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

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ABSTRACT

A ground based (1-g) 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 will allow the critical exponent η to be determined. The transmitted and reference light intensities can be measured to 0.1% and the fluid temperature can be controlled to 6.5 μK near room temperature. 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.

KEY WORDS: liquid-liquid equilibria; critical state; experimental method; turbidity; methanol; cyclohexane.

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1. INTRODUCTION

Critical Phenomena provides 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 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 non-effects) 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 further reduce gravitational field effects. 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 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 turbidity 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 predicted in order to explain light scattering measurements at small angles. An experimental determination of η can be done[6] 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 ($\eta \approx 0.036$), its effect can only be observed by an extraordinarily precise light scattering measurement very close to the critical point.[6] Just such a turbidity measurement is in progress and will provide a wealth of detail about the behavior of the system 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 determine correlation length. The analysis is simple if the light reaching the detector has only been scattered once. If the light has been scattered multiple times, then the analysis becomes very difficult. Shanks and Sengers [7] 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 has been confirmed by Bailey and Cannell [8] 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.[8]

Michael Fisher [9] first proposed the critical exponent η to describe how the correlation function behaves at T_c. Recent field theoretic analysis and partial differential approximates give the following theoretical values for γ, ν and η:

Table I: Theoretical values of the critical exponents.

γ	ν	η	Source
1.237 ± 0.002	0.630 ± 0.0015	0.0359 ± 0.0007	Ref. [10]
1.2390 ± 0.0025	0.630 ± 0.0015	0.033 ± 0.006	Ref. [11]
1.2395 ± 0.0004	0.632 ± 0.001	0.039 ± 0.003	Ref. [12]

While the theoretical predictions may 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 have attempted a measurement of the elusive exponent η using one of the three scattering probes. Tracy and McCoy examined the experimental results before 1975 and concluded [13] 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. 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 accurately calculate η from the scaling relation.

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. Most of the values are for liquid-liquid (LL) systems; others are liquid-gas (LG) or polymer blend (PB). Multiple scattering corrections were rarely done.

Probe	System	η	correct for multiple scattering?	Reference
γ	LG	0.03±0.03	No	[14]
γ	LL	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->0.046	Yes	[18]
γ,n	LL	0.042±0.007	No	[19]
γ	PB	0.038±0.003	No	[20]

In 1991, Ferrell [6] developed the theory that would allow turbidity measurements to be used to determine η, a parameter which appears explicitly in his formulation. The total incremental intensity of light scattered per unit length is defined as the turbidity τ, $\tau = L^{-1} \ln(I_0 / I)$ where L is the optical path length, I and I_0 are the transmitted and incident light intensities. The turbidity is related to critical phenomena by assuming Ornstein-Zernike scattering [21] far from the critical point and a modified [6] Fisher-Burford [22] form when very close to critical.

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

which becomes the following when very close to the critical point

$$\tau = \frac{2\tau_o t^{-\gamma}}{a} \left[L - 1 - \frac{\eta}{4} L^2 + 8.37\eta \right] \qquad t < 10^{-5} \qquad (3)$$

where

$$\tau_0 = \frac{\pi^3}{\lambda_0^4} \left[\frac{\partial n^2}{\partial \varphi} \right]^2 k_B T_c \chi_0 , \qquad (4)$$

$a = 2k_0^2\xi^2$, $L = \ln(2a)$, $k_0 = 2\pi n/\lambda_0$, n is the refractive index of the mixture, λ_0 is the vacuum wavelength of the light, ν, 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 $T >> T_c$.

The difference between Eq. (2) and (3) can best be illustrated on a plot of turbidity τ versus reduced temperature $t = (T-T_c)/T_c$. Values for the other constants can be taken from theory [10] in the case of critical exponents, or previous experiments on methanol-cyclohexane [17] for the other constants. 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 ν, γ and η appear explicitly in Eq. (3). The

scaling relation $\gamma = (2 - \eta)\nu$ can be invoked to reduce the number of adjustable parameters needed to fit the data, but it does not have to be.

Previous turbidity experiments [23] have without exception neglected η because data could not be taken sufficiently close to the critical point to warrant inclusion. The principle 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. 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."[6]

