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325343TURBIDITY OF A BINARY FLUID MIXTURE: DETERMINING  $\eta$ 

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## ABSTRACT

A ground based (1-g) experiment is in progress that will measure the turbidity of a density-matched, binary fluid mixture extremely close to the 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  $\eta$  to be determined. No experiment has determined a value of the critical exponent  $\eta$ , yet its value is significant to theorists in critical phenomena. Interpreting the turbidity correctly is important if future NASA flight experiments use turbidity as an indirect measurement of relative temperature in shuttle experiments on critical phenomena in fluids.

## INTRODUCTION

Although critical phenomena have been investigated for 100 years, it has only been in the last 20 years that comprehensive, quantitative models have begun to appear.<sup>1,2</sup> These models provided a framework for the observations made on a multitude of physical systems which had similar behavior near a critical point. The numerous theoretical extensions and experimental verifications which followed have provided a wealth of information but by no means has the understanding of critical points become complete. Numerous predictions remain untested or inadequately confirmed. One significant exponent prediction has still eluded experimental verification: the value of Fisher's "elusive exponent  $\eta$ ", which was predicted in order to explain light scattering measurements at small angles. An enhanced experimental technique is described that determines a value for  $\eta$  by measuring the total light being scattered (called the turbidity), in a density matched, binary fluid mixture of methanol and cyclohexane. In addition, the experiment will provide an important ground-based control for one aspect of an experiment on a recent shuttle mission: the ZENO project.

Since the correlation length is very large near the critical point compared to the molecular size, the behavior of a system is not determined by the type of gas but by its critical properties. It is these critical properties that have universal descriptors. For example, the correlation length  $\xi$  diverges close to the critical point as a power law  $\xi = \xi_0 t^{-\nu}$  where  $t \equiv (T - T_c) / T_c$ ,  $\xi_0$  is the amplitude describing the correlation length far from the critical temperature  $T_c$ , and  $\nu$  is a universal critical exponent ( $\nu \approx 0.64$ ). Not only will the critical exponents be the same for all gases near their critical point but also for many other thermodynamic systems that have a critical point (second-order phase transition). One example is a binary fluid mixture—two components which are partially miscible below a certain temperature and completely miscible above.

The development of renormalization group theory from earlier concepts of scaling and universality provided a theoretical framework for distinguishing systems, predicting critical exponent relations, approximating values for critical exponents, and obtaining amplitude relations. The current consensus is that liquid-gas systems, ferromagnets, and binary liquid mixtures all

belong to the same universality class— $n=1$  (spin dimension),  $d=3$  (spatial dimension) which corresponds to the three-dimensional Ising model. Despite this dramatic success, there are still fundamental gaps in our knowledge of these systems. The critical exponent  $\eta$  has a small predicted value ( $\eta \approx 0.03$ ) which has made its measurement extremely difficult. It is one of the last exponents to lack direct experimental verification.

## PREVIOUS WORK

Michael Fisher<sup>3</sup> first proposed the critical exponent  $\eta$  to describe how the correlation function behaves at  $T_c$ . Recent field theoretic analysis and partial differential approximants give the following values for  $\gamma$ ,  $\nu$  and  $\eta$ :

$\gamma$	$\nu$	$\eta$	Source
$1.238 \pm 0.003$	$0.631 \pm 0.003$	$0.038 \pm 0.014$	Nickel <sup>4</sup>
$1.241 \pm 0.002$	$0.630 \pm 0.0015$	$0.031 \pm 0.004$	LeGuillou and Zinn-Justin <sup>5</sup>
$1.2378 \pm 0.0006$	$0.6312 \pm 0.0003$	$0.0375 \pm 0.0005$	George and Rehr <sup>6</sup>

In the words of George and Rehr, who used partial differential approximants, " $\eta$  ... show(s) significant discrepancies with respect to the field-theoretic results" of reference 5.

While the theoretical predictions may not agree within their quoted uncertainty, the experimental situation is even less well-known. Three principal techniques have been used to look for  $\eta$  and they all involve scattering phenomena using either x-rays, neutrons, or light. Tracy and McCoy examined the experimental results before 1975 and concluded<sup>7</sup> that "no experiment to date unambiguously and directly establishes that the critical exponent  $\eta$  is greater than zero." At the same time, Cannell<sup>8</sup> published a measurement of  $SF_6$  which found  $\eta = 0.03 \pm 0.03$ . A high precision, angular light scattering experiment on the liquid mixture 3-methylpentane and nitroethane concluded<sup>9</sup> that  $\eta = 0.017 \pm 0.015$ ; "we cannot prove on the basis of the experimental data alone that  $\eta$  must be finite." Even the most recent x-ray scattering measurement,<sup>10</sup> done on the liquid mixture perfluoromethylcyclohexane and n-heptane finds  $\eta = 0.03 \pm 0.03$ . Turbidity measurements<sup>11</sup> have without exception assumed  $\eta = 0$  because data could not be taken sufficiently close to the critical point to warrant inclusion.

