

Turbidity very near the critical point of methanol-cyclohexane mixtures

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We have measured the turbidity of a critical mixture of methanol and cyclohexane extremely close to the consolute point. The data span the reduced-temperature range $10^{-7} < t < 10^{-3}$, which is two decades closer to T_c than previous measurements. In this temperature range the turbidity varies approximately as $\ln t$, as expected from the integrated form for Ornstein-Zernike scattering. A thin cell (200- μm optical path) with a very small volume (0.08 ml) was used to avoid multiple scattering. A carefully controlled temperature history was used to mix the sample and to minimize the effects of critical wetting layers. The data are consistent with a correlation-length amplitude $\xi_0 = 3.9 \pm 1.0 \text{ \AA}$, in agreement with the value 3.5 \AA calculated from two-scale-factor universality and heat-capacity data from the literature.

I. INTRODUCTION

At the present time, the theory of critical fluctuations in fluids predicts the viscosity and the fluctuation decay rate in the form of coupled integral equations with the wave vectors in these integrals scaled by the correlation length.¹ A careful test of the theory requires independent measurements of three quantities, the viscosity, the decay rate, and the correlation length, for the same fluid system asymptotically close to the critical point. As a first step in such a test, we have explored the technical problems encountered in simultaneously measuring the turbidity and the spectrum of quasielastic scattering in a thin sample of the binary liquid mixture methanol-cyclohexane extremely close to its consolute temperature (T_c).

In the present work we report turbidity (τ) results which span the reduced-temperature range $10^{-7} < t < 10^{-3}$ where $t \equiv (T - T_c)/T_c$. Because these data approach T_c so closely, we find a large range where, roughly speaking, $\tau \propto \ln t$, as expected from the Ornstein-Zernike theory. The amplitude of the correlation length derived from our data, $\xi_0 = 3.9 \pm 1.0 \text{ \AA}$, is in agreement with the value 3.5 \AA which we obtained from previously published heat-capacity data for this mixture and the concept of two-scale-factor universality.

In keeping with the present limited experimental objectives, we have not made a detailed study of the static structure factor. Instead, we have used the equations given by Puglielli and Ford² to relate the turbidity we measured to the correlation range for the case of Ornstein-Zernike scattering. For a mixture of the critical composition, the divergent part of the wave-vector-dependent osmotic susceptibility, χ_T , has the temperature dependence

$$\chi_T = \chi_0 t^{-\gamma} (1 + q^2 \xi^2)^{-1}. \tag{1.1}$$

Then the equation used to fit the turbidity τ is

$$\tau = \tau_0 t^{-\gamma} f(a), \tag{1.2}$$

where

$$f(a) = (2a^2 + 2a + 1)a^{-3} \ln(1 + 2a) - 2(1 + a)a^{-2}, \tag{1.3}$$

$$a = 2(q_0 \xi)^2 = 2(2\pi n \xi / \lambda_0)^2. \tag{1.4}$$

(Here n is the index of refraction of the mixture and λ_0 is the wavelength of light in vacuum.) The coefficient τ_0 is related to thermodynamic quantities via

$$\tau_0 = \frac{\pi^3}{\lambda_0^4} \left[\frac{\partial n^2}{\partial x} \right]_T^2 k_B T \chi_0. \tag{1.5}$$

(Here x is the mole fraction.) We measured $\tau_0 = 9.6 \times 10^{-6} \text{ cm}^{-1}$ for methanol-cyclohexane mixtures when $\lambda_0 = 6328 \text{ \AA}$. This value of τ_0 is almost identical to the corresponding coefficient of the turbidity divergence at the liquid-vapor critical point of sulfur hexafluoride. (The SF_6 data of Puglielli and Ford² are consistent with $\tau_0 = 9.3 \times 10^{-6} \text{ cm}^{-1}$ at 6328 \AA .) Thus, for the purpose of making turbidity measurements near a critical point, a methanol-cyclohexane mixture is an accurate model of the liquid-vapor system SF_6 . This model system is expected to show extremely weak stratification in the earth's gravitational field in contrast to SF_6 . The densities of methanol and cyclohexane are within 2% of each other and the directly determined excess volumes of mixing are less than 1% of the molar volume at all compositions just above the consolute temperature.³

We now turn to a description of the experimental techniques we have used and the problems that we encountered. Then we will compare our results with other measurements. We shall conclude with a comment concerning possible improvements in future work.

