Measuring Turbidity in a Near-Critical, Liquid–Liquid System: A Precise, Automated Experiment[1]

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A ground based ($1g$) experiment is in progress that measures the turbidity of the density-matched, binary fluid mixture methanol–cyclohexane extremely close to its liquid–liquid critical point. By covering the range of reduced temperatures $t \equiv (T - T_c)/T_c$ from 10^{-8} to 10^{-2}, the turbidity measurements should allow the Green–Fisher critical exponent η to be determined. This paper reports measurements showing $\pm 0.1\%$ precision of the transmitted and reference intensities, and $\pm 4\,\mu\mathrm{K}$ temperature control near the critical temperature of 320 K. Preliminary turbidity data show a nonzero η consistent with theoretical predictions. No experiment has precisely determined a value of the critical exponent η, yet its value is significant to theorists in critical phenomena. Relatively simple critical phenomena, as in the liquid–liquid system studied here, serve as model systems for more complex behavior near a critical point.

1. INTRODUCTION

Critical phenomena provide intriguing and essential insight into many issues in condensed matter physics because of the many length scales involved. As a result, critical point phenomena have been studied over a long period of time, with substantial recent effort toward modeling complex systems near a critical point. Large density or concentration fluctuations near a system's critical point effectively mask the identity of the system and produce universal phenomena which have been well studied in

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simple liquid–vapor and liquid–liquid systems. Such systems have provided useful model systems to test theoretical predictions which can then be extended to more complicated systems. Along various thermodynamic paths, several quantities exhibit a simple power-law dependence close to the critical point. The critical exponents describing these relationships are universal and should depend only on a universality class determined by the order-parameter and spatial dimensionality of the system. Liquid–gas, binary fluid mixtures, uniaxial ferromagnetism, polymer–solvent, and protein solutions all belong to the same universality class: the three-dimensional Ising model. The diversity of critical systems that can be described by universal relations indicates that experimental measurements on one system should yield the same information as on another.

The earth's gravitational field plays a significant role in highly compressible systems, such as a simple liquid near its liquid–gas critical point. Several individuals have reported on the effects (or noneffects) of gravity on turbidity measurements near a critical point. Leung and Miller [1] reported a significant gravitational effect on the turbidity when measured in a liquid–gas system. Xenon is such a system and could exhibit such effects as a turbidity which reaches its maximum before T_c is reached and an apparent η approaching one [1]. Cannell [2] argues that Leung and Miller overestimate the effect by a factor of 10 because of the assumptions used. However, both agree that measurements close to T_c ($t < 10^{-5}$) in a liquid–gas system would be significantly affected and prevent a valid determination of the critical exponent η. The only way to avoid such a difficulty for a liquid–gas system is to perform the experiment in a low-gravity, space shuttle environment [3].

However, gravity is much less important in other system types, such as a binary liquid mixture, not only because liquids are much less compressible but also because the liquids can be density matched to reduce gravitational field effects further. A binary liquid mixture exhibiting an upper critical consolute point has two components which are partially miscible below a certain temperature and completely miscible above. Below the critical temperature, a lower phase and an upper phase coexist in equilibrium where each phase is rich in one component and the order parameter usually chosen is volume fraction. Gravity causes a density (concentration) gradient which takes some time to establish [4]. The characteristic time depends on the density match; the better the match, the longer it takes. For methanol–cyclohexane, a stable concentration gradient would form only after months of waiting.

This paper details the technique and instrumentation used to measure the transmitted light intensity to 0.1% and control the temperature to a few microkelvins at room temperature. This capability will allow us to test

existing theory and also extend universal behavior into new areas. One significant theoretical prediction which has eluded convincing experimental verification is the value of Fisher's "elusive exponent η" [5], which was first proposed [6] to describe how the correlation function behaves at T_c. This exponent η could be called the critical correlation-correction exponent since it corrects the $1/r$ dependence exponent of the critical point's spatial correlation function, but we refer to η as the Green–Fisher exponent [7]. Recent field theoretical analysis and partial differential approximates give the theoretical values [8–10] for γ, v, and η shown in Table I. Ferrell [7] has suggested from his calculations that η might be measurable from turbidity measurements using his new analysis.

