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STUDIES OF MELTING, CRYSTALLIZATION, AND COMMENSURATE–INCOMMENSURATE TRANSITIONS IN TWO DIMENSIONS

Terminal Year Progress Report

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Abstract

The four year period of this contract was devoted to the study of two dimensional (2D) systems of particles in their fluid and crystalline phases and especially in their behavior on passage through the freezing/melting (F/M) transition. Monolayers of microspheres both on the surface of water and trapped in water films between parallel quartz plates were used in these studies. In addition, macroscopic-size steel spheres were used in similar studies jointly with Noel Clark's group. There was only partial agreement with the predictions of theory in the F/M behavior of these 3 systems. The air/water (A/W) interface experiments displayed a two-step continuous F/M transition in agreement with theory for 2.88 μm particles with a definite intermediate (hexatic) phase. An A/W system of 1.01 μm spheres exhibits what we interpreted to be a first order transition with a very narrow coexistence region in place of the hexatic phase. The trapped water film monolayer experiments using 1.01 μm spheres showed the same behavior, i.e. , a narrow range of two-phase coexistence and a first order F/M transition. The steel spheres displayed a definite first order F/M transition. In all these cases the observed defect behavior was more complex than theory predicts.

The techniques of electron-beam lithography and plasma etching were used to produce square arrays of wells and parallel linear channels on a quartz plate. This together with a second parallel smooth plate confined a monolayer if 1.01 μm spheres in a water film. For a plate separation of ≈ 3 μm the monolayer formed a triangular crystal structure incommensurate with the square and channel arrays. As the plate separation was reduced to ≈ 1.5 μm the spheres came into register with the arrays of wells and channels. The variation of electrostatic forces associated with the wells and channels was clearly evident in this commensurate/incommensurate transformation as the plate separation was varied in-and-out.

Damped lattice dynamics and hydrodynamics interactions were studied using the techniques of autocorrelation spectroscopy on a crystalline monolayer on the surface of water. Thermal relaxation times and Lamé coefficients were obtained.

Experiments were initiated to measure the variation of the surface tension of an A/W interface containing a crystalline monolayer at different states of compression.

The forth year of this contract was devoted to MAP studies in — collaboration with Paul Phillipson — related to the virtual dislocation-pair theory described in A. Armstrong's thesis, and a molecular dynamics simulation of a 2D liquid close to its freezing point was carried on jointly with Noel Clark's group.

The experimental effort during this period was devoted to further developments of apparatus and techniques associated with colloidal monolayers at the A/W interface. Experiments are in progress to measure directly the isothermal compressibility and the pressure equation of state. Direct determinations are accessible by observing the gravitational compression of the monolayer from gaseous to compressed crystalline on the curved meniscus at the edge of the trough container.

1. Studies of the 2D Melting Process, Background

This program of research was a study of two-dimensional (2D) colloidal monolayers both on the surface of water and in thin water films trapped between fused-silica optical flats. The principle effort was devoted to the characterization of the freezing/melting process of these monolayers. The micron-size particles are observable through a microscope and their Brownian motion is sufficiently slow to be tracked with a video camera. Positional data of the individual spheres were obtained on video tape and digitized for computer analysis. A sequence of video frames provided the time progression of the individual spheres within the field of view. Translational and orientational correlation functions, the structure, and the Wigner-Seitz plots were determined for each density in the time sequence as the system was compressed or expanded through the density range from solid/crystalline to fluid (or the reverse). The Wigner-Seitz plots provided the defect structures and their variations as the surface pressure changed.

Kosterlitz, Thouless [1], Halperin, Nelson [2], and Young [3] provided us with a rather distinct theory for 2D melting which we refer to as the KYHNY theory. This theory predicts that in 2D the melting/freezing process may be two successive continuous transitions (in contrast to the single first order transition familiar in 3D). In the crystalline phase the system has quasi-long-range order (QLRO) and the translational correlation function $g(r)$ has power law decay, $g(r) \sim r^{-\eta}$. Here the system has long-range orientational order and the orientational correlation function $g_6(r)$ is asymptotically constant. As the system is expanded through the first continuous transition $g(r)$ decays exponentially, implying short-range order (SRO), and $g_6(r)$ displays power law decay (QLRO) in this new intermediate phase which is called the **hexatic** phase. As the system is further expanded through the second continuous transition the system looses its orientational order and $g_6(r)$ displays exponential decay (SRO). The system now has neither translational nor orientational order and is in the fluid state.