II. EXPERIMENTAL DETAILS

A. Sample cell

The sample cell was constructed from two Homosil fused quartz windows⁴ as shown in Fig. 1. These windows were bonded to a fused quartz spacing ring with a glass frit (Vitta Corporation⁴). The spacing ring was ground to be 0.2 mm thick. It defined the path length through the sample. The surface-to-volume ratio of this cell was 100 cm^{-1} .

The cell was filled and the concentration was adjusted several times until the critical concentration was achieved. This process was facilitated using the demountable seals illustrated in Fig. 2. Two flat indium disks were cut with a diameter considerably exceeding the 1-mm diameter of the loading ports. Aluminum boots were constructed to fit over these seals. Pressure was applied to the boots with the retaining screws until the indium flowed. When correctly sealed, the indium would wet the glass around the holes uniformly. No radial leakage path could be observed. These seals were effective even though the pressure within the cell increased almost 1 atm upon warming the cell from room temperature to well above T_c .

The sample cell, as well as all glassware, metal, and plastic parts used in the sample loading were soaked in an 8% solution of Micro Laboratory Cleaning Solution⁴ for 20 min at 100°C . All pieces were rinsed in distilled water until the glass surfaces were uniformly wetted. They were then dried in an evacuated, heated dessicator for a minimum of 12 h and transferred to a dry nitrogen environment while still hot. This procedure was used to clean the cell and to decrease the chance of accidental contamination of the sample by water, an impurity known to strongly affect the properties of methanol-cyclohexane mixtures.

B. Materials

Mallinkrodt "SpectrAR" spectrophotometric grade solvent cyclohexane and Baker analyzed reagent "photorex" absolute methanol were used to prepare the mixture.⁴ Both components came sealed, and were specified by their manufacturers to contain no more than 0.02% water impurity. No special effort was made to further purify these

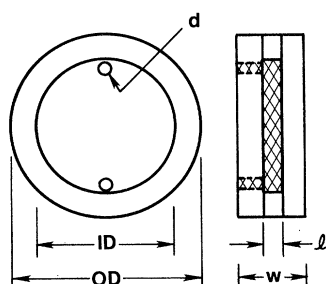


FIG. 1. Sample cell. The important dimensions are the following: inside diameter, $ID=2.22 \text{ cm}$; outside diameter, $OD=2.86 \text{ cm}$; overall thickness, $w=0.66 \text{ cm}$; optical path, $l=0.02 \text{ cm}$; and filling hole diameter, $d=0.1 \text{ cm}$. The fluid filled volume is shaded.

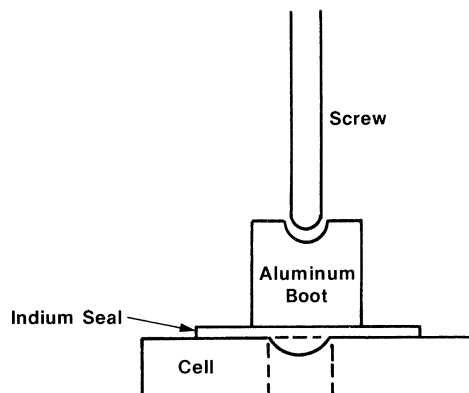


FIG. 2. Sealing mechanism.

components. Care was taken to open the bottles only in a dry nitrogen atmosphere and in the presence of a silica-gel dessicant. The critical concentration was determined by observing the behavior of the meniscus near T_c . We found it to be 0.2898 by volume of methanol. This value is 1% higher than that reported in the literature,^{5,6} though recent investigations^{3,7} do not differ significantly from this figure. The sample concentration was 0.07% (by volume) low in methanol. With this concentration the meniscus would remain within the 1-mm-diam field of view at reduced temperatures of 10^{-8} . The critical temperature was at 45.83°C after the sample cell was loaded; however, an upward drift in T_c was subsequently discovered.