An experimental determination of η can be done from the total light being scattered (turbidity), in a density-matched, binary fluid mixture of methanol and cyclohexane. Because of the small value of η ($\eta \approx 0.033$), its effect can be observed only by an extraordinarily precise light scattering measurement very close to the critical point. Just such a turbidity measurement is in progress and will provide a wealth of detail about behavior very near the critical point for a model system in a controlled environment.

Light scattering studies of fluids can take two forms: measuring the light intensity as a function of angle $I(\theta)$ or measuring the transmitted light intensity ($\theta = 0$), which determines the turbidity. By looking at one or several angles from the incident beam, the scattered light intensity can be used to determine the correlation length. The analysis is simple if the light reaching the detector has been scattered only once. If the light has been scattered multiple times, then the analysis becomes very difficult. Shanks and Sengers [11] have looked at the effect of double scattering on the light intensity $I(\theta)$ in binary fluid mixtures and conclude that corrections are necessary even when using matched refractive indices and/or very small sample volumes. This was confirmed by Bailey and Cannell [12], who have developed a simulation to correct for multiple scattering. Thus, while measuring the light scattered as a function of angle, a relatively small amount of multiple scattering can be a significant percentage of the light observed and it is essential to correct the data for multiple scattering [12].

Table I. Theoretical Values of the Critical Exponents, Which Assume the Scaling Relation $\gamma = (2 - \eta) v$

γ	v	η	Ref. No.
1.237 ± 0.002	0.630 ± 0.0015	0.0359 ± 0.0007	8
1.2390 ± 0.0025	0.630 ± 0.0015	0.033 ± 0.006	9
1.2395 ± 0.0004	0.632 ± 0.001	0.039 ± 0.003	10

While the theoretical predictions agree within their quoted uncertainty, the experimental situation is less well-known. Three principal techniques have been used to look for η and they all involve scattering phenomena using either x-rays, neutrons, or light. To determine η, the experiment must reach large values of $k\xi$, where k is the scattering vector, which varies as the reciprocal of the wavelength λ, and ξ is the correlation length. X-rays and neutrons can achieve large values of k but those experiments have difficulty in getting close to the critical point (large ξ). Moreover, the wavelength of the incident radiation must be long compared to the range of the interatomic forces, which is difficult to do in present x-ray and neutron scattering experiments. Light scattering, on the other hand, has relatively long wavelengths (smaller k values) and must resort to a very close approach to the critical point (large ξ). If light intensity is measured as a function of angle, then a close approach to the critical point is precisely where the problem of multiple scattering is most pronounced.

A variety of investigators has attempted a measurement of the elusive exponent η using one of the three scattering probes. Tracy and McCoy [13] examined the experimental results before 1975 and concluded that "no experiment to date unambiguously and directly establishes that the critical exponent η is greater than zero." Table II summarizes several experimental attempts since then [14–20]. Angular scattering of photons or neutrons can determine the exponents γ and ν, but only after careful consideration of multiple scattering effects, which limits the precision and hence the ability to calculate η accurately from the scaling relation.

In 1991, Ferrell [7] gave a new analysis of the problem in which η appears explicitly and could be determined from turbidity measurements.

Table II. Experimental Determinations Put an Upper Bound of 0.06 for η from Light (γ), X-Ray (x), or Neutron (n) Scattering as a Function of Angle

Probe	System	η	Correct for multiple scattering?	Ref. No.
γ	LG[a]	0.03 ± 0.03	No	14
γ	LL[b]	0.017 ± 0.015	2nd order	15
x	LL	0.03 ± 0.03	No	16
γ	LL	0.045 ± 0.010	No	17
γ	LL	$0.027 \rightarrow 0.046$	Yes	18
γ, n	LL	0.042 ± 0.007	No	19
γ	PB[c]	0.038 ± 0.003	No	20

[a] Liquid–gas system.
[b] Liquid–liquid system.
[c] Polymer blend.