The theory also predicts that dislocation pairs exist in the crystalline phase which dissociate (*unbind*) at the first transition so that the hexatic phase contains free dislocations. These dislocations (or disclination pairs) unbind at the second transition to become free disclinations yielding the disordered fluid phase.

2D melting/freezing was studied in three different systems each with quite different particle interactions:

A. Monolayers of microspheres on the surface of water contained in a trough with movable barriers so the colloidal system could be compressed or expanded isothermally through the phase transition(s).

B. Monolayers of microspheres suspended in water and trapped in a thin film between two parallel fused-silica plates. The crystal was melted by free expansion.

C. Monolayers of steel balls ($\frac{1}{16}$ inch dia.) confined between two charged conducting plates one of which is transparent. The particles are caused to move by mechanically fluctuating the lower (metal) plate. This provided the system with an adjustable *temperature*.

In each case the observations were compared with the predictions of KTHNY.

1.A Freezing/Melting Transition of a Colloidal Monolayer on the Surface of Water [4,5,6,7,8]

In these experiments two separate systems were studied as they were slowly compressed or expanded between the fluid and crystalline phases. One contained 2.88 μm spheres and the other 1.01 μm spheres on the surface of pure water. The correlation functions for the 2.88 μm spheres conformed with the predictions of the KTHNY theory. A definite intermediate phase was observed. On the other hand disclinations unbinding was not observed at the second transition (the intermediate to fluid transition). The defected structural change was more complex but perhaps related to the KYHNY scenario: chains of dislocations terminated at the two ends by disclinations of opposite polarity are joined on occasion by additional dislocations thus extending the separation between the terminating disclinations.

The 1.01 μm monolayer did not have a distinct intermediate phase. The QLRO of both the translational and orientational correlation functions was lost at about the same number density. Here regions of solid were seen to grow smaller while regions of fluid grew larger as the system continued to expand through the transitional region, suggesting a narrow range of coexistence and a first order transition. At this density the system is so highly defected that it probably violates the assumptions governing the KTHNY theory.

This work was the thesis research of Allen Armstrong [9].

1.B The Freezing/Melting Transition of a Colloidal Monolayer in a Thin Water Film Trapped Between Parallel Silica Plates [7,8,10,11,12]

In this experiment the free expansion melting of two different crystalline samples of 1.01 μm spheres were observed between parallel plates. Both gave essentially the same results. The translational and orientational correlation functions behaved in accord with the KTHNY theory, however the defect plots (Wigner-Seitz diagrams) show little conformity. Dislocation unbinding at the solid-to-fluid phase transition was definitely not observed. Vacancies appear to play a important role in the process between parallel plates. They are spontaneously generated in the *intermediate* phase and formed rather stable structures at the higher densities. The *intermediate* phase showed liquid areas surrounded by crystalline areas. As the density decreased in the expansion process the liquid areas expanded at the expense of the crystalline areas. This suggests that the intermediate phase is a coexistence region and not the hexatic phase. In this case the transition would be first order and not continuous, and the existence of a hexatic phase cannot be determined solely on the behavior of the correlation functions.

Other conflicts with the predictions of KTHNY: at the second transition (*intermediate*-to-fluid) it was impossible to observe the dissociation of dislocations into two free disclinations of opposite polarity. The system was too highly defected at these densities to identify such a process. Defects were spontaneously created in the form of dislocation clusters, pairs, and dislocation loops characteristic of grain boundaries.

These experiments were Yeke Tang's thesis problem [12].