C. Temperature control and measurement

In order to achieve μK temperature control at 46°C , great care was given to the design of both the thermostat and the controlling electronics. To reduce temperature gradients, we used a multilayered thermostat designed with three actively thermostated outer shells and one passive inner shell. The thermostat was not evacuated; each metal shell was insulated from its neighbors by a 1 mm air gap. Typically, the shells were 5 mm thick. Temperature measurement was accomplished with ac ratio transformer bridges and thermistor sensors. Long-term temperature stability of $\pm 15 \mu\text{K}$ was observed over 18 h and stability of $\pm 2 \mu\text{K}$ over 20 min periods were not uncommon. The sample's turbidity changes in response to a 1 mK change in the set point of the innermost active shell indicated an equilibration time of no more than 3 min.⁸

The primary source of uncertainty in t was introduced by the observed upward drift in T_c . When the sample was held within 100 mK of T_c , this drift was virtually linear with an average rate of $500 \mu\text{K}/\text{d}$ ($21 \mu\text{K}/\text{h}$). Because T_c steadily increased, the drift could not be explained as a preferential loss of a sample component. More likely, it was due to residual water migrating from the quartz cell into the sample. This explanation is supported by the observation of a nearly discontinuous increase in T_c upon heating the sample to 50°C . These jumps were attributed to the accelerated desorption of the water from the walls which would be expected at the elevated temperature.

Over the course of several months of measurements, T_c increased by 0.16 K. If this were a result of water desorption, the quantity of water required would be 43 parts per million by volume⁷ which corresponds to about 14 monolayers of water for each interior surface of the sample cell. Dry synthetic quartz surfaces are known to adsorb much larger quantities of water at typical laboratory conditions.⁹

The standard deviation of a measurement of t , σ_t , can be found by combining in quadrature three quantities: (1) the imprecision in the determination of T_c (see below), (2) the imprecision in the measurement of temperature, and (3) the product of the drift rate and the time required for a turbidity measurement (15 min). We estimate the uncertainty in t to be

$$(\sigma_t/t)^2 = 1.7 \times 10^{-16} t^{-2} + 8 \times 10^{-8}. \quad (2.1)$$

The uncertainty is 1% at $t = 1.3 \times 10^{-6}$ and 100% at $t = 1.3 \times 10^{-8}$.

D. Determination of the critical temperature

After a great deal of experimentation, we selected a method of measurement of the "momentary" critical temperature which exploited the rapid thermal response of the inner stages of the thermostat and the sample as well as the secular increase in T_c . We note that the sample's turbidity responds reversibly to small changes in the set point of the thermostat (with a 3 min lag), as long as the sample is maintained above T_c . Furthermore, the turbidity of this thin sample is a weak function of t . To determine T_c we set the thermostat to a temperature just above the expected critical temperature and monitored the turbidity. As the critical temperature slowly increased, a distinct break occurred in the turbidity versus time record. Then the turbidity began a more rapid, linear, increase as a function of time. In this regime, the increase in turbidity did not respond to small changes in the set point of the thermostat. The break in the turbidity versus time curve was taken to be T_c . It could be located with a precision corresponding to $\pm 3 \mu\text{K}$.

E. Mixing the sample

Before taking each series of data the sample was heated to 50°C ($t = 10^{-2}$) and maintained at that temperature for at least 12 h. During this time the thermostat was placed so that the optical axis of the sample cell was vertical. (A small bubble level facilitated this.) Thorough mixing via diffusion will occur under these conditions.

Excursions of the sample below T_c were sufficiently small (much, much less than 1 mK) and of sufficiently short duration (a few minutes) that the sample did not demix on a macroscopic scale. The sample was quickly restored to a one-phase state by heating it 100 mK above T_c without displacing the optical axis from its usual horizontal position.

If the sample's temperature is abruptly reduced from 100 mK above T_c to 1 mK above T_c , the turbidity abruptly increases as expected on the time scale of a few minutes. This is followed by a small, slow decrease in turbidity with a time constant on the order of 5 h. We attribute the slow decrease in turbidity to the slow formation

of wetting layers, a phenomenon which is known to be ubiquitous near critical points.^{10,11} At equilibrium, such layers are expected to have a thickness which is at least on the order of a correlation length and may be several micrometers. Other experiments on methanol-cyclohexane mixtures suggest methanol-rich layers would form on the quartz walls of our cell and around the small vapor bubble in the cell.¹¹ This would tend to deplete the methanol concentration elsewhere in the sample cell. Both layers would reduce the turbidity. To minimize the influence of layer formation on our data, we preceded each measurement close to T_c by an equilibration period 100 mK above T_c where the correlation length is 0.06 μm and the layers observed with other mixtures are quite thin.¹² After the equilibration period, we abruptly reduced the sample's temperature towards T_c and recorded the turbidity data within a few minutes, a time much shorter than that required for the wetting layers to thicken at temperatures very close to T_c .

