Progress Report

CRITICAL SCATTERING OF LASER LIGHT

BY THIN FLUID FILMS

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Abstract

A novel close spaced Fabry-Perot interferometer has been developed which contains the fluid under study between the mirrors. The interferometer-cell has been used to make the first successful measurement of the anomalous refractive index of a binary fluid mixture near its consolute critical point. The cell has also been used to determine the coexistence curve for a binary mixture and the associated critical index β .

Intensity autocorrelation spectroscopy of laser light scattered from Brownian particles suspended in a binary mixture has been used to study the effective shear viscosity of the fluid near its critical point. A theory has been developed which includes a momentum dependent shear viscosity and takes into account effects due to surface interactions between the particles and the fluid. This theory explains our observations and is consistent with the results of earlier tracer diffusion measurements in a critical mixture.

Progress Report

I. Introduction

During the present contract period we have established that the internal reflection technique for studying critical behavior of fluid boundary layers is much less promising than the approach which uses a closely spaced Fabry-Perot (CSF-P) interferometer. As a result essentially all of the effort on thin film research during this contract period has been expended on the development and application of the CSF-P interferometric technique to the study of fluid critical behavior. Several technical problems involving the CSF-P cell design had to be overcome. Thus the first successful experiments involving the CSF-P method have just been performed. We have observed the anomalous change in the refractive index of a critical mixture near its critical point. This is the first observation of an anomalous refractive index in the region of a critical point to our knowledge.

Experiments on CO_2 that were specified in the proposal were not done for reasons stated in Section III of this Report. These experiments will be delayed until further work is done with binary fluid critical mixtures using the CSF-P cell.

Most of the experiments proposed for the investigation of Brownian motion in a critical mixture have been completed and several interesting and originally unanticipated results have evolved from these studies. The momentum dependence of the diffusion coefficient has been observed and the effect of the suspended particles on the anomalous shear viscosity has also been observed. The particle rain effect (a nucleation phenomenon) interface between the two phases of the isooctane-nitroethane mixture below the critical temperature depending upon impurities and the rapidity of passing through the critical point. Experiments proposed using very small microspheres have not been done as proposed and remain as a future problem.

Programs covering the area of Brownian motion will be covered in Section II of this Report, and progress covering the Application of the CSF-P cell to the study of critical phenomena will be discussed in Section III together with a discussion of the internal reflection spectroscopic method.

II. Light Scattering Studies of Brownian Motion in Critical Mixtures

The initial results of this study [1] provided evidence that light scattering from Brownian particles in a critical mixture could be used to investigate the fluid viscosity and particle diffusion behavior in the critical region. During the present contract period, this work was extended to study the diffusion coefficient of Brownian particles much further into the critical region, as a function of momentum transfer (scattering angle) as well as temperature. These results will be reported in an article to be published in the December issue of the Physics of Fluids (preprint appended to this report) and in a substantial article which details both the experimental and theoretical aspects of this work. The latter article is under preparation and will be submitted to the Physical Review.

The progress made on this problem during the present contract period may be summarized as follows: During the latter part of the first contract period we established that the diffusion coefficient of Brownian particles in a critical mixture could be related to the anomalous shear viscosity of the fluid. We showed from these studies, that the anomalous shear viscosity varied logarithmically with the coherence length, ξ , in agreement with the theoretical prediction of Perl and Ferrell [2]. Subsequently, we demonstrated that upon closer approach to the critical mixing temperature, the diffusion coefficient for suspended particles becomes strongly momentum dependent. In particular, we found an enhancement of the effective anomalous shear viscosity, and a strong κ dependent rounding off of the viscosity anomaly in the critical region. The conclusion we drew from this is that there are two different phenomena at work, one responsible for the enhancement effect, and the second, for the strong κ dependent modifications in the viscosity anomaly. The theoretical model developed to explain our results is sketched briefly in the Physics of Fluids article and at greater length in Dr. Kenneth Lyons' Dissertation (appended) and in the detailed article in preparation. With this two component theoretical model for particle diffusion behavior in critical mixtures, we are able, not only to explain our light scattering results, but also to reconcile these with the results of tracer diffusion studies in critical mixtures [3] and the microphotography results of a Russian group [4].