The total incremental intensity of light scattered per unit length is defined as the turbidity $\tau = L^{-1} \ln(I_0/I)$, where L is the optical path length and I and I_0 are the transmitted and incident light intensities. The turbidity was related to critical phenomena by Puglielli and Ford, who assumed Ornstein-Zernike scattering [21] far from the critical point:

$$\tau = \tau_0(1+t)\,t^{-\gamma}\left\{\frac{2a^2+2a+1}{a^3}\ln(1+2a)-\frac{2(1+a)}{a^2}\right\}\quad \text{for }\eta = 0,\quad t > 10^{-5}$$

$$(1)$$

An expression for the turbidity explicitly involving η was developed by Calmettes et al. [22], which is incorrect close to the critical point [23]. In 1991, Ferrell [7] used a correct treatment with a modified Fisher-Burford [24] form when very close to the critical point to obtain:

$$\tau = \frac{2\tau_0 t^{-\gamma}}{a}\left\{L-1-\frac{\eta}{4}L^2+8.37\eta\right\},\qquad t < 10^{-5}\tag{2}$$

where $\tau_0 = (\pi^3/\lambda_0^4)[\partial n^2/\partial\phi]^2\,k_B T_c \chi_0$; $a = 2k_0^2\xi^2$; $L = \ln(2a)$; $k_0 = 2\pi n/\lambda_0$; $t = (T-T_c)/T_c$; n is the refractive index of the mixture; λ_0 is the wavelength of the light in vacuum; v, γ, and η are critical exponents; and τ_0 is a quantity dependent on the system. The ξ_0 dependence enters in a complicated fashion through a. The compressibility dominates far from T_c, so the turbidity has a simple power-law dependence, $\tau = (8/3)\,\tau_0 t^{-\gamma}$ for $T \gg T_c$. We should note that Eq. (2) includes a prefactor to the bracketed expression developed by Ferrell [7] because of the definition of turbidity which he used.

The difference between Eqs. (1) and (2) can best be illustrated on a plot of turbidity τ versus reduced temperature $t = (T-T_c)/T_c$, where the scaling relation, $\gamma = (2-\eta)\,v$, was used with $v = 0.63$. For this illustration, Eqs. (1) and (2) were matched at $t = 10^{-5}$ to correct for the different values of γ and hence τ_0. Having $\eta \neq 0$ results in lower turbidity values at small reduced temperatures (close to the critical point), but identical turbidity values as when $\eta = 0$ when at large reduced temperatures (see Fig. 1). An advantage of measuring the turbidity is that all three critical exponents v, γ, and η appear explicitly in Eq. (2).

