	1.37942
0.182	1.38612	1.37316	0.01296	1.37964
0.209	1.38644	1.37317	0.01327	1.3798
0.305	1.38676	1.37194	0.01482	1.37935
0.406	1.38745	1.37124	0.01621	1.37934
0.502	1.38804	1.37067	0.01737	1.37935
0.579	1.38849	1.37022	0.01827	1.37935
0.67	1.38912	1.37001	0.01911	1.37956
0.694	1.3891	1.36962	0.01948	1.37936
0.797	1.3895	1.36923	0.02027	1.37936
0.916	1.39025	1.36887	0.02138	1.37956
0.923	1.39013	1.36877	0.02136	1.37945
1.167	1.39106	1.36802	0.02304	1.37954
1.799	1.39348	1.36693	0.02655	1.3802
2.749	1.3959	1.36506	0.03084	1.38048
3.792	1.39762	1.36369	0.03393	1.38065
4.686	1.39849	1.36263	0.03586	1.38056
5.59	1.40014	1.36171	0.03843	1.38092
6.573	1.40169	1.36086	0.04083	1.38127
7.645	1.40297	1.36029	0.04268	1.38163
8.656	1.40434	1.35987	0.04447	1.3821
9.451	1.40534	1.35959	0.04575	1.38246
10.329	1.40606	1.35909	0.04697	1.38257
11.312	1.40729	1.35891	0.04838	1.3831
12.423	1.40818	1.35835	0.04983	1.38326
13.265	1.40904	1.35806	0.05098	1.38355
14.126	1.40955	1.35771	0.05184	1.38363
15.183	1.4107	1.35752	0.05318	1.38411
16.212	1.41167	1.35721	0.05446	1.38444
17.207	1.41249	1.35704	0.05545	1.38476
18.205	1.4132	1.35675	0.05645	1.38497
-0.241 ( $T > T_c$ )	1.37951			
-0.661	1.37926			
-1.363	1.37888			
-2.403	1.37825			
-3.436	1.37765			

Although we could determine the critical temperature to  $\pm 2.5$  mK by visual observation, a more precise value could be determined by using the method of Kouvel and Fisher [31] which assumes scaling and requires taking the numerical derivative of the data taken below  $T_c$ . The quantity  $T^* = [(1/\Delta n)d\Delta n/dT]^{-1} = (T_c - T)/\beta$  can then be constructed, allowing a least squares fit to determine  $T_c$  (independent of  $\beta$ ) to  $\pm 0.5$  mK and to a value consistent with that observed visually. We will show in the next section that the scaling assumption used above is not violated over the temperature range measured with this mixture.

### 3.2. Data analysis

From the refractive index data taken above and below  $T_c$  the shape of the coexistence curve, the critical concentration and the rectilinear diameter can be determined. From table 1 and the data taken above  $T_c$ , the coexistence curve was plotted. See fig. 2. The average of the refractive indices above and below the meniscus is a measure of the mean density of the fluid and is called the rectilinear diameter of the coexistence curve. A straight line drawn through the

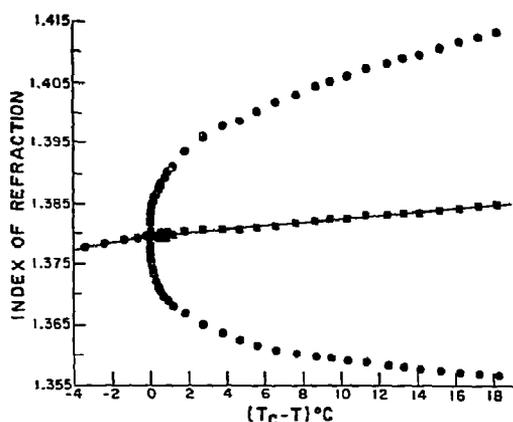


Fig. 2. The coexistence curve of methanol-cyclohexane as given in table 1. The data above the critical temperature ( $T_c = 45.474^\circ\text{C}$ ) has a slope of  $5.82 \times 10^{-4}/^\circ\text{C}$  and an intercept with the coexistence curve of 1.37966. The rectilinear diameter (average of the refractive index above and below the meniscus) is the (■) points and line bisecting the coexistence curve. The line is a least squares fit to  $(n_1 + n_2)/2 = A + B'(T_c - T)$  with  $A = 1.37956$  and  $B' = 2.96 \times 10^{-4}/^\circ\text{C}$  and where  $n_1$  and  $n_2$  are the refractive indices above and below the meniscus respectively.

data points above  $T_c$  intersects the rectilinear diameter at a point on the coexistence curve indicating that we are very close to the critical concentration. We found the critical refractive index, from the rectilinear diameter extrapolated to the critical temperature, to be  $1.37956 \pm 0.00005$ . From the data above the critical point the refractive index at the critical point is extrapolated to be 1.37966. By using the Lorentz-Lorenz relation (see the Appendix), the critical concentration was determined to be  $29.04 \pm 0.1\%$  by weight methanol.

