TURBIDITY OF A BINARY FLUID MIXTURE: DETERMINING η

Donald T. Jacobs
Physics Department
The College of Wooster
Wooster, Ohio 44691

59-34

75

(i

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 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. 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 systems near a critical point.

INTRODUCTION

Comprehensive, quantitative models of critical phenomena have been developed[1,2] that provide a framework for the observations made on a multitude of physical systems which have similar behavior near a critical point. The numerous theoretical extensions and experimental verifications 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 precise experimental verification: the value of Fisher's "elusive exponent η", which was predicted in order to explain light scattering measurements at small angles. An enhanced experimental technique is described that determines a value for η 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 molecule but by its critical properties. It is these critical properties that have universal descriptors. For example, the correlation length ξ diverges close to the critical point as a power law $\xi = \xi_0 t^{-\nu}$ where $t \equiv (T - T_c)/T_c$, ξ_0 is the amplitude describing the correlation length far from the critical temperature T_c, and ν is a universal critical exponent ($\nu \simeq 0.63$). 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 liquid 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, uniaxial 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. One of these is the critical exponent η, which has a small predicted value ($\eta \approx 0.038$) that has made its measurement extremely difficult. It is one of the last exponents to lack direct experimental verification.

PREVIOUS WORK

The critical exponent η describes[3] how the correlation function behaves at T_c. Recent field theoretic analysis and partial differential approximants predict the following values for the critical exponents γ, ν and η:

γ	ν	η	Source
1.237 ± 0.002	0.630 ± 0.0015	0.0359 ± 0.0007	Nickel and Rehr[4]
1.2390 ± 0.0025	0.630 ± 0.0015	0.033 ± 0.006	LeGuillou and Zinn-Justin[5]
1.2395 ± 0.0004	0.632 ± 0.001	0.039 ± 0.003	Fisher and Chen[6]

While the theoretical predictions may just 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. Tracy and McCoy examined the experimental results before 1975 and concluded[7] that "no experiment to date unambiguously and directly establishes that the critical exponent η is greater than zero." At the same time, Cannell[8] published a measurement of SF_6 which found $\eta = 0.03 \pm 0.03$. A high precision, angular light scattering experiment by Chang, Burstyn and Sengers[9] on the liquid-liquid mixture 3-methylpentane and nitroethane found $\eta = 0.017 \pm 0.015$; the authors conclude "we cannot prove on the basis of the experimental data alone that η must be finite." A recent x-ray scattering measurement,[10] done on the liquid mixture perfluoromethylcyclohexane and n-heptane finds $\eta = 0.03 \pm 0.03$. The most recent light scattering measurement was done by Bailey[11], a Ph.D. student of Cannell, on 3-methylpentane and nitroethane, which is a popular system because the close refractive index match of the components greatly reduces (but not eliminates) multiple scattering corrections.

Bailey determined the exponents γ and ν, which if the scaling relation $\gamma=\nu (2-\eta)$ is assumed, gives values of η from 0.027 to 0.046. 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.

In 1991, Ferrell[12] developed the theory that would allow turbidity measurements to be used to determine η, a parameter which appears explicitly in his formulation. The turbidity measures the total amount of light scattered over all solid angle. 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 turbidity τ 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[12,13] and has different forms if η is or is not zero. The effect of η can best be illustrated by a plot of turbidity τ 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. Previous turbidity experiments[14] have without exception assumed $\eta = 0$ because data could not be taken sufficiently close to the critical point to warrant inclusion. An 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 provide a good determination of the exponent η.

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.