1.C The Freezing/Melting Transition of a Monolayer of Steel Balls with a Variable Temperature

The melting/freezing studies of this system exhibited a sharp first order phase transition. There was no evidence of an intermediate or hexatic phase [13]. Related to this problem, molecular dynamics simulations of 2D Leonard-Jonesium and a 2D induced dipole system were studied in real time. These computer experiments conformed with the steel ball experiments and revealed that the principal excitations producing particle diffusion are collective events involving chains of particles. In these events each particle is displaced in a snakelike fashion along the local chain direction by a distance of the order of an interparticle spacing. These *snake* events account for nearly all of the diffusion in the 2D systems near freezing [14].

This work was a joint effort between our group (R. Malzbender) and Noel Clark's group (B. Pouligny and N. Clark). Rainer Malzbender transferred to Noel Clark's group in 1988 after which the work was completed and will be published in July [15].

2. Commensurate-Incommensurate Phase Transitions in 2D

The techniques of electron-beam lithography and plasma etching were used to produce square arrays of wells (1.2 μm in diameter and 0.3 μm deep) and channels (0.3 μm deep) in fused silica optical flats. The wells were spaced 2.8 μm apart and the two sets of parallel channels had different widths and spacing. A water film containing 1.0 μm diameter spheres was then trapped between the etched flat and a smooth one. At a separation of ≈ 3 μm between the confining flats the microsphere suspension — at an appropriate concentration — would crystallize with a triangular structure incommensurate with the square well array as if both surfaces were perfectly smooth. As the plates were brought closer together, to about 1.5 μm, the spheres came into register with the square array and the channeled arrays as well. When the spacing was again increased back to its previous value the spheres reordered back into the incommensurate triangular structure. The influence of the strong electrostatic forces was clearly evident as the plates were moved in and out. The colloidal system is highly compressible and registration occurs very easily with the long range electrostatic forces between particles and traps (wells and channels) [16].

This work was discontinued in order that Yeke Tang could devote full time to the free expansion melting experiments (1.B above) for his thesis research.

3. Damped Lattice Dynamics and Hydrodynamic Interactions of a 2D Colloidal Crystal on the surface of Water [17]

A single layer of charged microspheres may be suspended at the air/water interface and will, at sufficient density, form an ordered hexagonal array. The electrostatics of the interfacial system in dominated by a long-range repulsive dipole potential which gives rise to ordering of nearest neighbor separations of ≈ 10 μm for particles having a radius of $a = 0.8$ μm. Laser light scattered from the lattice displays Bragg diffraction as well as a fluctuating diffuse background due to damped thermal lattice modes. The homodyne autocorrelation function of the quasielastically scattered light intensity characterizes the dynamics of the system which is predicted in the context of the harmonic model and the linearized Navier-Stokes equation for a viscous, incompressible fluid. Agreement between light scattering results and the theoretical predictions is demonstrated for a particular set of longitudinal modes.

The shortest thermal relaxation times were about $\frac{1}{10}$ seconds and were all overdamped. Thus none of the longitudinal modes propagate in this finite structure. (The transverse dispersion curves were not extracted from the data.) The Lamé coefficients were found, for two different crystals, to be

$$\mu = 3.51x10^{-6}\ \frac{dyne}{cm}$$

$$\lambda = 3.06x10^{-5}\frac{dyne}{cm},$$

for $a = 8.95$ μm;

$$\mu = 2.11x10^{-6}\ \frac{dyne}{cm}$$

$$\lambda = 1.88x10^{-5}\frac{dyne}{cm},$$

for $a = 9.9$ μm. These were determined from the static elastic properties fo the system. These values are about 4-orders of magnitude less than those for 3D colloidal crystals [18],[19] and agree reasonably with estimates based simply on number density and the dipole-pair interaction. Hurd's pair-interaction [20] was shown to reasonably describe the system forces where the sole fitting parameter was the sphere charge ($\approx 10^4\ e$), not an unreasonable value for these large spheres.