It has been predicted [32-34] and observed [35] that the rectilinear diameter (mean density) has some sort of an anomaly near the critical point. However, this was not seen in this experiment (see figs. 2 and 3a). In using the Lorentz-Lorenz relation it is necessary to know the size of the anomaly in the refractive index and in the density. The refractive index anomaly has been measured [36] for this system and is too small by an order of magnitude to be observable in this experiment. A precise measurement of the thermal expansion or density anomaly is in progress on these fluids and preliminary data [37] shows this effect to be too small by several orders of magnitude to have been measured.

To analyze the coexistence curve and determine what the critical exponent  $\beta$  should be, a "properly weighted" least squares fit to our data, shown in fig. 4, is required. (We show in the Appendix that  $\Delta n$  is pro-

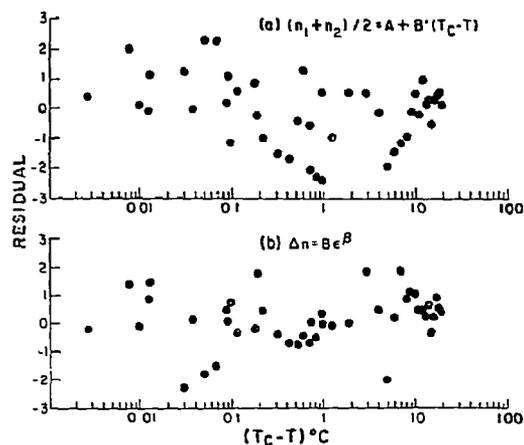


Fig. 3. The residuals from the fit to (a) the rectilinear diameter in fig. 2 and (b) our data in fig. 4. The residual is the amount the fitted line differs from the data point divided by the data point's error.

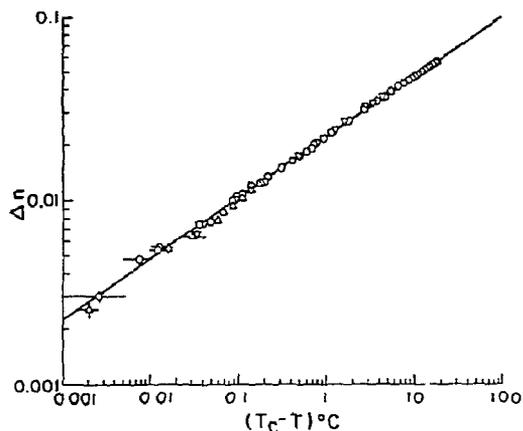


Fig. 4. The difference in refractive index (proportional to the volume fraction) above and below the meniscus as a function of  $T_c - T$ . The open circles are the data taken in this experiment, the triangles ( $\Delta$ ) are from ref. [39] and the inverted triangles ( $\nabla$ ) are from ref. [7]. The line is a fit to our data using simple scaling,  $\Delta n = Be^\beta$ , with  $\beta = 0.326 \pm 0.003$  and  $B = 0.143 \pm 0.008$  (uncertainties are three standard deviations).

portional to  $\Delta\phi$ , the change in volume fraction between the two phases. The proportionality constant is effectively independent of temperature so that our fit to  $\Delta n$  will give the same value for  $\beta$  as plotting the difference in volume fraction.) By “properly weighted” we mean that one needs [3] to propagate the temperature error into the refractive index error bars and take into account that one is fitting on a log-log scale and weight the points in the fit accordingly. We used the method described by Bevington [38] to obtain the fit (shown in fig. 4) to the function  $\Delta n = Be^\beta$  with  $\beta = 0.326 \pm 0.003$  and  $B = 0.143 \pm 0.008$  (the errors are three standard deviations). It is important to use a “properly weighted” fit to the data and also to have a sufficient number of data points over the temperature region studied so one can say with reasonable accuracy what is the best fit. Others [7,39] who have measured the coexistence curve for methanol–cyclohexane using refractive index techniques have fewer data points over a smaller temperature region and have inferred higher values for the critical exponent  $\beta$  ( $0.347 \pm 0.008$  and  $0.35 \pm 0.01$ ). However, their data are consistent with ours as shown in fig. 4 even though their values for  $\beta$  are different.