A cylindrical cell with quartz optical windows encloses the fluid mixture, which is sealed with Kalrez o-rings. The optical path length is about 2.0 mm. This length allows adequate resolution at t ~ 10^{-3} yet also gives good resolution at small reduced temperatures (t ~ 10^{-8}). The cell is temperature controlled by placing it within an onion-layer thermostat with low thermal mass stages for (relatively) fast changes in temperature. When properly controlled, such an enclosure can maintain the cell temperature to within ±10 μK at room temperatures (t ≈ 3×10^{-8}). The temperature is sensed by stable, calibrated Thermometrics thermistors. The stage holding the cell is 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. The outer stages 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 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 η, 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 (±2%) fluctuations in a 3mW, polarized HeNe laser is reduced by passing the beam through a laser power amplitude stabilizer before passing through a beam expander, spatial filter. The central portion of this beam is 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 intensities are measured using lock-in amplifiers tuned to the chopper frequencies. The thermostat, laser, power controller, and photodetectors 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 and control the temperatures of the stages and then measure the light intensities in a sequential process. Stability of the light intensity ratio of the two beams is less than 0.1%, and the cell temperature can be controlled to 30 μK. This stability and resolution are quite adequate for the turbidity. The process of collecting preliminary data and preparing a sample sufficiently close to the critical composition has begun.

CONCLUSION

This turbidity experiment should provide the best determination of the exponents v, γ and η, and amplitudes ξ_0 and χ_0. This research will be the investigation of the critical exponent η, on whose value the theorists disagree, and whose effect the experimentalists have been unable to definitively detect. The experiment outlined should provide the first evidence of a non-zero η 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.

REFERENCES

1 . S. C. Greer, *Acc. Chem. Res.* 11, 427 (1978); G. Ahlers, *Rev. Mod. Phys.* 52, 489 (1981).

2 . S.C. Greer and M.R. Moldover, *Ann. Rev. Phys. Chem.* 32, 233 (1981); A. Kumar, H.R. Krishnamur, and E.S.R. Gopal, *Phys. Rep.* (Netherlands) 98, 57 (1983).