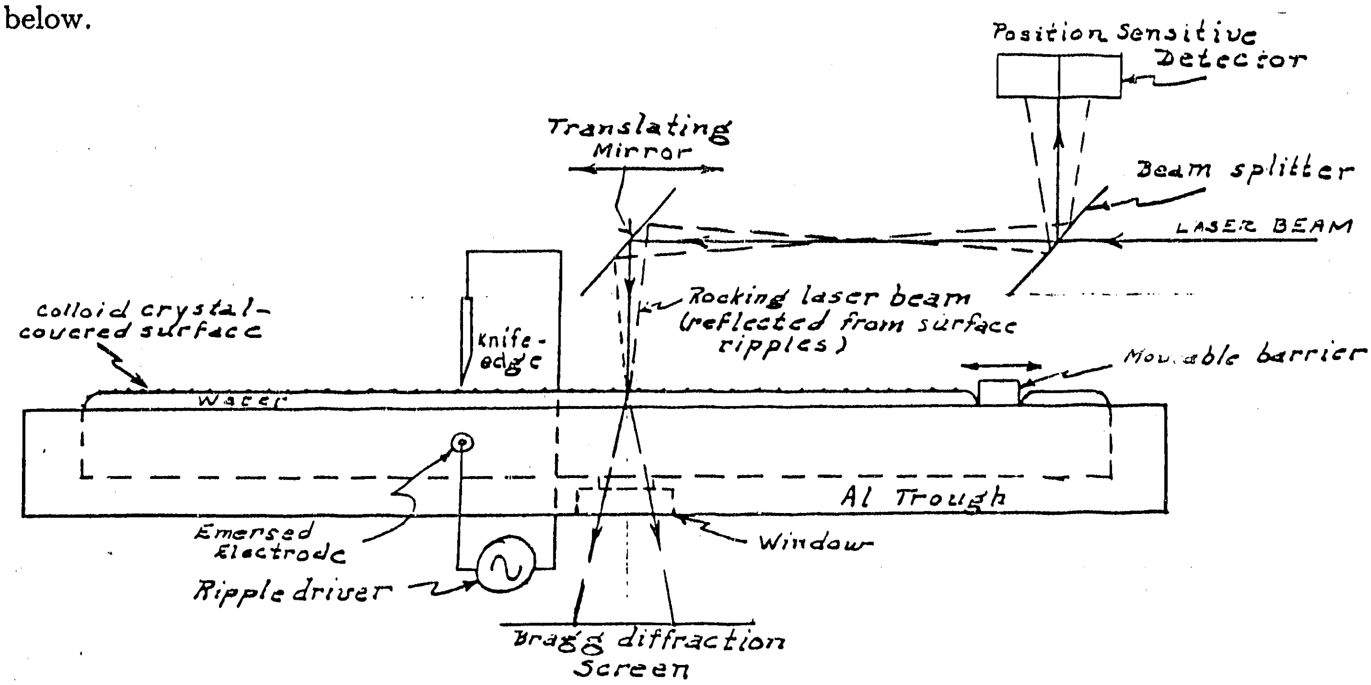
This was the thesis research of David Cohen. The details are given in his Thesis [21].

4. Surface Tension of an Air-Water Interface Containing a 2D Colloidal Crystal [22]

Although this experiment was not pursued far enough to consider it sufficiently complete to publish there were some interesting preliminary results well worth including here. The intention of the experiment was to study the variation in the surface tension (γ) of a water surface covered with a colloidal crystal at various stages of compression. The point was to compare the surface tension measured with calculated values using a model pair-interaction [20]. Also there is an interesting point in the compression where attractive van der Waals force become dominant over the combined dipole-dipole and monopole repulsive forces. Here the spheres are essentially in contact. Both phases have a triangular lattice structure. Our question was: does anything remarkable happen to γ at this apparently irreversible transition from a crystal with repulsive forces dominating to one with attractive forces dominating?

