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CRITICAL SCATTERING OF LASER LIGHT BY FLUID FILMS, AND INTERFACES

MASTER

Progress Report

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Abstract

Analysis of results of coexistence curve measurements for films of a 2,6-lutidine + water critical mixture, has resulted in the first general confirmation of the scaling theory description of Ising class fluid film critical behavior. For example, we have shown that (3,1) to (2,1) universality class transitions occur in these films as a result of finite size constraints upon the evolution of the correlation length, ξ. There exists a generalized law of corresponding states for films. The critical temperature-shift exponent and the crossover temperature critical exponent agree with the values predicted by scaling theory. The 2D regime coexistence curve amplitude dependence upon film thickness is consistent with scaling theory. There exists an unanticipated interaction between the fluid films and the interferometer mirrors in contact with them. This is manifested in a uniform, film thickness dependent, displacement of the entire coexistence curve structure in temperature. We have completed construction of an ellipsometer to be used in studies of the interface between a solid surface and a critical fluid. In addition, we have assembled, and are currently evaluating, a system for studying the intensity autocorrelation of light scattered from critical fluid films. Progress has been made toward developing mathematical techniques for analyzing non-exponential correlation functions in terms of expansions in orthogonal polynomials.

I. Introduction

Progress during the current contract year has been dominated by significant development of our understanding of the effects of restricted geometry on the static critical properties of fluid films. The results of our research on this fundamental problem have appeared in two Physical Review Letters[1,2] and in the Proceedings of the 2nd USA-USSR Light Scattering Symposium.[3]

II. Studies of Thick Fluid Film Critical Behavior

A. Effects of Finite Size on Static Critical Phenomena in Fluid Films

Our investigation of the thickness dependence of coexistence curves for films of a 2,6-lutidine + water critical mixture is largely complete. Since several short papers outlining this work have been published[1-3], we will limit the following discussion.

This research is unique in that all predictions of scaling theory for critical films have been tested, and with the single exception of the thickness dependence of the 2D domain coexistence curve amplitude, have been confirmed. In the latter case we were able to provide reasonable support for the behavior predicted by theory.

A surprising result of this work is the evidence it provides for the existence of an unanticipated effective solid surface-fluid interaction. This acts concurrently with, but in a sense orthogonal to, the ξ constraint finite size effect considered by scaling theory for films. The finite size effects associated with the ξ constraint are manifested in the (3,1) to (2,1) universality class crossovers (3D to 2D) and in shifts of the internal structure of the coexistence curves (see attached reprints for explanation). The solid surface-fluid effect appears as a uniform temperature translation of the entire coexistence curve structure. It is specific-surface dependent, but

in a restricted way. The amplitude and sign of the effect change when the surface in contact with the fluid is changed from a metal (Ag) to a dielectric (SiO_2). However, the value of the scaling exponent is unchanged. The origin of this new effect is not understood at present.

B. Selection of a Binary Fluid System for Future Film Studies

We have developed a screening procedure, based upon criteria evolving from our research on 2,6-lutidine + water, which enables us to identify especially promising fluid mixtures from tabulated bulk data. This is significant in light of our attempts to reexamine the cyclohexane + methanol system (C+M) and in terms of the requirement that we study the effect of finite size on a system with an upper critical point. (2,6-lutidine + water has a lower critical point.)

Application of this screening procedure shows that the mixture diiodomethane + cyclohexane, which has an upper critical point, is an extremely attractive candidate for future work. It should have a broad range of useable film thickness, primarily due to its large refractive index-coexistence curve amplitude.

C. Films of Cyclohexane + Methanol

Our original experiments with critical fluid films studied the mixture C+M[4]. Although no scaling crossovers were observed, the films displayed mean field scaling behavior, a result at variance with theoretical predictions. During the present contract period we have reexamined films of C+M for two essential reasons: 1) In light of our extensive experience with the 2,6-lutidine + water films, we are skeptical of the early results, and 2) C+M has an upper critical point, and thus remains a possible candidate for further study. The results of initial experiments have been discouraging, and our current position is that inherent characteristics of the C+M system are

responsible for the lack of success.