3. M.E. Fisher, *J. Math. Phys.* 5, 944 (1964); M.S. Green, J. Chem. Phys. 33, 1403 (1960).

4. B.G. Nickel and J.J. Rehr, *J. Stat. Phys.* 61, 1 (1990).

5. J.C. LeGuillou and J. Zinn-Justin, *J. Physique* 50, 1365 (1989).

6. M.E. Fisher and J.-H. Chen, *J. Physique* 46, 1645 (1985).

7. C.A. Tracy and B.M. McCoy, *Phys. Rev. B* 12, 368 (1975).

8. D.S. Cannell, *Phys. Rev. A* 12, 225 (1975).

9. R.F. Chang, H. Burstyn, and J.V. Sengers, *Phys. Rev. A* 19, 866 (1979).

10. Y. Izumi, *Phys. Rev. A* 39, 5826 (1989)

11. A. Bailey, Ph. D. thesis (UCSB, 1993).

12. R.A. Ferrell, Physica A177, 201 (1991).

13. V.G. Puglielli and N.C. Ford, Jr., *Phys. Rev. Lett.* 25, 243 (1970).

14. D.T. Jacobs, *Phys. Rev. A* 33, 2605 (1986); R.B. Kopelman, R.W. Gammon, and M.R. Moldover, *Phys. Rev. A* 29, 2048 (1984); C. Houessou *et al.*, *Phys. Rev. A* 32, 1818 (1985).
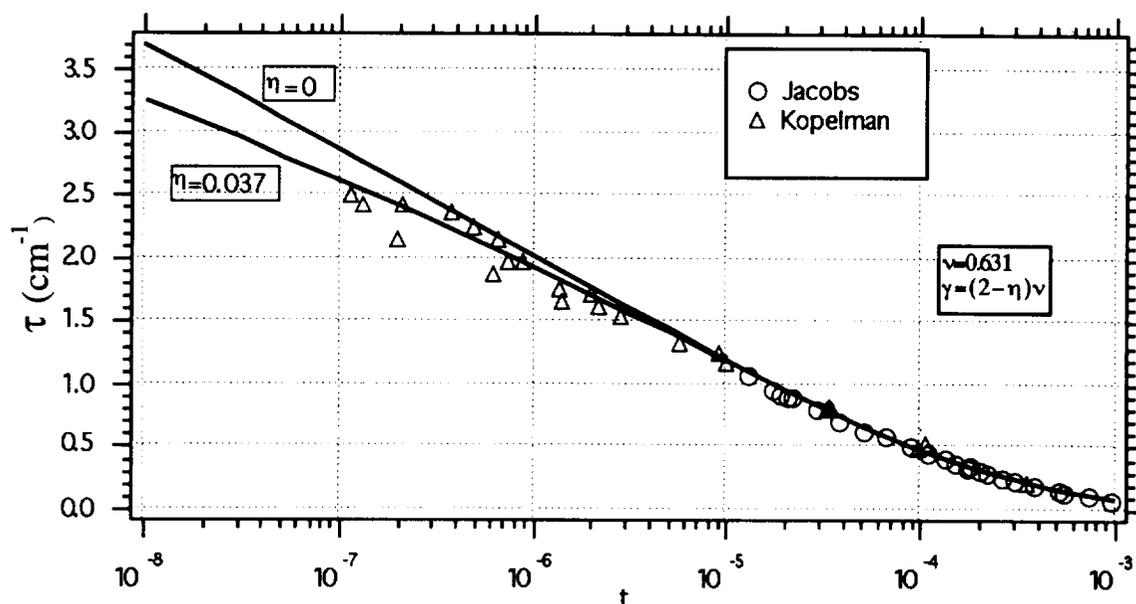
Figure 1: Theory and published data for the turbidity τ of Methanol-Cyclohexane. The upper line is from Ref. 13 when the critical exponent $\eta=0$; the bottom line is from Ref. 12 when $\eta=0.037$. Both curves use the same parameters and constants with the constraint that the scaling relation $\gamma=\nu(2-\eta)$ holds. An effect due to η can only be detected close to the critical point (small reduced temperature, t).
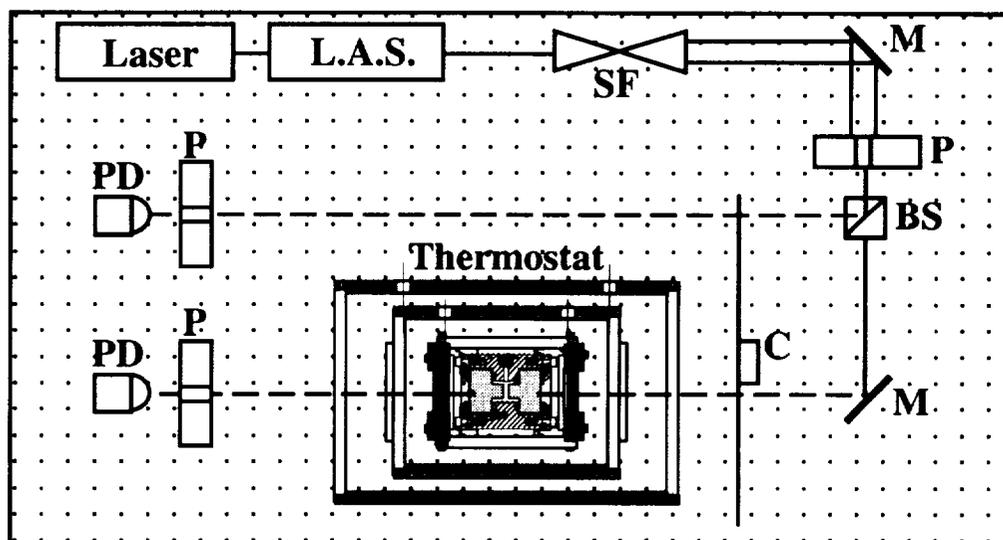

Figure 2: Optical Schematic. The laser beam passes through a laser amplitude stabilizer (L.A.S.) and a beam expander/spatial filter (SF) before the central portion is divided by the beam splitter (BS). Part of the beam goes through the outer ring of slots of an optical chopper (C) and around the fluids to provide a reference. The rest goes through the inner ring of slots on the chopper before passing through the fluids in the center of the thermostat. The beams are detected by photodiodes (PD) connected to lock-in amplifiers. Mirrors (M) and pinholes (P) are also shown.