Nucleation Phenomena in Critical Mixtures

In the previous progress report, we reported the first observation of a critical nucleation phenomenon near the mixing phase transition of a binary fluid mixture (nitroethane-isooctane). We believe, however, that this phenomenon is related to an ion nucleation effect reported by Pisareu and Biryukov [5]). Significant progress was made toward understanding this critical "particle rain" effect during the present contract period.

In the earlier work, we observed the particle rain near T_c to be downward into the nitroethane-rich phase. However, in later work the rain "fell" consistently upward into the isooctane-rich phase. The only difference between the two sets of observations was that the purity of the fluid components was improved in the later work. This observation, plus the results of a number of studies made which enabled us to discount several other possibilities, has led us to the following model of the effect: There exists a surface energy interaction between the particles and the fluid components which slightly favors one component. The fact that the direction of the particle rain can be reversed by a small amount of homologous impurity present in the fluid is taken as evidence that the surface energy imbalance is very small, and the presence of impurities (primarily nitromethane), even though similar chemically to nitroethane, was enough to reverse the direction of the effect. Very near the critical point, the small surface energy affinity of the particles for the isooctane causes the particles to act as effective nucleation sites for the formation of isooctane droplets. When the single phase system with uniformly distributed particles is cooled through T_c , even in a step as small as 0.001°C , the trapped particles are all carried up into the isooctane rich phase. A simple calculation of the minimum surface tension coefficient for trapping of a particle by the fluid gives us $\gamma > 10^{-7} \text{ erg/cm}^2$. This is a very reasonable result. For example, the surface energy of the mixture methanol-cyclohexane has been measured [6], and for $T_c - T = 0.001^\circ\text{C}$, $\gamma \approx 5 \times 10^{-6} \text{ erg/cm}^2$. The ramifications of this effect for our studies of the anomalous shear viscosity in critical mixtures were very important. The "rain" effect provided clear evidence for the existence of a surface energy of interaction between the particles and the fluid components. This in turn played a significant part in the theoretical interpretation of the viscosity enhancement effect we observed near the critical

point in the binary mixture system nitroethane-isooctane. A short note describing this critical nucleation process, and our tentative explanation, is being prepared for the Journal of Surface Physics.

III. Critical Phenomena Observed in a Fluid Contained Within a Fabry-Perot Interferometer

The first Fabry-Perot cell was designed and fabricated in the previous contract period. It was designed for pure fluids (CO_2) at high pressures, with fixed spacings of the flats that could only be adjusted over at most a few wavelengths of light for the purpose of setting the flats parallel.

During this contract period we designed and built a second cell for critical mixtures at about one atmosphere of pressure. The conditions for this sort of system were thought to be more convenient in the developmental stages, and also they allowed us to move easily design the Fabry-Perot so that the flats could be translated over rather large distances such that the mirror spacings could be adjusted from about 2mm to 1 micron or less. The advantage here is not only convenience. It allows us to search for shifts in the critical point as a function of wall spacing. With fixed spacers the fluid would have to be changed at each spacing. This could introduce different impurities and the possibility of temperature shifts in T_c by virtue of the impurities rather than because of a change in wall spacing. It took some time to attain a workable design. A further slow down in progress came about because the coatings of the optical flats, which are in contact with the fluid, peeled off. Our new coatings are performing quite satisfactorily. Figure 1 shows a simplified diagram of the cell. Gross adjustments are made with adjusting screws and fine tuning is accomplished by means of three piezoelectric transducers located symmetrically about the periphery of one of the flats. This flat is captured in a metal cage and is suspended by a Kel-F diaphragm so that it effectively floats on the fluid. The diaphragm also acts as one of the seals. The temperature controller controls the temperature of the cell to about ± 0.2 m°k. The cell has a heat shield around it separately thermostated and the entire assembly is contained within a vacuum.

We proceeded to make detailed measurements of the refractive index in the critical region of a binary mixture with the new apparatus rather than

of turbidity and correlation spectra as proposed for this contract period. The reason for this change in plan was because of new theory worked out by Hocken and Stell [7] for the refractive index near a critical point. This theoretical work, if correct, suggested that we should be able to detect the anomalous refractive index quite easily. Also, if the theory applies it should allow us to measure the critical indices n and u in a very simple way, compared to using turbidity or correlation spectroscopic methods.