Previous turbidity experiments [25] have, without exception, neglected η because data could not be taken sufficiently close to the critical point to warrant inclusion. The principal advantage of measuring the turbidity is that multiple scattering is not important because once the light is scattered out of the beam, it does not matter how many times it is scattered after that. Shanks and Sengers [11] have done detailed numerical calculations
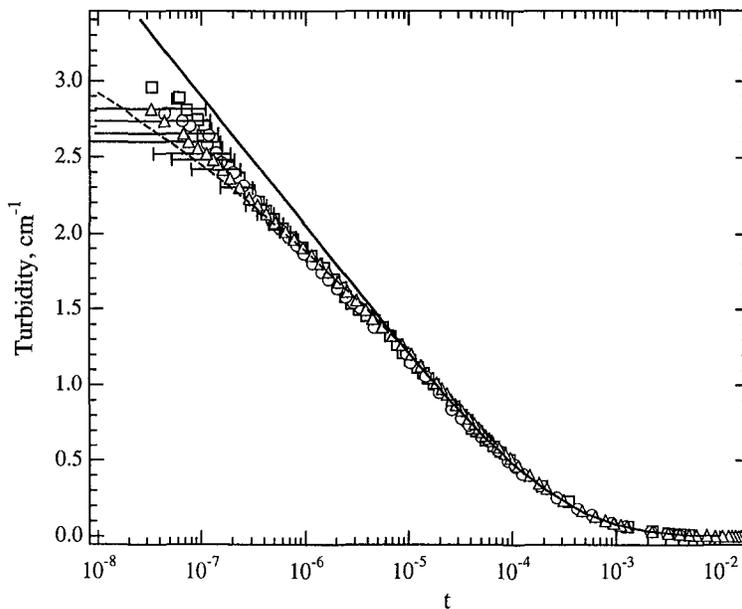
Fig. 1. Theory and preliminary data for the turbidity τ of methanol–cyclohexane. The upper (solid) line is from Eq. (1), where the critical exponent $\eta = 0$; the bottom (dashed) line is from Eq. (2) when $\eta = 0.033$. Both curves use the same parameters and constants, with the constraint that the scaling relation $\gamma = \nu(2 - \eta)$ holds. An effect due to η can be detected only close to the critical point [small reduced temperature, $t = (T - T_c)/T_c$]. Three experimental runs are shown—Run 1 (squares), Run 2 (circles), and Run 3 (triangles)—with representative error bars on Run 3. The error in the turbidity is smaller than the symbol size in this plot.

for double scattering as a function of angle in methanol–cyclohexane and find the contribution to be zero as $\theta \to 0$. Thus, if the single scattered light can be excluded from the detector, then multiple scattering effects can be neglected when measuring the turbidity. A precise measurement of the turbidity very close to the critical point can now be done, "making the turbidity method of determining η feasible in an earth-bound environment for a gravity-balanced binary liquid, such as methanol–cyclohexane" [7].

In order to determine the critical exponent η, the turbidity must be measured precisely for a critical composition sample when within micro-kelvins of the critical point. We report here the success in temperature control and in measuring the turbidity on one near-critical composition sample with a fixed optical path length.

2. EXPERIMENT

The critical exponents can be determined from a turbidity measurement, which can avoid multiple scattering effects since the total light scattered from the beam gives the turbidity and having that light scatter more than once is irrelevant provided it does not scatter back into the detector. The binary fluid mixture methanol–cyclohexane combines similar densities $(\Delta\rho/\bar\rho = 0.016)$, which minimizes the effect of gravity, with quite different refractive indices, which allows significant light scattering near the critical point and an easily measured turbidity. This system has also been studied extensively with published measurements of the turbidity, viscosity, surface wetting, dynamic light scattering, coexistence curve, and excess molar volume. The critical composition is 29.0%, by weight, methanol, with a critical temperature of about 45°C, depending on the amount of water present [26]. For these experiments, the fluid mixture will need to be relatively pure (99.9+%) and as free of water as possible. The 0.6-ml sample used for the preliminary measurements reported here was $(30.2 \pm 0.2)\%$ by mass methanol.

The thermostat is an onion-layer design which, when properly controlled, is capable of maintaining temperatures to within $\pm 10\,\mu$K at room temperatures $(t \approx 3\text{x}10^{-8})$. Each stage is controlled with a thermistor and heater, allowing a feedback network using external electronics. The outer two stages use a digital control network where the voltage across each YSI thermistor carrying a constant current of $100\,\mu$A is measured by a precision digital voltmeter (Keithley 2001) and transmitted to a computer which determines the correct voltage to be applied to that stage's heater. The innermost stage and the cell have their temperature sensed by stable, calibrated Thermometrics thermistors. The stage immediately surrounding the cell is controlled using an AC bridge with one arm an ESI 73 ratiotransformer and a Stanford Research 830 lock-in amplifier as a null-detector coupled to an analog PID controller in order to achieve the desired precision in temperature control $(t \sim 10^{-8})$. The cell is not actively temperature controlled but is monitored by an identical bridge using an SR 850 lock-in amplifier. The cell temperature can be controlled within $10\,\mu$K as shown in Fig. 2.

