LIGHT-SCATTERING STUDIES OF
LOWER-DIMENSIONAL COLLOIDAL-PARTICLE AND
CRITICAL-FLUID SYSTEMS

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Abstract

We have extended the theoretical description of the lattice excitations in crystals formed of charged colloidal particle suspensions (CCPS) to include the effects of bounding surfaces. One of the new features that arises in a CCPS crystal confined by surfaces to form a film, is that propagating lattice waves cannot exist at the center of the Brillouin zone. Techniques have been developed to form systems of colloidal particles in monolayers on a water surface and on membranes. Transitions from gas to liquid to two dimensional solid phases have been observed in both classes of system. The two dimensional solid phases range from single crystals having a hexagonal lattice with long range translational order, to hexatic forms with short range translational order and long range orientation order, to amorphous or glass-like structures. The Rayleigh scattering studies on thin films of a critical mixture of 2,6lutidine + water have been extended to a film of thickness 0.5 μm . The dynamical critical behavior of this film remains strictly three dimensional to within 2 mK of the extrapolated critical point, where an apparent first order transition occurs.

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I. Introduction

Our interest is concerned with studying those modifications of a physical system's properties that result when one spatial dimension is reduced until it is comparable to some significant characteristic length. To this end, we have proposed a variety of experiments on two classes of lower dimensional system. They are:

- a. Lower dimensional charged colloidal particle suspensions (CCPS)

We use the acronym CCPS as a generic term referring to any monodisperse collection of charged polymer microspheres, either in aqueous suspension, or in liquid interfaces. By forming CCPS in films and in liquid interfaces, lower dimensional conditions can be realized.

- b. Lower dimensional critical fluid films-

A confined film formed of a critical binary fluid mixture should show the influence of confinement, when the correlation length of the concentration fluctuations becomes comparable to the film thickness.

In this report, we discuss the initial progress made on these studies.

II. Studies of Thin Film Colloidal Particle Suspensions

In this part of the program we will take advantage of the expanded length scale (typical interparticle separations of $\sim 1 \mu\text{m}$) and slowed time response (initial response time of $\approx 1 \text{ msec}$) of CCPS to study lower dimensional behavior in both the liquid and crystalline states of CCPS films.

During the first six months of the contract period we have made progress in our theoretical understanding of the effects on the lattice dynamics of CCPS crystals due to the presence of walls. These results bear directly on the experiments we've proposed to study the influence of film thickness on the melting/crystallization transition, and on supercooling and nucleation in CCPS films. We've succeeded in developing a consistent formalism for determining the frictional response of the solvent to CCPS crystal lattice excitations, for both long and short wavelengths. One of the new features that arises when a CCPS crystal is bounded to form a film, is that propagating lattice waves cannot exist at $q = 0$, but only within some bounded range of non zero q . We've submitted a manuscript covering these results to Physics of Fluids, and a copy is attached to this report.

II. Systems of Colloidal Particles on Interfaces

Work was done in two principal areas:

- a) The development of techniques to observe the crystal structures formed by colloidal particles on the surface of water, to observe the particle dynamics, and to determine the interparticle forces.
- b) The development of techniques, to observe the crystal structures formed by colloidal particles on membranes, to observe the particle dynamics, and to determine the interparticle forces.
- a) Colloidal Particles on the Surface of Water

In 1980, Pieranski reported observations of two dimensional (2D) colloidal crystals on the surface of very shallow ($< 3 \mu\text{m}$) layers of pure water¹. These crystals exhibited remarkably large lattice constants- 3 to 5 colloid sphere diameters- quite comparable to those lattice constants observed in 3D CCPS crystals².

We have observed similar 2D colloidal crystals on the surface of water (see Fig. 1), where in our case, the lattice constants for the hexagonal structure could be varied over a range of 2 to 5 sphere diameters. Our experiments differ from those of Pieranski in that the crystals are formed on water of rather arbitrary depth ($\approx 1\text{cm}$) in a miniature Langmuir trough that was constructed and fitted to a microscope stage.

Our observations can be summarized as follows: Immediately upon introducing the colloid suspension onto the water surface, it covers the entire surface as a 2D gas-like system which rapidly forms crystalline rafts having very small lattice constants (spheres almost touch) floating in a sea of more tenuous crystals of large lattice constant (2 to 10 sphere diameters). By reducing the microsphere number density of the applied suspension, the entire surface can be covered with the large lattice constant system. The small lattice constant, well ordered crystals, are disrupted by networks of grain boundaries. The large lattice constant systems are usually not as well ordered, and are suggestive of the hexatic phase³, with configurations displaying short range translational order, but having extended correlations in the orientation of crystallographic axes (see Fig. 1). In some instances, completely amorphous configurations, with short range translational and orientational order are observed; probably associated with

Fig. 1 2.02 micron diameter microspheres on the surface of water. System is in a hexatic phase, with short range translational order and long range orientational order.

contamination of the water. If we change the surface area available to the spheres by moving the Langmuir trough barriers, we find that the surface number density changes almost linearly with change in surface area. There seems to be no loss of spheres from the surface on this compression process.