F. Optical arrangement and data acquisition

The optical components used to measure the sample's turbidity were a laser, a beam splitter to divide the beam into a reference beam and a sample beam, and two identical detectors consisting of 25-mm-diam silicon solar cells. The laser used was a Spectra-Physics⁴ Model 125 helium-neon laser which produced 21 mW at 6328 Å. A neutral-density filter inserted between the laser and the beam splitter reduced the input intensity to 2 mW. The reference beam went directly from the beam splitter to one detector. The sample beam was weakly focused (with a 40 cm focal length lens) through windows into the sample within the thermostat. The light scattered by the sample and absorbed within the thermostat heated the innermost shell 0.21 mK/mW. This heating induces a small temperature offset ($t = 10^{-6}$) between the innermost shell and the one just outside it. The fluctuations in this offset ($\delta t < 3 \times 10^{-8}$) are negligible and its temperature dependence is quite weak. With the 40 cm focal length input lens, the beam diameter was 170 μm in the sample. The beam waist is 7 cm long and the beam's full angular spread is 4.4 mrad.

The turbidity τ is simply related to the ratio of the light intensity incident upon the sample I_0 to the light intensity transmitted I_T through a thickness l of sample

$$\tau l = \ln(I_0/I_T). \quad (2.2)$$

Using the techniques described below, we actually measured and recorded the quantity E :

$$E = \ln(i_R/i_T), \quad (2.3)$$

where i_R is the photocurrent produced by the reference beam detector and i_T is the photocurrent produced by the transmitted beam detector. If the photocurrents are accurately proportional to the light intensity incident on the detectors, the relationship between E and the turbidity is

$$E = \tau l + E_0. \quad (2.4)$$

E_0 is an instrumental constant, which, in principle, could

be determined by the arduous process of calibrating the beam splitter and both solar cell detectors and by measuring the reflectance of the lens and windows between the beam splitter and the sample detector. Instead, we have chosen to determine E_0 by analyzing the data in the fashion described in Sec. III.

It has been shown that the current generated by a solar cell is insensitive to ambient temperature variations and is accurately proportional to the incident light intensity over five decades in current, provided that the current is passed through an external short circuit.¹³ We approached this ideal condition by passing the current from each solar cell into a 308 operational amplifier used as a current-to-voltage converter. A precision resistor (20 k Ω) was used as the transimpedance element and an input nulling circuit was added to ensure that the current was accurately zero in absence of illumination. Typically, this circuit presented a load resistance of 0.067 Ω to the silicon solar cell.

The outputs of the two current-to-voltage converters were fed into an analog ratio circuit [Evans Associates Model 4122 (Ref. 4)] to compute the instantaneous photocurrent ratio and its logarithm. The output of this circuit was sent through a low-pass filter (1 sec time constant) and then recorded with a suitably expanded scale. (The photocurrent ratio changes less than 6% throughout the range $10^{-7} < t < 10^{-3}$.)

We verified the accuracy of the analog circuitry by changing the light intensity incident on the beam splitter by 100%. The computed ratio changed by 2%. Thus, the expected laser fluctuations of $\pm 1\%$ would cause errors in the ratio of $\pm 0.02\%$. This small quantity is much less than the very slow fluctuations which we observed in the sample's extinction and which we attribute to statistical fluctuations in the turbidity of the very small illuminated volume (5×10^{-6} cm⁻³).

III. DATA REDUCTION AND RESULTS

The photocurrent ratio data are plotted as a function of t in Fig. 3. The same data are converted to turbidity via Eq. (2.3) and plotted again in Fig. 4.