The range in measured surface tension was $72.4\ \frac{dynes}{cm}$ to $61.2\ \frac{dynes}{cm}$ for a corresponding range in lattice constant of 5.7 μm to 4.0 μm for the repulsive crystal. The surface tension was just that for pure water for the largest lattice constant as expected. The diameter of the spheres was 1.60 μm. Although this particular crystal was not compressed into a van der Waals crystal a second crystal was formed using a new sample of spheres. It was compressed directly into a van der Waals crystal. This coated surface had a surface tension of $56.7\ \frac{dynes}{cm}$ (lattice constant 1.6 μm). Further compression created corrugation: straight parallel flutes of equal spacing (diminishing with still more compression). This monolayer film had sufficient resilience to be cycled back-and-forth between tight corrugations and a flat film; it had sufficient strength to be picked up with a pair of tweezers.

The technique used to measure γ was essentially that of C. H. Sohl, et al. [23] which they used to measure the surface tension of liquids. Our version is shown in the figure below.



Surface tension, shear viscosity, and surface wave amplitude measurement apparatus

The surface wavelets are produce by applying a low frequency (100—1000 Hz) voltage between the knife edge and the immersed electrode (electrocappillarity). The He/Ne laser beam is directed normal to the quiescent water surface. When the oscillating voltage is applied the rocking motion of the laser beam provides the wavelet amplitude. Standing waves introduced by the right hand barrier provide a means of measuring the wavelet wavelength using the calibrated translator supporting the mirror.

For a small amplitude surface wave the surface displacement in given, to a good approximation, by

$$\zeta(x,t) = \zeta_0 e^{-\alpha x} e^{i(kx-\omega t)}.$$

Here k and ω are related through the dispersion relation

$$k^3 \approx \frac{\rho\omega^3}{\gamma},$$

and the damping factor can be related to the shear viscosity η by

$$\alpha \approx \frac{4}{3}\eta\frac{\omega}{\gamma}.$$

This work was discontinued in order that David Cohen devote full time to his thesis research described in the previous section.

5. Work Done During the Terminal Year of This Contract.

5A. Defect Dynamics and Virtual Dislocation Pairs

Allen Armstrong worked jointly with Noel Clark's group (M. Glaser, P. Beale, and Noel Clark) on a molecular dynamics simulation of a 2D liquid close to its freezing point [24]. The liquid was looked upon as a highly defected solid. This work is described in the Proceedings of the 4th Nishinomiya-Yukawa Memorial Symposium 1989 [25].

Allen also worked with Paul Phillipson in a separate study of 2D maps of a particle moving under the influence of discrete and fluctuating impulses in a double well potential.

The details are found in the June 11 issue of Physics Letters A – not yet available [26]. Copies of the original manuscript are included with this report.

The above problems both relate to 2D melting and to the virtual dislocation theory described in Allen's thesis [9].

5B. The Direct Measurement of the Isothermal Compressibility and the Pressure Equation of State

The experimental effort was devoted to improvements in the apparatus and techniques of the water-air interface studies, and to the direct experimental determination of elastic properties, the isothermal compressibility, and the pressure equation of state for a colloidal monolayer on the surface of water. This direct measurement is available to us by virtue of the curvature of the water meniscus along the inner edge of the trough.

At low number density the monolayer has a random (fluid-like) distribution of microspheres in the top flat area of the water surface and the density increases down the surface of the meniscus toward the edge of the trough. Thus there is a band about 1 cm wide all along the trough edge within which a fluid monolayer on the top is compressed into an ordered crystalline solid toward the bottom by the earths gravitational field. From a measurement of the contour of the surface $z = f(x)$ and number density $\rho(z)$ at a set of locations along the surface the relationship between $\rho(z)$ and the potential energy of a sphere $(m_e g z)$ may be determined. In the low density fluid region this is just $\rho(z) = \rho_0 e^{\frac{-m_e g z}{k_B T}}$, where m_e is the effective mass of a sphere, z is the vertical distance above the point where ρ has the measured value ρ_0 and z is chosen to be zero. There is a corresponding equation for the pressure.