Preliminary measurements of the refractive index of the critical mixture cyclohexane-methanol were made, an effect not previously observed, to our knowledge. These results agree qualitatively with the results of the theoretical calculations of Hocken and Stell on xenon [7].

The Fabry-Perot system has also proven to be useful in providing a vivid display of conditions of equilibrium or non-equilibrium (homogeneity and non-homogeneity) over the entire fluid film under study. A particularly interesting effect occurs when the system is very near the critical point and the interference pattern has disappeared. At this point the system scintillates with the scintillations growing and decaying at a rate which is slow and observable to the eye. The rise and decay time seems to be slower the closer the fluid is to its critical point. The displays which were observed in previous test cells implemented changes in design to eliminate temperature gradients. The previous test cells were also used to obtain the coexistence for cyclohexane-methanol by observing the relative displacement of fringes above and below the interface between the coexisting fluid phases. In this experiment, the flats are set at a specific wedge to give straight interference fringes perpendicular to the interface between the phases. A preliminary value for the critical index β was determined to be $0.35 \pm .02$. An improved value should be obtained with the new cell.

The Behavior of the Refractive Index Near the Critical Point

Interesting features in the refractive index near a critical point were brought to our attention some time ago by the work of Larson, Mountain, and Zwanzig [8] and more recently by a very recent article by Hocken and Stell [7]. In this latter publication the real and imaginary parts of the refractive index are calculated specifically for xenon in the region of its

critical point. They assume the pair correlation function $h(r)$ to be a homogeneous function of $\kappa = \frac{1}{\xi}$ and of r for small κ and r^{-1} :

$$h(r) \sim A \frac{f(\kappa r)}{r^{1+\eta}}, \quad f(0)=1.$$

The critical index η has its usual meaning. Hocken and Stell found that if $h(r)$ has this form then $(n-n_b)$ is itself homogeneous of degree $1+\eta$ in κ and $k = 2\pi/\lambda$:

$$(n-n_b) \sim k^{1+\eta} F(\kappa/k).$$

Here n is the refractive index, n_b is the refractive index if there were no critical phenomena and λ is the wavelength of the incident light. They further show that $(n-n_b)$ can be represented by an expansion in the variable κ/k and that for $\kappa/k > 1$

$$(n-n_b) \approx (\text{const.}) \left(\frac{\kappa}{k}\right)^{\eta-1}.$$

Additional terms must be retained in the expansion for smaller values of κ/k . Their calculations show that n (real-part) increases at the critical point but remains finite.

We have made preliminary measurements of the anomalous increase of n in the region of the critical point of a critical mixture of cyclohexane and methanol. A deliberate wedge was introduced in the spacing between the flats of the cell to give straight interference fringes. The location of the fringes was determined as a function of temperature with a measuring telescope. The spacing of the flats was about 0.6 mm, the wedge about 8×10^{-5} radian which gives a fringe spacing of about 3 mm. As a sample, Figure 2 shows the raw data on one of the fringes. The position of the fringe is plotted versus the temperature difference $(T-T_c)$. The position of a fringe can be measured with a precision of ± 4 microns easily at temperatures $30\text{m}^\circ\text{K}$ or greater from T_c and ± 10 microns within $30\text{m}^\circ\text{K}$ of T_c . This means that the instrument has a potential capability of measuring a change in n of 1×10^{-6} .

Refer to Figure 2. We scan from a temperature above T_c down through T_c . The contraction of the cell resulting from this lowering of the temperature causes a general shift of the fringes to the right in the Figure. This is the dominant effect at temperatures far from T_c . The change in the background refractive index n_b is linear in the range of the scan and also shifts the fringe to the right but only slightly ($\frac{dn_b}{dT} \approx 0.005$ $^\circ\text{K}^{-1}$). The combination of these two effects was determined by an experiment

performed in a temperature interval outside the critical region. As the experiment proceeds in the critical region toward T_c , n apparently increases since the fringe moves more slowly to the right, finally stops and moves in the opposite direction. Using this preliminary data we have subtracted away the cell contraction and background refractive index changes together with a small but rather steady systematic shift which we have not yet completely identified but which can be measured. With these corrections we have drawn a smooth curve through the data points and have taken a few points along this curve to construct a refractive index ($n-n_b$) versus temperature ($T-T_c$) curve for a quick assessment of the general behavior of the refractive index in the critical region. This curve is shown in Figure 3. Insufficient data was taken on the systematic shift to make full use of the data, but the scan rate is such that over a period of 20 minutes and in a temperature region including the highest three points of Figure 2, the anomalous part of the fringe shift is 84 to 169 microns compared to the expected systematic fringe shift of about 25 microns. This systematic fringe shift at the present time can vary as much as 33% from one hour to the next. This gives us the calculated shift of the curve (points in squares) shown on the Figure. The error incurred by scanning too rapidly can not be assessed until further experiments are done at a slower scan rate.