## TURBIDITY

A binary fluid mixture exhibiting an upper consolute point will be one phase, homogeneous, and essentially clear when the mixture is well above its critical consolute temperature  $T_c$ . The constant transmitted light intensity at these temperatures is referred to as  $I_0$ . As the temperature of the fluids approaches  $T_c$ , concentration fluctuations, "droplets," begin to form and cause the transmitted light intensity  $I$  to be reduced. The total incremental intensity of light scattered per unit length is defined as the turbidity  $\tau$ . The turbidity is dependent upon the transmitted light intensities  $I$  and  $I_0$  by

$$\tau = L^{-1} \ln(I_0 / I)$$

where  $L$  is the optical path length. The turbidity is related to critical phenomena by assuming Ornstein-Zernike scattering<sup>12,13</sup> and has different forms if  $\eta$  is or is not zero. The effect of  $\eta$  can

best be illustrated by a plot of turbidity  $\tau$  versus reduced temperature  $t$  (see Figure 1). Having  $\eta \neq 0$  is expected to result 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. An advantage of measuring the turbidity is that all three critical exponents  $\nu$ ,  $\gamma$  and  $\eta$  appear explicitly in the theoretical expressions. While the scaling relation  $\gamma = (2 - \eta)\nu$  can be invoked to reduce the number of adjustable parameters needed to fit the data, it does not have to be and some of the analysis will be devoted to determining all three exponents.

## EXPERIMENT

The binary fluid mixture to be measured in this experiment is methanol and cyclohexane. These fluids 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. 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.

The thermostat is an onion-layer design with low thermal mass stages for (relatively) fast changes in temperature. When properly controlled, such an enclosure is capable of maintaining temperatures to within  $\pm 10 \mu\text{K}$  at room temperatures ( $t \approx 3 \times 10^{-8}$ ). The temperature is sensed by stable, calibrated Thermometrics thermistors. Each stage will be controlled with a thermistor and heater allowing a feed-back network using external electronics. The outer stages can use a digital control network where the resistance of each thermistor is measured by a precision digital voltmeter and reported to a computer which determines the correct voltage to be applied to that stage's heater. The cell will be controlled using an AC bridge with a lock-in amplifier as a null-detector coupled to a PID controller in order to achieve the desired precision in temperature control ( $t \sim 10^{-8}$ ).

The cell design is a cylindrical cell with BK-7 optical windows enclosing the fluid mixture, which is sealed with Kalrez o-rings. The optical path length would be a fixed value of 2.0 mm. This length would allow adequate resolution at  $t \sim 10^{-3}$  yet also give good resolution at small reduced temperatures ( $t \sim 10^{-8}$ ).

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.

To obtain  $\eta$ , we use an optical system capable of measuring the turbidity with a resolution that can distinguish between the various theoretical predictions. With the small path length cell, the most stringent measurements will be at temperatures far from the critical temperature where the light scattering is weak. The ( $\pm 2\%$ ) fluctuations in a 3mW, polarized HeNe laser is reduced by passing the beam through a laser power amplitude stabilizer before being 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 voltages are measured using lock-in amplifiers tuned to the chopper frequencies. The thermostat, laser, power controller, and photodetector are placed on an optical table to minimize vibration and noise. Fig. 2 illustrates the optical system.

The interfacing software (written in LabVIEW) accesses the instruments via a GPIB and allows the computer to set the lock-in amplifiers and then measure the light intensities and room temperature over long periods of time. Early problems with room temperature drift and vibration of the light intensity have been solved and the stability of the intensity ratio of the two beams is less than 0.1% over a long period of time (40 hours as shown in Fig. 3). This stability and resolution are quite adequate for the turbidity measurement in progress.