#### 4. Comments and conclusions

It has been shown that refractive index techniques are a valuable probe into critical behavior and that the difference in refractive index between two phases is effectively the same as the difference in volume fraction – the preferred order parameter in coexistence curve measurements in binary liquid mixtures.

There has been recent evidence that corrections to scaling as predicted by Wegner [2] are necessary for pure fluids and binary mixtures to explain the coexistence curve data. As seen in fig. 3b, a simple scaling relation works well for this data with corrections terms not significantly improving the fit [40]. It has been suggested [15] that extended scaling is not important in binary mixtures until  $\epsilon > 10^{-2}$  whereas it is necessary for pure fluids [12,13] for  $\epsilon > 10^{-4}$ . Our data corroborates this view. Since gravity effects [16] and corrections to scaling [17] can affect the coexistence curve fits in a similar manner, care must be taken in analyzing the data to correctly explain its features.

This result for  $\beta$  is in very good agreement with recent renormalization group calculations [18,19] for the Ising model and with recent measurements on pure fluids [13] and binary mixtures [14,15]. These results provide evidence that pure fluids and binary mixtures belong to the same universality class as the Ising (lattice-gas) model. This is particularly important since it allows the results of binary mixtures, where gravity effects are generally smaller and corrections to scaling do not appear until very far from the transition, to be compared to Ising model predictions much more simply.

#### Acknowledgement

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#### Appendix: Relation between $n$ and $\phi$

The index of refraction of a mixture of liquids is related to the volume fraction by the Lorentz–Lorenz relation

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

where  $n$  is the refractive index of the mixture,  $V$  is the total volume,  $\alpha_i$  is the polarizability per unit mass of the  $i$ th component and  $M_i$  is its mass. If we consider two components for which anomalies in the density and refractive index are small, then we have, above the critical point,

$$(n^2 - 1)/(n^2 + 2) = [(n_1^2 - 1)/(n_1^2 + 2)]\phi_1 + [(n_2^2 - 1)/(n_2^2 + 2)](1 - \phi_1). \quad (\text{A.1})$$

Below the critical point,

$$(n_u^2 - 1)/(n_u^2 + 2) = A_1\phi_1^u + A_2(1 - \phi_1^u), \quad (\text{A.2})$$

and

$$(n_L^2 - 1)/(n_L^2 + 2) = A_1\phi_1^L + A_2(1 - \phi_1^L). \quad (\text{A.3})$$

Here  $A_1 = (n_1^2 - 1)/(n_1^2 + 2)$ ,  $A_2 = (n_2^2 - 1)/(n_2^2 + 2)$ ,  $n_1$  ( $n_2$ ) is the refractive index of component 1 (2), and  $\phi_1$  ( $\phi_2$ ) is the volume fraction  $V_1/V$  ( $V_2/V$ ). The indices  $u$  and  $L$  designate the quantity in the upper ( $u$ ) or lower ( $L$ ) phase when the system is below  $T_c$ . If one subtracts eq. (A.3) from (A.2), the result is

$$[(n_u^2 - 1)/(n_u^2 + 2)] - [(n_L^2 - 1)/(n_L^2 + 2)] = (A_1 - A_2)(\phi_1^u - \phi_1^L),$$

which can be written as

$$\frac{3n_u^2 - 3n_L^2}{(n_u^2 + 2)(n_L^2 + 2)} = (A_1 - A_2)(\phi_1^u - \phi_1^L).$$

This gives the relationship between the volume fraction difference and the refractive index difference as

$$(\phi_1^u - \phi_1^L) = \left( \frac{3(n_u + n_L)}{(A_1 - A_2)(n_u^2 + 2)(n_L^2 + 2)} \right) (n_u - n_L), \quad (\text{A.4})$$

without approximation, assuming eqs. (A.2) and (A.3). The quantity  $k = 3(n_u + n_L)/[(A_1 - A_2)(n_u^2 + 2)(n_L^2 + 2)]$  is only slightly temperature dependent. For our fluids if  $T_c - T = 18.205$  K then  $k = 10.59$ . When  $T_c - T = 0$ ,  $k = 10.48$  and there is a change in  $k$  of 1% over a temperature interval of 18 K. The uncertainty in  $(n_u - n_L)$  ranges from 0.4% to 10% over the same 18 K range. The small systematic error in assuming  $k$  to be a con-

stant is thus small compared to our experimental uncertainty, and so the change in volume fraction is proportional to the change in refractive index between the two phases.

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