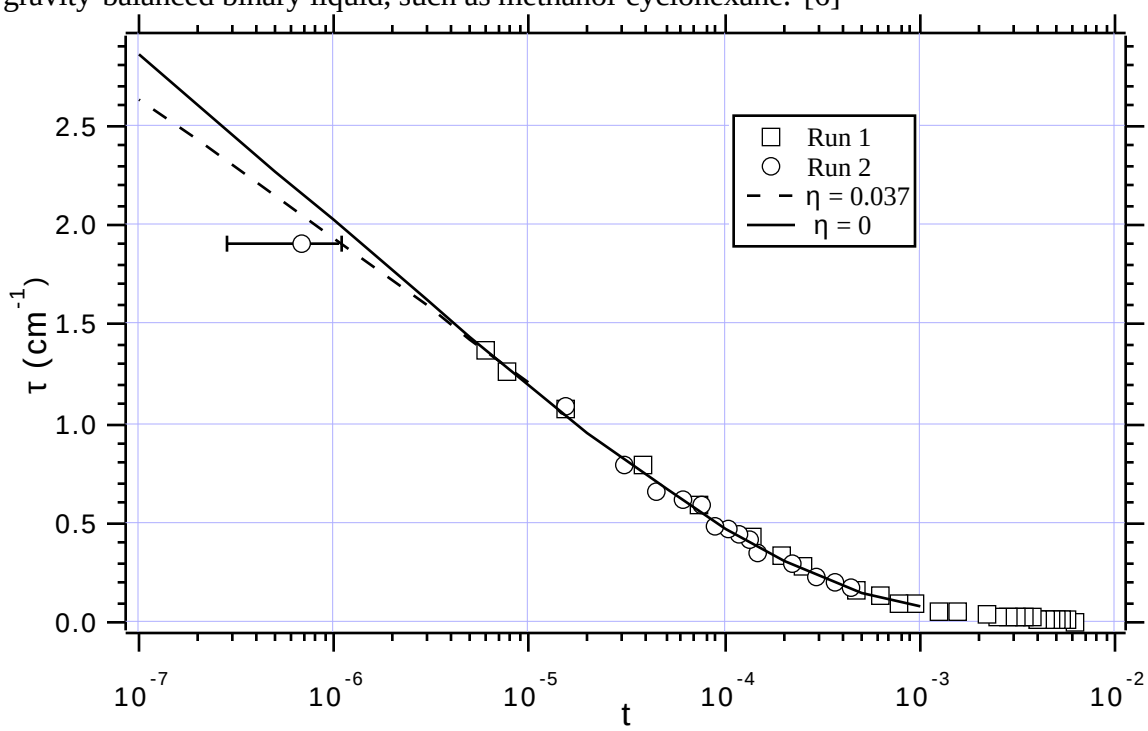

Fig. 1. Theory and preliminary data for the turbidity τ of Methanol-Cyclohexane. The upper (solid) line is from [21] when the critical exponent η=0; the bottom (dashed) line is from [6] when η=0.037. Both curves use the same parameters and constants with the constraint that the scaling relation $\gamma=\nu\ (2-\eta)$ holds. An effect due to η can only be detected close to the critical point (small reduced temperature, t).

In order to determine the critical exponent η, the turbidity must be measured precisely for a critical composition sample when within microKelvins of the critical point. We report

here the success in temperature control and in measuring light intensities that have allowed some preliminary data to be collected.

2. EXPERIMENT

The turbidity measurement can avoid multiple scattering effects since the total light scattered from the beam gives the turbidity. Since the turbidity measures all the light scattered from the main beam, having that light scatter more than once is irrelevant provided it does not scatter back into the detector. Shanks and Sengers[7] have done detailed numerical calculations for double scattering as a function of angle in methanol–cyclohexane and find the contribution to be zero as $\theta \rightarrow 0$. Thus, if the single scattered light can be excluded from the detector, then multiple scattering effects can be neglected when measuring the turbidity.

The binary fluid mixture methanol and cyclohexane combine 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.[24] For these experiments, the fluid mixture will need to be relatively pure (99.9^{+}%) and as free of water as possible. The 0.6mL sample used for the preliminary measurements reported here was 30.2% by mass Methanol.

The thermostat is an onion-layer design which, when properly controlled, is capable of maintaining temperatures to within ±10 μK 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 μA is measured by a precision digital voltmeter (Keithley 2001) and reported 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 10μK as seen in Fig. 2.