The optical cell is cylindrical with the fluid mixture enclosed by optical windows and sealed with Kalrez o-rings. The optical path length used here is a fixed value of 10.8 ± 0.1 mm. A small Teflon-coated stir bar rests in the bottom sidewall of the cell and oscillates back and forth through a small angle due to an external, computer controlled, rotating magnet beneath the thermostat. The fluids are thus mixed for a short time immediately after a temperature change.
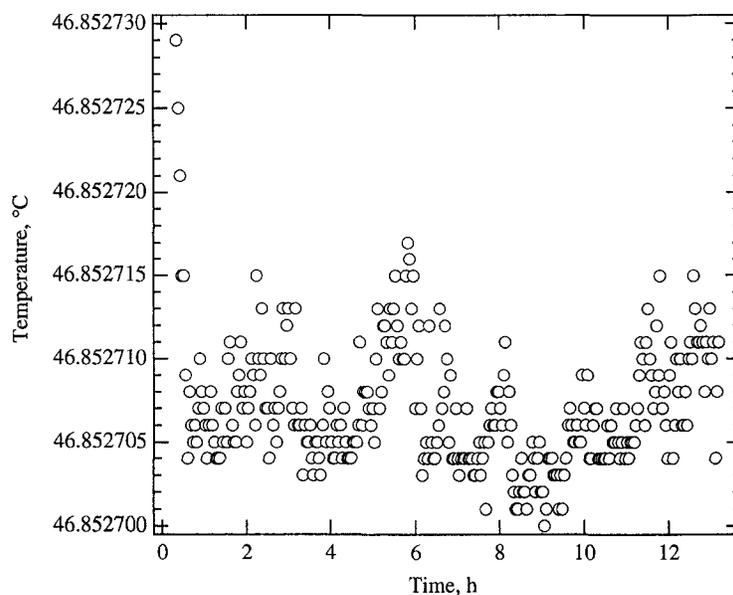
Fig. 2. The resulting cell temperature after a 1-mK temperature step using our thermostat. The temperature varied less than $\pm 10\,\mu$K, with a standard deviation of $3.3\,\mu$K over a period of 12 h.

The turbidity is determined from the transmitted light intensity I when the fluids are close to T_c, compared to the transmitted intensity I_0 when the fluids are well into the one-phase region. The nominal ($\pm 2\%$) intensity fluctuations in a 2-mW, polarized HeNe laser (Melles Griot 05LHP121) are reduced by passing the beam through a laser power amplitude stabilizer (Cambridge Research Instrumentation LS100). The resulting beam passes through a beam expander/spatial filter with the central section split with one part passing through the fluids and the other part traveling around the thermostat to provide a reference intensity. A light chopper (New Focus 3501) is used to sample the two beams at different frequencies. The light not scattered from the fluids in the cell passes through a pinhole before the beams are directed through a diffuser and a 632.8-nm-bandpass filter before striking photodiode detectors. The current from the photodiodes is measured using SR 510 lock-in amplifiers tuned to the chopper frequencies. The thermostat, laser, power controller, spatial filter, and photodetectors are placed on an optical table to minimize vibration and noise. Figure 3 illustrates the optical system.