## CONCLUSION

This turbidity experiment should provide the best determination of the exponents  $\nu$ ,  $\gamma$  and  $\eta$ , and amplitudes  $\xi_0$  and  $\chi_0$ . This research will be the investigation of the critical exponent  $\eta$ , on whose value the theorists cannot agree, and whose effect the experimentalists have been unable to definitively detect. The experiment outlined should provide the first evidence of a non-zero  $\eta$  and perhaps resolve which theoretical value is correct. This experiment also provides a good proving ground for the acquisition and analysis of turbidity data similar to that obtained in the shuttle experiment ZENO. Finally, a rigorous understanding of the turbidity very close to the critical point may allow its use as a temperature probe in future shuttle experiments on near-critical fluids, or at the very least, as a definitive indicator of the critical point.

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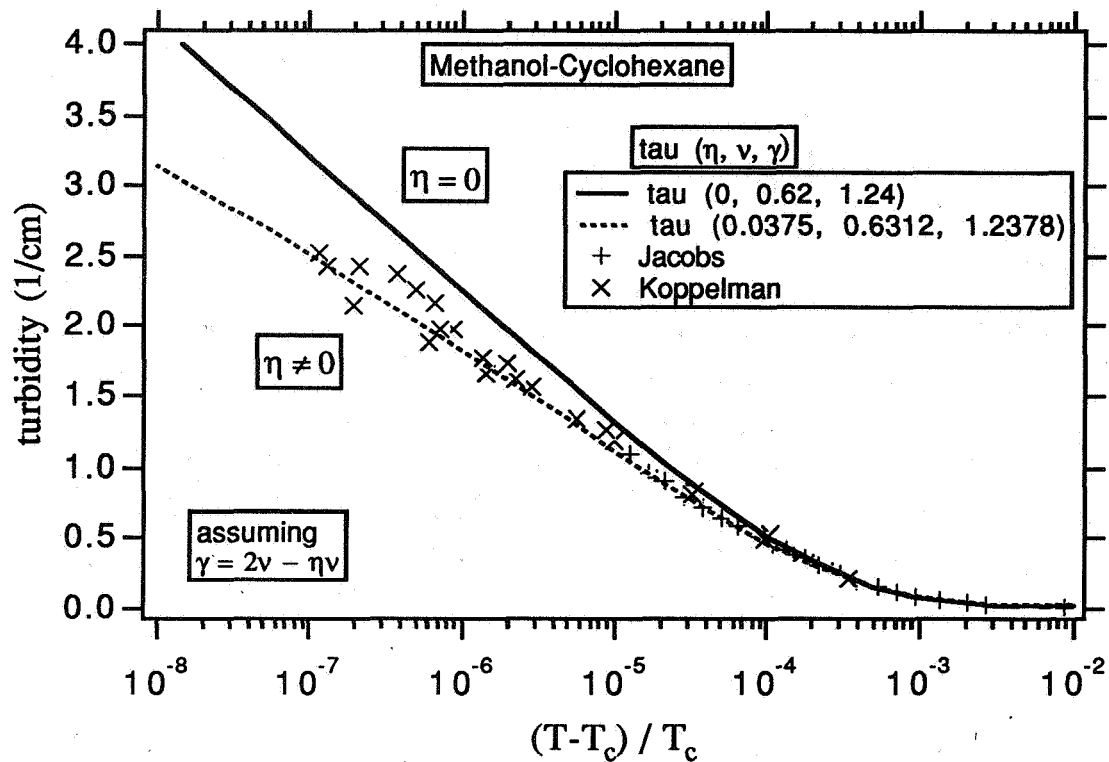


Fig. 1. Theory and published data for the turbidity of Methanol-Cyclohexane. The upper (solid) line is the theoretical curve when the critical exponent  $\eta = 0$ , while the lower (dashed) curve assumes it is 0.0375. The data are from reference 11 and are more consistent with  $\eta \neq 0$ , but a value of  $\eta$  can not be determined from the existing data.