We applied the screening procedure discussed earlier to C+M. It shows that the mixture is not especially promising in the first place. In particular, the refractive index-coexistence curve amplitude is small. This insures that 2D behavior will occur only for very small values of the refractive index difference between phases (a factor of two smaller than for 2,6-lutidine + water). The range of film thickness over which 2D effects should appear is much narrower that for 2,6-lutidine + water. Although this fact alone does not preclude detection of universality class crossovers, it does present a severe challenge to our experimental technique.

A second inherent difficulty concerns critical perfect wetting (CPW). The symptoms association with CPW were first described by Heady and Cahn[5], and Cahn[6] has developed a phenomenological theory to describe it. In our case, the phenomenon would result in a layer of one of the phases being interposed between the other phase and the interferometer mirrors. If the wetted layer thickness was an appreciable fraction of the total film thickness, our experiment would not measure the true film coexistence curve.

There is an accumulating body of observation which strongly suggests that CPW occurs for C+M. We have observed the symptoms which Heady and Cahn described, and we have observed what might be CPW at the liquid-vapor-glass contact in a glass cell. Moldover[7], in an attempt to measure CPW layer thickness in C+M, observed what he believes is CPW with very long equilibration times. We have carried out time lapse photographic studies of the phase boundary structure in 10 μm C+M films. The results are consistent with the existence of long equilibration time CPW.

In summary, our studies of C+M have been confronted with persistent difficulties which we now believe are intrinsic to the system. We have suspended further work on this mixture.

D. Intensity of Light Scattered by Critical Fluid Films

(Refer to Section I-C. of proposal for current year.)

The versatile scattering system which will enable us to measure the intensity of light scattered from fluid films has been constructed. Testing of the system should be completed by the end of this contract period, and then first measurements will be made on 2,6-lutidine + water films.

E. Intensity Autocorrelation Studies of Critical Fluid Films

(Refer to Section I-B. of proposal for current year.)

We have completed construction of the apparatus required to carry out the first Rayleigh scattering studies on critical fluid films. An evaluation of the system at this time shows: 1) The temperature control meets our requirements, however temperature gradients of the order of 1 mK/cm persist within the sample cell. 2) There are fluid losses from the sample cell, but the loss rate is low enough to enable us to carry out pilot studies, probably by the end of this contract period. Additional related progress accomplished during the present contract period is detailed in Section VIII of this report.

III. Ellipsometry Applied to Critical Fluid Films and the Solid-Fluid Interface

(Refer to Section V of the previous progress report and Section II of the current year proposal.)

The apparatus for the ellipsometric study of the critical fluid-solid interface has been completed and measurements to test the system performance have been made on several simple (unfilmed) interfaces such as glass/water and glass/methanol. Ellipsometric measurements of the interface between a critical 2,6-lutidine + water mixture and a solid (optical glass) should be

underway by the beginning of the upcoming contract period. A discussion of some of the technical progress made on this part of our program is included in Section VIII of this report.

IV. Particle Diffusion in Fluid Films and Diffusion in Interacting Particle Suspensions

(Refer to Section IV of the current proposal.)

A. Interacting Particle Suspensions

A study of the crystallography of colloidal crystals comprised of ordered monodisperse charged polymer spheres has been published in Nature[8] by Allan Hurd of our group, along with Noel Clark and a former member of our group, Bruce Ackerson. This work is related to the proposed program of study on interacting particle systems, and was supported under the contract for the present period. Reprints are attached.

B. Particle Diffusion in Fluid Films

B.1. Non-Interacting Particle Diffusion in Films

(Refer to Section IV of previous progress report.)

This experiment was originally intended to serve as a prototype to test the feasibility of carrying out Rayleigh scattering studies on critical fluid films. It has satisfied that function, revealing a host of significant technical problems that required solution before the critical fluid film studies could begin. In addition, our first experimental results made it apparent that, if taken seriously, this experiment could serve as an interesting test of hydrodynamic theoretical treatments of microscopic particle diffusion in films and solid-fluid interfaces.