By combining Eqs. (1.2)–(1.4) and (2.4), the attenuation can be expressed as the following:

$$E = E_0 + \tau_0 t^{-\gamma} f(a). \quad (3.1)$$

This function was fit to the data using a widely available nonlinear least-squares program.¹⁴ The critical exponents were fixed at the theoretical values as determined by renormalization group techniques:¹⁵ thus we assume $\xi = \xi_0 t^{-\nu}$ and $\gamma = 1.241$ and $\nu = 0.630$. The index of refraction was taken to be the value measured by Jacobs:⁶ $n = 1.37966$. The fitted parameters were τ_0 , ξ_0 , and the instrumental parameter E_0 . T_c was not a fitted parameter. The data are best described by the values $\tau_0 = 9.62 \times 10^{-6}$ cm⁻¹, $\xi_0 = 3.87$ Å, and $E_0 = 1.0613$. The function resulting from the fit is shown as a solid curve in Figs. 3 and 4. The difference between the fitted function and the data are shown on the top part of Fig. 4.

One measure of the uncertainty in the fitted value of ξ_0 is the diagonal term in the error matrix.¹⁴ By this mea-

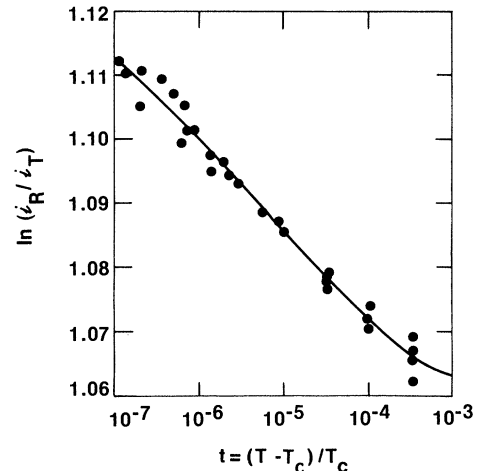


FIG. 3. The natural logarithm of the ratio of photocurrents as a function of the reduced temperature. The solid curve represents Eq. (3.1).

sure we obtain $\xi_0 = 3.87 \pm 0.97$ Å. In fact, the correlation between ξ_0 and τ_0 is extremely high. This is a consequence of our decision to use such a short optical path

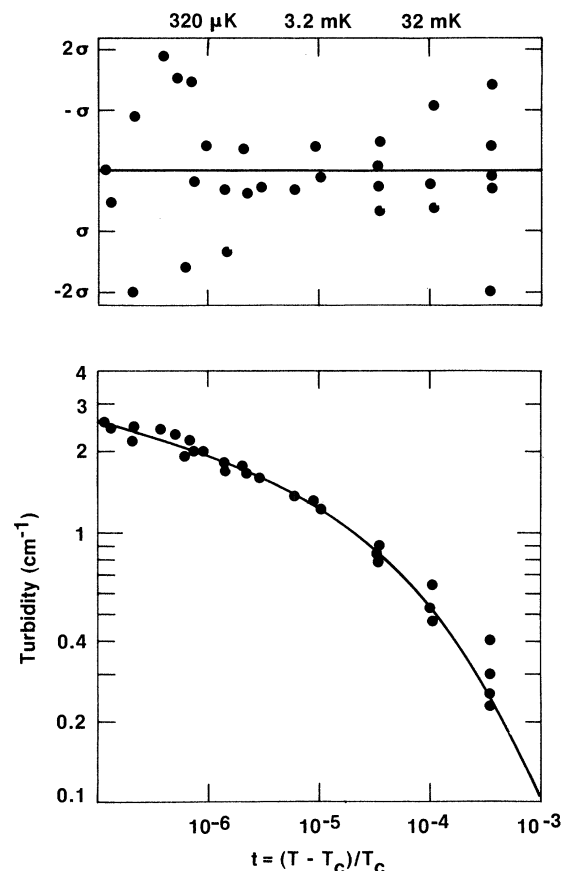


FIG. 4. Bottom: Turbidity as a function of the reduced temperature. The solid curve represents Eq. (3.1) with the parameters: $\xi_0 = 3.87$ Å, $\tau_0 = 9.62 \times 10^{-6}$ cm⁻¹, and $E_0 = 1.0613$. Top: The data points are subtracted from the fitted curve and the differences (in units of 0.101 cm⁻¹) are plotted as a function of t .