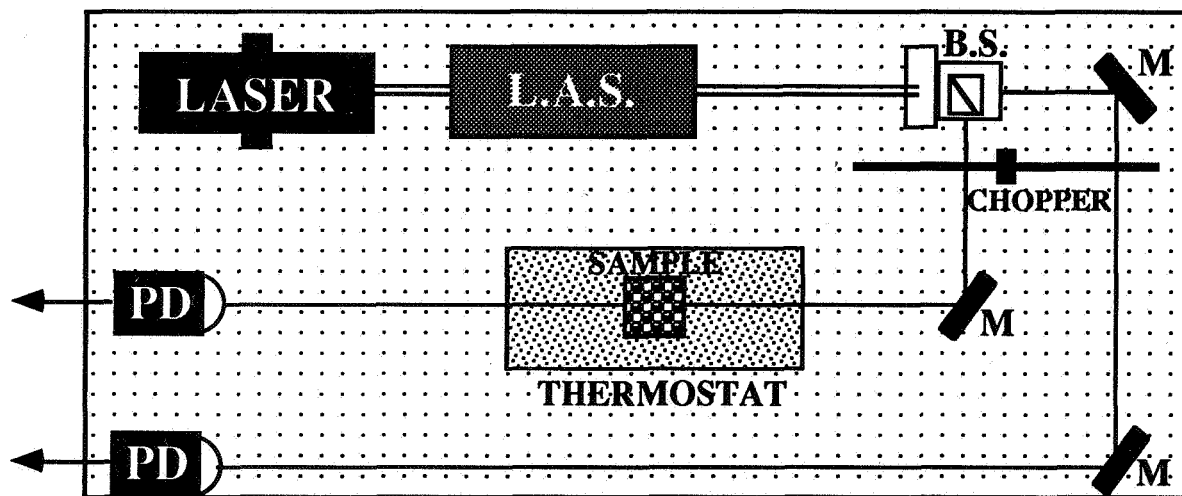


Fig. 2. Optical schematic. The laser beam passes through a laser amplitude stabilizer (L.A.S.) before striking the beamsplitter (B.S.). Each beam is chopped at a different frequency. The photodiodes (PD) detect the light and provide a signal to lock-in amplifiers whose reference frequency is locked to the chopper.

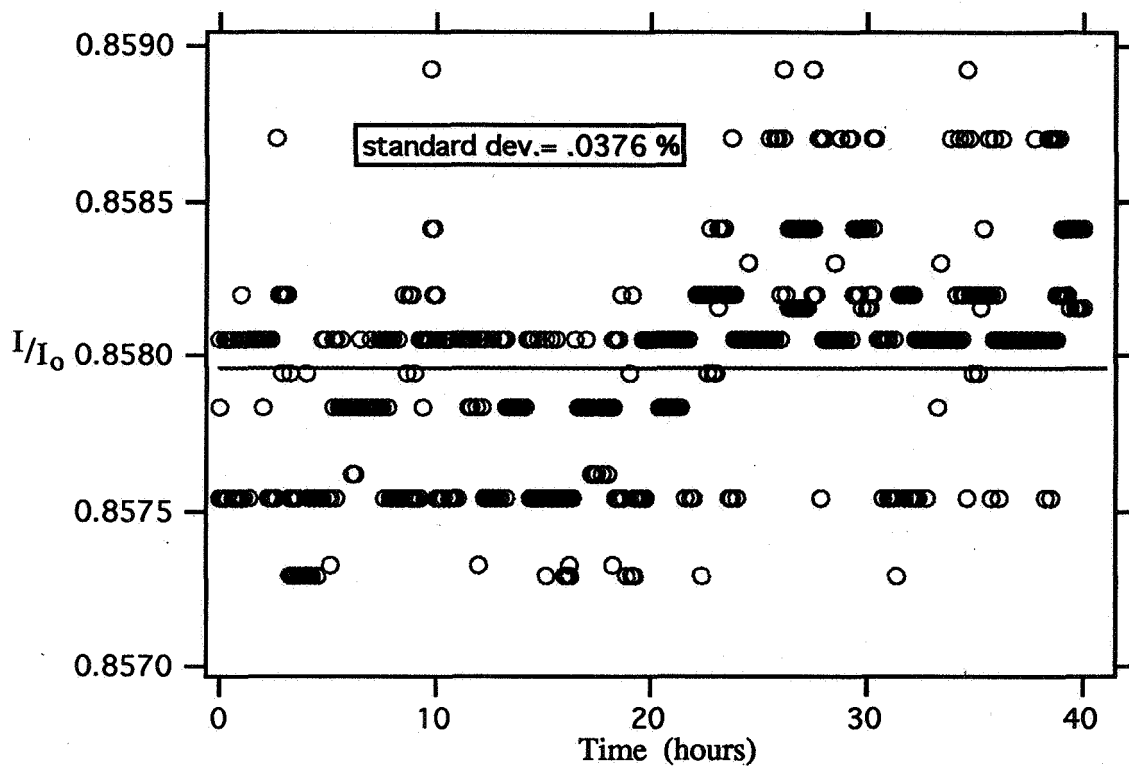


Fig. 3. Measured ratio of laser light intensities through air using photodiodes and lockin-amplifiers when the two beams of Fig. 2 are chopped. This demonstrates the techniques' stability and resolution.