As reported in our previous progress report, the trend in the mean diffusion constant (i.e. the first cumulant of the autocorrelation function) as a function of spacing can be well described by a hydrodynamic theory due to H. Faxen[9], good to zeroth order in the Reynolds number. Faxen used a

perturbation method (the "method of reflections") to find an estimate of the friction factor for a sphere moving through a fluid parallel to two bounding walls, as a function of the ratio of the total gap to the sphere radius, L/a, and the eccentricity, e, the distance from the center of film divided by the film thickness. In particular, we discovered that our first cumulant data seem to fit the case where the spheres are centered (e=0) on the average, implying that some transverse forces, either direct or hydrodynamic, exist. Of greater potential importance is the behavior of the second cumulant for small film thicknesses. For L/a less than about 4, the deviation from a pure autocorrelation function becomes significant. This indicates that spheres of non zero eccentricities contribute to the spectrum, and in fact gives a clue to the relative magnitude of the wall potentials compared to the thermal energy of the particles.

Largely because of this, we deferred publication of our first cumulant results and launched an effort to develop techniques to enable reliable measurements of second cumulants. (Progress in developing experimental and analysis techniques for optimizing the process of extracting information from non exponential autocorrelation functions is included in Section VIII of this report.)

Considerable effort has been applied to develop an understanding of the transverse forces responsible for the observed non exponentiality. The hydrodynamic forces can come from rotational-translational Brownian motion coupling, and from fluid inertia effects.[10] The direct forces are either electrical or steric, and are much easier to understand. Consequently, it is appropriate that the sample characteristics be chosen so that direct forces dominate the transverse hydrodynamic forces. This can be done by cleaning the colloids by ion exchange, then titrating with NaOH to the desired conductance.

It is necessary that the interaction range be much less than the interparticle separation to insure independent particle diffusion, but large enough to dominate the hydrodynamic forces. The distribution of eccentricities will then be given simply by a Boltzmann factor, exp(-U/kT), where U is the known double layer potential.

It is anticipated that the experimental work on this specific problem will be completed during the present contract period.

B.2 Interacting Particle Diffusion in Films

Progress has been of a technical nature, and is treated in Section VIII of this report. For information on the rationale of these studies, refer to Section IV of the proposal for the current year.

V. Index of Refraction Anomaly

(Refer to Section I-E. of proposal for current period.)

Work on these measurements was largely suspended to enable us to concentrate on the critical fluid film studies.[1-3] However, we were able to evaluate the improved cell discussed in our last report, and we find that mechanical relaxation of the interferometer separation is reduced in the new cell by a factor of ten over earlier designs. We anticipate completing these measurements during the next contract period.

VI. Measurement of the Coexistence Curve of a Binary Fluid

(Refer to Section III of current year proposal.)

We proposed an alternate method for determining the critical exponent β for 2,6-lutidine + water, where the requirement for the measurement followed from the need to have a "large sample" value for β, which could be compared with our film results far from the critical point. The alternate method was considered because of difficulties experienced during the previous contract period in applying the prism cell technique. These difficulties were

manifested in a steady decrease of the critical separation temperature of the mixture when it was placed in the nickel plated-aluminum prism cell.

However, during the present contract period, in an example of stubborness carried to extremes, we gold plated the nickel-aluminum cell, and in addition, build an all glass prism cell. The first change affected a significant reduction in the T_c drift, and the second, eliminated it. We are now carrying out successful coexistence curve measurements for 2,6-lutidine + water, and preliminary results indicate that β is in agreement with values found for other binary mixtures, and with the value we find for films of the same system in the 3D scaling regime. As a result, we will not proceed with the alternate method discussed in the current year proposal.

VII. Autocorrelation Spectroscopy in the Very Short Time Domain

(Refer to Section V of current year proposal.)

The feasibility of using a Michelson interferometer as an autocorrelation spectrometer to investigate the short time dynamics of fluids, has been evaluated. The interferometer can be constructed without undue difficulty and it will enable determination of the electric field autocorrelation function over times ranging from considerably less than 1 ps, to 1 ns. However, the technique seems to offer no advantages relative to the use of a double grating Raman spectrometer to determine $S(k,\omega)$ over the relevant frequency domain. Thus, we have discarded the idea of developing a Michelson interferometer-autocorrelator.