There are slight differences between the values of ($n-n_b$) measured using different fringes in the same experiment. At this point, these differences are thought to be due to differences in the conditions of "equilibrium" in the different regions of the cell examined by the separate fringes. Nucleation occurs at different temperatures for each fringe. This point of initial nucleation was chosen as the critical temperature. This point appears as a stipling of the fringes. For the 4 fringes observed, the points of nucleation occurred over a range of about 25 m°K. Only two runs have been made on two different days and the scan rates were high, 0.44 m°K/min. and 0.37 m°K/min. for purposes of a quick determination of the problems.

The behavior of the measured corrections, the ease and precision with which they can be measured and the range of nucleation temperatures leads us to conclude from the present data that the large excursions in the fringe position, Figure 2, at temperatures within 30 m°K of T_c are due to non-equilibrium conditions. We attribute these large excursions to an excessively large temperature scan in this region and we suspect the data at temperatures within 30 m°K of T_c to be unreliable. On the other hand, the behavior of

this limited data at temperatures $30\text{m}^\circ\text{K}$ above T_c and greater is considered reliable. We will now repeat the experiment at slower scanning rates and see if the range in temperatures of the nucleation points narrows, and if the values of $(n-n_b)$ obtained from the 4 fringes give closer agreement in $(n-n_b)$ determined from them. The sample data that we have given in Figure 1 was for the fringe that nucleated last, i.e., had the lowest critical temperature (according to our criterion for T_c). This fringe also has the smallest change in refractive index. It appeared to be the fringe least likely to be experiencing non-equilibrium conditions.

It should perhaps be noted that the apparatus was designed for the flats to be in horizontal planes for the purposes of observing gravitational effects and for stability. Our first experiments have the flats in vertical planes for purposes of observing the interface between the two coexisting phases when $T < T_c$.

Further experiments using radiation of different wavelengths should provide a test of Hocken and Stell's relationship $(n-n_b) \propto (k/k)^{\eta-1}$. If it tests valid then we can determine η . With η known we could then proceed to find ξ and the critical index ν from the temperature variation assuming a simple power law relationship for ξ . ($\xi = \xi_0 \left(\frac{T-T_c}{T_c} \right)^{-\nu}$.) If these relationships are found to hold then we have a very simple means of measuring the critical indices η and ν by merely observing the motion of a fringe with a measuring telescope. We can also use the cell for determining the coexistence curve and the index β .

We hope to complete this work on the anomalous refractive index for large spacings (bulk fluid) in the present contract period and submit the results for publication. We will submit the design and performance details of the Fabry-Perot cell as a separate publication. During the time left in this contract period we would also like to move to smaller spacings between the flats and look for shifts in the critical temperature.

Other Work in Progress

A separate temperature controlled cell has been constructed and is being used to determine precise critical concentrations and also for relating the concentration to the refractive index.

Total Internal Reflection Spectroscopy

Contrary to our plans in the proposal for this period, little work was done with the internal reflection elements mostly due to the demands in time of the Fabry-Perot developmental work. Some problems arose with the optical company who fabricated these prisms. We had difficulty in finding a suitable optical cement for gluing the prisms onto the cell windows. All of those that we have tried have been affected by the cyclohexane-methanol mixture. We chose this mixture because the difference in refractive index between cyclohexane and methanol is particularly large which would give us maximum sensitivity for turbidity measurements with the internal reflection element. Further, we would like to study the same fluids in both the Fabry-Perot and internal reflection systems for purposes of comparison at this developmental stage. If a suitable cement or masking material can not be found we will have to use some other critical mixture.

Because of the success of the Fabry-Perot system, priority on our time will remain with this work.

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FIGURE 1. FABRY-PÉROT CELL