($l=200\ \mu\text{m}$) that almost all of our data are necessarily confined to the region very close to T_c where the weak temperature dependence of the turbidity is predicted to be

$$\tau = \frac{\tau_0 t^{0.019}}{\xi_0^2} \ln(1 + 4q_0^2 \xi_0^2 t^{-1.26}). \quad (3.2)$$

If τ_0 were determined by additional data taken farther from T_c (in the range spanned by many earlier turbidity measurements on other fluids) the present data and theoretical framework could have been used to determine ξ_0 (and E_0) with a precision on the order of 2% of ξ_0 .

IV. COMPARISON WITH OTHER RESULTS

The value of ξ_0 which we have obtained may be compared with four other values of ξ_0 . Three are derived from quite different optical measurements on methanol-cyclohexane mixtures and the fourth is obtained from our reinterpretation of heat capacity data.

Sorensen *et al.*¹⁶ measured the quasielastic spectrum of scattered light. They obtained values of ξ_0 between 2.38 and 2.85 Å, depending upon the model they used to interpret their data. The corresponding values of ν ranged from 0.627 to 0.654. Hartley *et al.*¹⁷ measured an anomaly in the real part of the index of refraction and obtained the value $\xi_0=4.7\ \text{Å}$ with $\nu=0.60$. Yosida¹⁸ measured the intensity of light scattered at 90° and obtained the value $\xi_0=4.1 \pm 0.5\ \text{Å}$ with $\nu=0.65$.

The fourth value of ξ_0 results from combining specific heat data with the concept of two-scale-factor universality. The hypothesis of two-scale-factor universality predicts that a universal relationship exists between the scale factor for the correlation length and the two scale factors required to describe the thermodynamic anomalies near critical points. In favorable cases, experiments near liquid-vapor critical points¹⁹ and liquid-liquid consolute points^{20,21} are consistent with this hypothesis with an accuracy on the order of $\pm 5-10\%$ of ξ_0 . We shall employ this hypothesis in the form

$$\xi_0 = R_\xi \left[\frac{M_w k_B}{\rho_c \alpha A} \right]^{1/3}. \quad (4.1)$$

Here R_ξ is the appropriate "universal" amplitude ratio, whose theoretical value for fluids is 0.270 ± 0.01 (calculated by renormalization group techniques);²² M_w is the average molecular weight of the mixture (0.0689 kg/mole); ρ_c is the critical density ($753.6\ \text{kg/m}^3$ from the data of Ref. 3); and α and A are the parameters characterizing the specific heat divergence as T_c is approached from above. Anisimov *et al.*²³ measured the heat capacity of methanol-cyclohexane mixtures and expressed their results in the form

$$C_{px} = At^{-\alpha} + B = 4.3t^{-0.125} + 132\ \text{J mole}^{-1}\ \text{K}^{-1}. \quad (4.2)$$

We can estimate the value of A that Anisimov *et al.*

would have obtained if they had chosen $\alpha=0.110$ (in agreement with current theoretical estimates¹⁵) by observing that both α and A are determined by dC_{px}/dt at values of t on the order of $10^{-3 \pm 1}$. Thus the correlation between α and A imposed by their data is approximately

$$-t \frac{dC_{px}}{dt} = \alpha A t^{-\alpha} \approx 1.275\ \text{J mole}^{-1}\ \text{K}^{-1}. \quad (4.3)$$

From Eq. (4.3) we estimate $A=5.42\ \text{J/mole K}$ if $\alpha=0.110$; hence we obtain $\xi_0=3.47\ \text{Å}$ via Eq. (4.1). We expect ξ_0 obtained by this route has an accuracy near $\pm 10\%$, similar to the accuracy attained when other high quality calorimetric data have been used to estimate ξ_0 . (The C_{px} data in Ref. 21 have been analyzed with many values of α . For these data, our procedure for estimating A upon changing α from 0.125 to 0.110 leads to an error which is less than $0.05A$. Such a small error in A leads to a 2% error in ξ_0 .)

The primary source of error in determining ξ_0 from the three optical methods and from the C_{px} data is the uncertainty about which theoretical model to use in the analysis (and which numerical values to be used for the parameters in the model). We have not critically reviewed this field; however, we observe that there are fewer assumptions made in analyzing the C_{px} data than in analyzing the optical data. We expect the various values of ξ_0 would become more nearly consistent if all the optical data were reanalyzed using the more recent values of the theoretical parameters.