VIII. Technical Progress

A. Technical Progress on Intensity Autocorrelation Spectroscopy Applied to Fluid Films

Our proposed program of light scattering studies on fluid films is separable into two parts: the first consists of applying intensity autocorrelation spectroscopy to probe microparticle diffusion in fluid films,

where the long range intent is to characterize the dynamics of suspensions of interacting particles under conditions which insure the elimination of multiple scattering. In the absence of multiple scattering it should be possible to analyze the effect of the screened interparticle Coulomb interactions upon the particle dynamics, over a particle density range encompassing gas-like, liquid-like, and solid-like behavior. The second part of the program consists of a pioneering effort to apply light scattering to study the dynamical scaling properties of a constrained critical fluid film as it undergoes a (3,1) to (2,1) universality class transformation. This work is an essential extension of our studies[1-3] of the effects of restricted geometry on the static scaling behavior of critical fluid films.

There are several technical problems common to the two parts of the program. The first concerns the very general question: "What is the most effective technique for extracting meaningful physical information from non exponential autocorrelation functions?" As reflected in the extensive literature on the subject, this question has a significance which extends beyond the limits of our interests. Other shared technical aspects include the problem of controlled heterodyning in the thick film system, the real time determination of film thickness, and the development of appropriate computer software for the analysis of experimental results. Progress accomplished in these areas during the current contract year is treated below.

A.1 Unbiased Estimators for a Set of Statistics of Multiexponential Decays.

The problem of analyzing nonexponential decays in intensity autocorrelation functions has long been a barrier to applying quasielastic light scattering to such problems as the characterization of particle size distributions and the dynamics of interacting Brownian particles. The traditional method of cumulant expansions yields estimates of the algebraic

moments of the distribution of decays present, $\langle \Gamma^n \rangle$, but due to truncation of the cumulant expansion they suffer from systematic bias. In general, cumulants are defined only in the limit of zero delay time, forcing the experimenter to extrapolate to the required limit with no specific guidelines for weighting the values. Furthermore, errors in the background correction severely affect the values of second and higher moments. Recent advances in direct Laplace inversion provide promising methods for the direct evaluation of the distribution function, but they often suffer from ill-conditioning and nonuniqueness. Penalty functions which are employed to solve these numerical problems, serve to restrict the range of applicability and bias the results.

During the present contract period, we have shown that expansions in orthogonal polynomials have no truncation errors, do not require extapolations, are insensitive (above zeroth order) to incorrect background corrections, and can be tailored to avoid numerical problems. The resulting functional moments, $\langle B_1(\Gamma) \rangle$, have perhaps a less convenient interpretation than the algebraic moments, but are <u>not</u> affected by the systematic bias introduced by truncation of the expansion. For example, in cumulant analysis, values of $\langle \Gamma^m \rangle$ for different order fits will in general disagree, due in part to truncation of the series. In the orthogonal polynomial case, truncation errors are nonexistent. Hence, the same value of $\langle B_1(\Gamma) \rangle$ will be obtained for first, second, third, or any order fit greater than one.

Finally, the numerical advantages of orthogonal polynomials have been demonstrated in practice. The orthogonality forces the normal equations inherent in any linear least square problem to degenerate to diagonal form, thereby eliminating the dangerous (from the standpoint of round-off) and time consuming step of evaluating a determinant.

We are presently comparing the orthogonal polynomial expansion technique with other methods which are currently used for analyzing non exponential decays. The initial results of the comparisons are encouraging.

A.2 Heterodyning

(Refer to previous progress report, Sect. IV.)

A single beam technique using flares present in the optical flats has been improved to the point that it is now viable for sufficiently small film thicknesses. The major breakthrough came in simply observing the scattering intensity through a microscope focused at the plane of the photomultiplier cathode. This technique graphically reveals the spatial coherence of the light, so that collection optics can be designed and tuned for optimum operation. Observing the coherence properties is an invaluable aid in understanding the process of heterodyne detection, to say nothing of the confidence it lends to the experimenter involved in the process of optical system line-up and wave front matching. We have also carried out a theoretical study of the effects, on the first two cumulants of the autocorrelation function, of mixing efficiency, the coherence area factor, and the local oscillator efficiency.