Pieranski proposed that the forces between microspheres were strictly repulsive, and due to the dipoles produced by the charged spheres and their associated counterion clouds.¹ He took no account of capillary forces in his analysis. Marcerou⁴ has developed a theory that appears to apply to the interaction of charged colloidal particles on a liquid interface and on membranes as well. These forces are related to the energy of elastic distortion of the surfaces. Marcerou's treatment looks especially applicable to the systems that we observe. However, in order to make an adequate assessment of his theory or some variation of it, by comparison with our experiments, it will require that we obtain a more accurate determination of the ionic content of our water solutions and of the charges on the colloidal spheres.

b) Colloidal Particles on Membranes

Our development of techniques for producing hexagonal crystals of colloidal particles on freely suspended soap films has provided us with a visual means of studying crystal defect formation in this model system.

We find that multi-domain crystalline rafts can be stressed to the point where line dislocations suddenly appear and propagate in response to the stress. Upon removal of the stress, the dislocation may disappear in a healing process. We observe melting phenomena occurring in the contact regime between two colliding crystalline rafts. After a short time interval, the two original multi-domain crystals move as a single rigid unit, the regime of collision contact having completely healed into normal crystalline material.

Statistical mechanics relates the number of vacancies n in a crystal at equilibrium to the total number of atoms (microspheres) N in the system (a single domain) by

$$n/N = \exp\left(\frac{-E^{\circ} + E^{\text{ph}}}{kT}\right)$$

where E^0 is the energy required to extract a single sphere from the crystal, and E^{ph} is the vibrational energy per mode. If we count the average number of vacancies for an ensemble of crystalline domains, we estimate $E^0 \approx 0.1$ eV if we neglect E^{ph} relative to E^0 ; i.e. the bonding is roughly four times kT at room temperature. We expect the crystal binding to be appreciably weaker for crystals on the surface of water.

Although the soap membranes are easy to work with in air, their dynamics is complicated by the film thinning process. Initially, a rather thick layer of water solution is trapped between the two soap film layers, and this thins rapidly and non uniformly.

Bilipid membranes are expected to behave more simply. They are also potentially more significant, because bilipid membranes are important structures in biological cells. Bilipid membranes in water are, in a sense, the reverse of freely suspended soap membranes in air. The polar "heads" of the lipid layers point outward into the aqueous solution, and the hydrophobic "tails" of the two lipid layers are contiguous. There is no water sandwiched between them as there is in the soap membrane in air, and there should be no problem with thinning instabilities.

A cell has been constructed, the purpose of which is to produce bilipid membranes containing colloid particles from a lipid monolayer on the surface of water. This cell was designed to accommodate both light scattering experiments as well as studies based on direct microscope observations.

We have nearly completed construction of a wedge plate interferometer which will be used to study surface irregularities in CCPS monolayers and membranes. The interferometer is composed of two highly reflecting optical flats, one below the surface of the liquid supporting the monolayer or bilayer, and parallel to it, and the other above the surface at a slight wedge angle. Such an interferometer can detect surface thickness irregularities with a sensitivity of about $10 \text{ \AA}$. We have successfully used such interferometers to study critical phenomena in thin films of critical fluid mixtures⁵. The applications proposed for this interferometer during the upcoming contract period will be discussed in the attached Proposal. However, we expect that testing of the system will be completed by the end of the current contract period.

IV Dynamical Properties of Lower Dimensional Critical Fluids

We have succeeded in taking good intensity autocorrelation data from a 0.5 μm thick, trapped film of a 2,6lutidine + H_2O critical mixture. This represents a reduction in film thickness by a factor of four from the result we reported earlier.⁶ For this new film, the finite size domain is defined by $k\xi \geq 3$, and thus, we might expect departures from 3D critical dynamics to occur for values of the wavenumber-correlation length product greater than about 3. We managed to measure the reduced Rayleigh linewidth⁶, at eight values of $k\xi$, ranging between $k\xi \approx 3$ and $k\xi \approx 10$, and at eight $k\xi$ values within the hydrodynamic regime ($k\xi < 1$).

We've drawn several conclusions from these results. The 0.5 μm film behaves dynamically as a bulk (3D) critical system, and seems to approach to within 2mK of a true 3D critical point, T_c^{film} . There is no evidence of "off loading"; throughout the film critical regime, it behaves as if it were at the critical composition to within the precision of our measurements. When the film temperature is shifted closer to T_c^{film} ($T_c^{\text{film}} - T \leq 2\text{mK}$), the film heads toward another type of transition, which does not exhibit critical scattering, and for which hysteresis is observed in the phase separation. This combination of observations suggests that the film enters a first order transition just before T_c^{film} is reached.

A manuscript detailing our results to date on these studies is being prepared for Physical Review A.

V. Summary of Progress and Prospects for the First Year

Allan Armstrong was added to the program as a Graduate Student R.A. in October, 1982. Allan was assigned to work on studies of the properties of colloidal particles on membranes. Russell Walker, who transferred to C.U. from Cal Tech, will start in June on an R.A. he will begin work on the problem of melting/crystallization, and supercooling of thin CCPS films. We hope to be able to add a third student, beginning in June.

We expect that a significant part of the progress made during the first contract year will occur during June and July, when both PIs are able to contribute on a full time basis. Once we can develop a cadre of trained Graduate Students, then past experience indicates that progress should be sustained throughout the year.

IV. Principal Investigator Time and Effort Estimates

William O'Sullivan-100% effort, last two weeks of August, 1982;
20% effort (est.) for 1982-1983 Academic Year:
100% effort for the last week in May, and for
June and July, 1983. (2.5 months of summer salary
are funded by the contract.)

Richard Mockler- 100% effort for August, 1982, 20% effort (est.)
for 1982-1983 AY, and a planned 100% effort for the
last week in May, and for June and July, 1983.
(2.5 months of summer salary are funded by this
contract.)

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