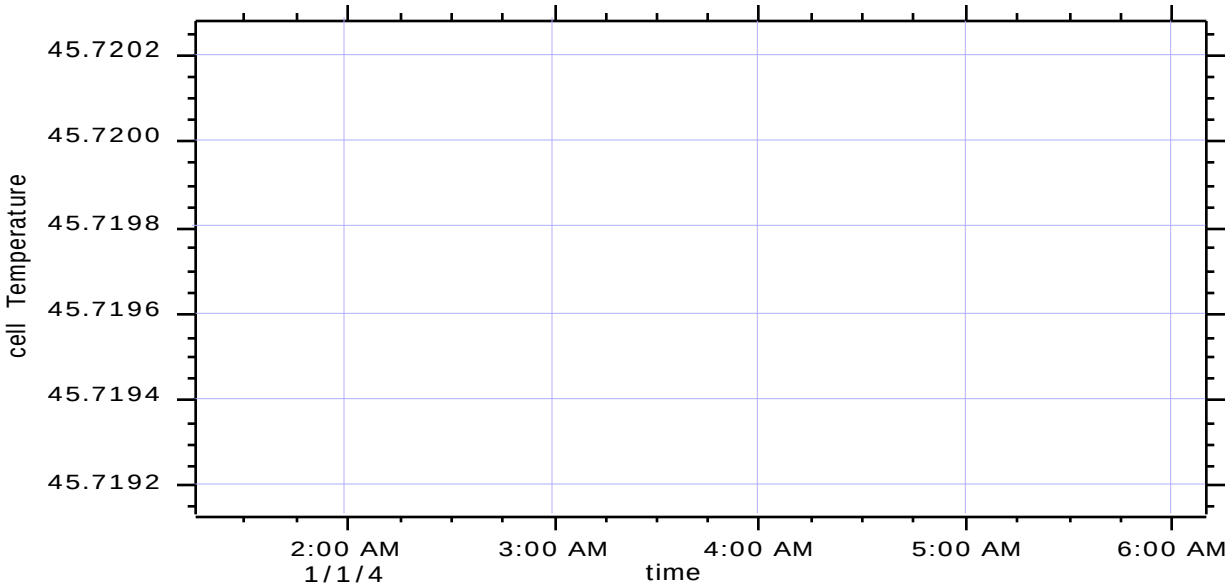

Fig. 2. The resulting cell temperature after a 1mK temperature step using our thermostat. The temperature varied less than ±10μK with a standard deviation of 6.5μK from 3AM to 6AM.

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±0.1mm. A small teflon coated stir bar rests in the bottom of the cell and sloshes the fluids for a short time immediately after a temperature change

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 relatively large (±2%) fluctuations in a 3mW, polarized HeNe laser are reduced by passing the beam through a laser power amplitude stabilizer. 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 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 632.8nm bandpass filter before striking photodiode detectors. The current from the photodiodes are 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.

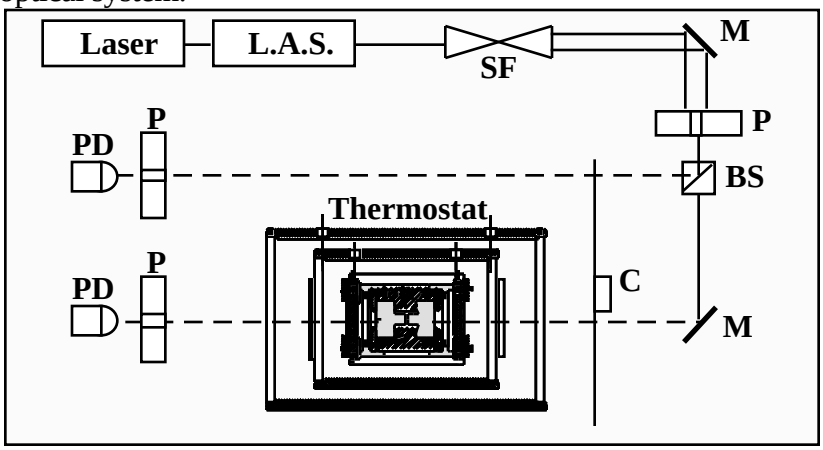

Fig. 3. Optical schematic. The laser beam passes through a laser amplitude stabilizer (L.A.S.) before passing through a spatial filter/beam expander (SF) and then striking the beamsplitter (B.S.). Each beam is chopped at a different frequency. The photodiodes (PD) detect the light and provide a signal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

The instruments measuring the light intensity and monitoring the temperature are interfaced to a Macintosh Quadra 950 computer using the 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 transmitted intensity measurements.

3. RESULTS

Turbidity data is taken on a near-critical composition of Methanol-Cyclohexane in the one-phase region. Starting from well above the critical temperature, each temperature setpoint is allowed to come to equilibrium, in times varying from 30 to 90 min., before the light intensity through the fluids and the reference intensity are measured and averaged. 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. Our preliminary data converted to values of turbidity and reduced temperature are shown in Fig. 1. We have not attempted to fit this data and the lines in Fig. 1 are from theory using published parameter values [10,23].

In taking this data, we have realized that we will need to take data less frequently and allow the fluids more time to relax to equilibrium. The critical temperature was also found to drift upwards at a constant rate of 0.15 mK/hr which may be due to water contamination from the cell walls. The method of approaching the critical temperature will have to be changed if we are unable to completely eliminate this drift.

The preliminary data does show the promise of the techniques being used and has better resolution in both temperature and turbidity than previously reported. [23] The agreement with theory and previous measurements is remarkable. With some modification of the procedure, a close approach to the critical point can be accomplished and a value of the critical exponent η can be determined.

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