During the current contract year we have carried out an analysis of a fiber-optic heterodyne system which uses a double-input , single-output fiber optic T-coupler as a mixer for the scattered light and the reference signal. The scattered light is collected and introduced into the T-coupler via one input fiber, the local oscillator via the second input fiber, and the combined signal is conveyed to the detector via the output fiber. This system has the advantage that it eliminates the optical components usually found in a heterodyne spectrometer, such as lenses, beam splitters, and mirrors, thus simplifying the alignment of the optical paths. Also, by passing both the

scattered light and the local oscillator through fibers, one expects better wavefront matching and a higher optical mixing efficiency. We anticipate that technical evaluation of this system will begin during the present contract period.

A.3 Film Thickness Measurements in Real Time

The variable film thickness cells, designed for the microparticle diffusion studies and for the critical fluid film studies, each display a small but persistent drift in film thickness. As a result it will be useful to be able to make frequent in situ measurements of the film thickness during the course of a measurement.

The spacing, or film thickness measurement technique has been refined significantly, by taking advantage of the fact that the order number of an extinction in a ray reflected by the flats must be an integer. Thus, under the most favorable conditions, a one micron spacing can be measured in seconds to within 1% (10 Angstroms). In addition, a multiwavelength scheme has been designed to handle the submicron spacings which show no extinctions inside the critical angle.

A.4 Software Development

In general, the correlator analysis program has been improved and updated as a continuing process. Helpful parameters have been added for both heterodyning and homodyning and the fitting routines were replaced with improved software (FORSYT, below). For colloids, the hydrodynamic radius calculation now includes an important (2-5% per degree) temperature correction.

Subprograms of general utility that have been written and added to the Scientific Subroutine Library are:

a) PLGUER -- calculates Laguerre polynomials,

b) BICOEF -- calculates binomial coefficients,

c) FACTRL -- calculates n!

d) SBESS1, 2 -- calculates spherical Bessel functions,

e) FORSYT, FSYT2 -- and associated support routines do polynomial fits of arbitrary order to data by orthogonal polynomials. These routines constitute a substantial improvement over determinantal routines.

B. Ellipsometry

A variable spacing sample cell was machined from a Corning ceramic, selected for its low thermal expansion coefficient, its resistance to corrosion and its easy machinability. However, the cell persisted in leaking fluid at a rate of about 0.5 mg/hr., due to the failure of the ceramic to seal against a teflon coated O-ring. The ceramic will be coated, either with teflon or with gold plating to solve the sealing problem. In the interim, we have built a simpler stainless steel cell which does not have the variable spacing feature of the ceramic cell, but which is adequate for the interface studies. This cell is now being used in measuring simple (unfilmed) interfaces, such as glass/water, and glass/methanol, in order to test and calibrate the optics.

The dispersion and prism angles of the high index prism were determined to 0.00004 and to 0.005 degrees, respectively, using two methods. Absolute angular measurements of the prism angles were performed using a high precision mill index. A dispersion curve was calculated from a least squares fit to both melt data and data obtained by applying the minimum deviation angle method for several emission lines. The latter method also yielded values for the prism angles.

Several improvements of the light detection system have been made, which should result in improved signal to noise ratios and enhanced measurement precision. Light detection up to now has been accomplished by a photodiode,

two stage amplifier and a DC meter. In principle, a light intensity range spanning six orders of magnitude can be detected. However, DC and low frequency noise combine to limit this range, forcing the incorporation of several improvements. A circuit has been designed, and will be in operation by the end of this contract period, which takes a reference signal directly from the laser output and divides it into the measured signal, thus corecting for laser power fluctuations. The present 0.5 mw laser will be replaced by one with a 5mw output, and finally, we will use lock-in detection in which a Faraday rotator is used to modulate the angle of polarization of the light.

C. Temperature Controller

A simple, inexpensive temperature controller, capable of controlling temperatures to better than 100 μK, has been developed by Mark Handschy of our group. A manuscript has been submitted for publication to J. Phys. E., and copies are appended to this report.

Reprints + Preprints removed

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