V. SUMMARY

We have measured the temperature dependence of the turbidity in a new regime which is closer to the critical point than previous experiments. In this regime the turbidity exhibits a weak temperature dependence as expected. We have compared our data with the integrated form of the Ornstein-Zernike theory to obtain an estimate of the correlation-length amplitude $\xi_0=3.9 \pm 1.0\ \text{Å}$. This value of ξ_0 is close to the value $\xi_0=3.47\ \text{Å}$ which we estimated from the C_{px} data of Anisimov *et al.* The precision of our measurement of ξ_0 could be greatly increased if our data extended further from T_c . This would have been possible if our sample cell were designed to have a second optical path through the fluid sample, which greatly exceeded the $200\ \mu\text{m}$ path we used.

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- ¹H. C. Burstyn, J. V. Sengers, J. K. Bhattacharjee, and R. A. Ferrell, *Phys. Rev. A* **28**, 1567 (1983).
- ²V. G. Puglielli and N. C. Ford, Jr., *Phys. Rev. Lett.* **25**, 143 (1970).
- ³A. N. Campbell and S. C. Anand, *Can. J. Chem.* **50**, 1109 (1972).
- ⁴In order to describe materials and experimental procedures adequately, it was occasionally necessary to identify commercial products by manufacturers's name or label. In no instance does such identification imply endorsement by the National Bureau of Standards, nor does it imply that the particular product or equipment is necessarily the best available for the purpose.
- ⁵Y. Yosida and A. Ikushima, *J. Phys. Soc. Jpn.* **45**, 1949 (1978).
- ⁶D. T. Jacobs, D. J. Anthony, R. C. Mockler, and W. J. O'Sullivan, *Chem. Phys.* **20**, 219 (1977); D. T. Jacobs, Ph.D. thesis, University of Colorado, 1976.
- ⁷J. L. Tveekrem and D. T. Jacobs, *Phys. Rev. A* **27**, 2773 (1983).
- ⁸R. Kopelman, Ph. D. thesis, University of Maryland, 1983.
- ⁹S. Dushman, *Scientific Foundations of Vacuum Technique*, 2nd ed., edited by J. M. Lafferty (Wiley, New York, 1962), p. 469 and pp. 459–491.
- ¹⁰M. R. Moldover and J. W. Schmidt, *Physica D* (to be published).
- ¹¹M. R. Moldover and J. W. Cahn, *Science* **207**, 1073 (1980).
- ¹²D. Beaglehole, *J. Chem. Phys.* **73**, 3366 (1980); C. Frank and S. E. Schnatterly, *Phys. Rev. Lett.* **26**, 763 (1982); D. Beysens and S. Leibler, *J. Phys. (Paris) Lett.* **43**, L133 (1982).
- ¹³P. G. Witherell and M. E. Faulhaber, *Appl. Opt.* **9**, 73 (1970).
- ¹⁴P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences* (McGraw-Hill, New York, 1969).
- ¹⁵J. Zinn-Justin, in *Phase Transitions, Cargese, 1980*, edited by M. Levy, J. C. Le Guillou, and J. Zinn-Justin (Plenum, New York, 1981), pp. 349–370; J. C. Le Guillou and J. Zinn-Justin, *Phys. Rev. B* **21**, 3976 (1980).
- ¹⁶C. M. Sorensen, R. Mockler, and W. O'Sullivan, *Phys. Rev. A* **16**, 365 (1977).
- ¹⁷C. Hartley, D. Jacobs, R. Mockler, and W. O'Sullivan, *Phys. Rev. Lett.* **33**, 1129 (1974).
- ¹⁸Y. Yosida, *Phys. Lett.* **65A**, 161 (1977).
- ¹⁹J. V. Sengers and M. R. Moldover, *Phys. Lett.* **66A**, 44 (1978).
- ²⁰E. Bloemen, J. Thoen, and W. Van Dael, *J. Chem. Phys.* **73**, 4628 (1980).
- ²¹G. Sanchez, M. Meichle, and C. W. Garland, *Phys. Rev. A* **28**, 1647 (1983).
- ²²C. Bervillier and C. Godreche, *Phys. Rev. B* **21**, 5427 (1980).
- ²³M. A. Anisimov, A. V. Voronel', and T. M. Ovodova, *Zh. Eksp. Teor. Fiz.* **61**, 1092 (1971) [*Sov. Phys.—JETP* **34**, 583 (1972)].