The instruments measuring the light intensity and monitoring the temperature are interfaced to a Macintosh Quadra 950 computer using the
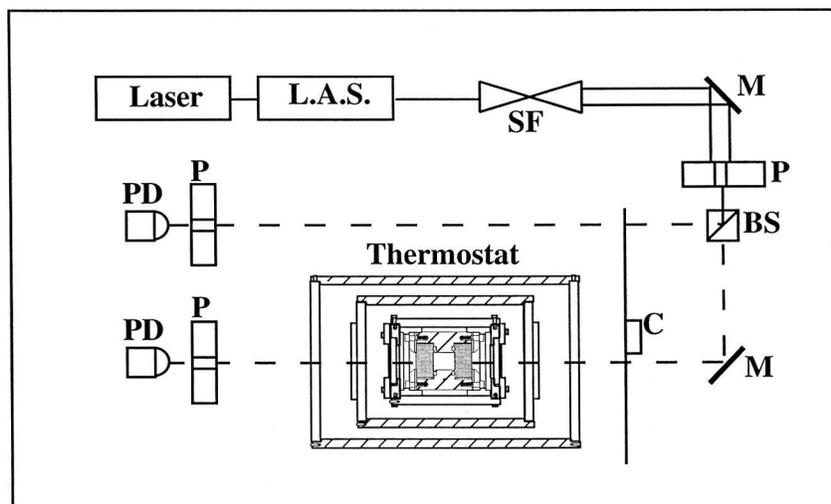
Fig. 3. Optical schematic. The laser beam passes through a laser amplitude stabilizer (L.A.S.) before passing through a spatial filter/beam expander (SF) and then striking the beamsplitter (BS). Each beam is chopped at a different frequency. The photodiodes (PD) detect the light and provide a signal to lock-in amplifiers whose reference frequencies are locked to the chopper C.

GPIB. The computer takes, stores, and analyzes data while it is controlling the experiment through digital-to-analog converters (in the SR 510 lock-ins) which are used to set the voltage on the Kepco power supplies attached to the heaters. The program is written in the pictorial language LabVIEW, which is a robust programming language ideally suited to data acquisition and control. Each instrument (lock-ins, ratiotransformers, D/A converters, scanner, and voltmeter) has its own "sub VI," a virtual instrument that acts as a subroutine. These routines are interwoven to provide the proper logic for temperature control and measurement, and for transmitted and reference intensity measurements.

3. RESULTS

Turbidity data have been taken on a near-critical composition of methanol–cyclohexane in the one-phase region. Starting from well above the critical temperature, each temperature setpoint allows the fluids to come to equilibrium, in times varying from 2.8 h for temperature steps less than 10 mK and 4 h or more for larger steps. When the temperature is changed to a new setpoint, the stir bar is activated for a short time to slosh the fluids and then stopped to eliminate flow cells; however, the fluids take

at least an hour to recover from sloshing. The light intensity through the fluids is used to determine when the fluids reach equilibrium.

Three runs of data have been collected over six decades of reduced temperature, with two of the runs approaching the critical temperature within 25μK. The critical temperature was found to drift upward over a period of months at a rate of 0.1 mK $\cdot$ h^{-1}, which may be due to water contamination [26] leaching from the cell walls. When our temperature was within 10 mK of critical, the cell temperature was fixed and the critical temperature drift allowed a slow, quasistatic equilibrium approach to the critical point. A large decrease in the transmitted intensity signaled the transition temperature, which could be determined with a precision of 20μK. The transition temperature was taken as the critical temperature in this experiment and the drift in the transition temperature between runs was 90μK $\cdot$ h^{-1}. Our preliminary data converted to values of turbidity and reduced temperature are shown in Fig. 1. We have not attempted to fit these data, and the lines in Fig. 1 are from theory using the theoretical value for the exponent v [9] with the requirement that the scaling relation $\gamma = (2 - \eta) v$ holds; the other parameter values used in Eqs. (1) and (2) are $\tau_0 = 5.96 \times 10^{-6}$ cm^{-1}, $\xi_0 = 0.34$ nm, and $k_0 = 0.0137$ nm^{-1}.

These preliminary data show the capabilities of the techniques being used and have a better resolution in both temperature and turbidity than previously reported [25]. The agreement with theory and previous measurements is remarkable. Additional data need to be taken for other composition samples and different path length cells before a precise value of the critical exponent η can be determined.

ACKNOWLEDGMENTS

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