This is closely related to an experiment done by Crandall and Williams [27] where they observed the gravitational compression of a 3D colloidal suspension of microspheres in a culture tube (These were some of the first — if not the first — quantitative measurements on colloidal microspheres). Their 3D system was totally crystalline and they measured

Young's modulus which in their system was equivalent to the bulk modulus B ($B \equiv \kappa_T^{-1}$, where κ_T is the isothermal compressibility.) Our measurements should yield the elastic coefficients for the 2D crystal as well as the isothermal compressibility and pressure equation of state for the fluid.

The curved surface introduces some complications relative to spheres that are completely immersed as those of Crandall and Williams. The normal component of force holding the sphere at the surface is composed of a hydrostatic-buoyancy force $\vec{f}_h$ (outward), a capillary force $\vec{f}_c$ (outward or inward depending on the slope of the liquid surface at the position of the sphere and such that the contact angle between the sphere and water is everywhere the same), a repulsive dipole-dipole force $\vec{f}_d$ (outward for an outward concave surface) which depends on the lattice constant and sphere charge, an osmotic force $\vec{f}_{os}$ (outward) which is due to the ionic concentration gradient in close proximity to the sphere, and the normal component of the gravitational force $(\vec{f}_g)_\perp$ (inward or zero for our system). The forces $\vec{f}_h$, $\vec{f}_c$, $\vec{f}_d$, and $\vec{f}_{os}$ are all normal to the surface except for a small finite size effect that we shall ignore. Let

$$\vec{f}_B = \vec{f}_h + \vec{f}_c + \vec{f}_d + \vec{f}_{os}.$$

This can be reduced to

$$\vec{f}_B \approx \vec{f}_h + \vec{f}_c$$

since $\vec{f}_d$ and $\vec{f}_{os}$ are small compared to $\vec{f}_h$ and $\vec{f}_c$. The tangential force on a sphere tending to move it down the slope of the meniscus is then

$$f_T = (f_g - f_B sin\theta)cos\theta = (mg - f_B sin\theta)cos\theta$$

where θ is the angle between $-\vec{f}_g$ and the line tangent to the surface at the sphere and in a plane containing $\vec{f}_g$ and $\vec{f}_B$. Thus the effective mass for a sphere is

$$m_e \approx [m - (\frac{f_B}{g})sin\theta]cos\theta.$$

κ_T and P can also be determined by assuming that a pair-interaction may be applied to the system in which case the two following relationships apply:

$$\kappa_T = \frac{1}{\rho}(\frac{\partial \rho}{\partial P})_T = \frac{2\pi}{k_B T}\int_A [g(r) - 1]r dr + \frac{1}{\rho k_B T},$$

$$P = \rho k_B T[1 - \frac{\pi \rho}{3 k_B T}\int r \frac{du(r)}{dr} g(r) r dr].$$

Here $g(r)$ is the pair (translational) correlation function that can be obtained from the individual video frames used in determining ρ for the direct measurement of κ_T and P. (The form and technique is described in Section 1 and references [7,11,12]). $u(r)$ is the pair potential energy and is required explicitly only for the pressure equation. A comparison of the results of these calculations and the direct measurements of κ_T and P would give a test of the applicability of a pair potential and also a test of the explicit form used for this potential (initially chosen as the Hurd potential [20]).

This work is still in progress. The results and a detailed description of the experimental procedure will be forwarded to you on completion.

References

[1] J. M. Kosterlitz and D. J. Thouless, J. Phys. C **6**, 1181 (1973).

[2] D. R. Nelson and B. I. Halperin, Phys. Rev. B **19**, 2457 (1979).

[3] A. P. Young, Phys. Rev. B **19**, 1855 (1979).

[4] A. Armstrong, R. Mockler, and W. J. O'Sullivan, Bull. Am. Phys. Soc. **31**, 281 (1986).

[5] A. Armstrong, R. Mockler, and W. J. O'Sullivan, J. Phys.: Condensed Matter **1**, 1707-1730 (1989).

[6] A. Armstrong, R. Mockler, and W. J. O'Sullivan, Bull. Am. Phys. Soc. **33**, 436 (1988).

[7] Y. Tang, A. Armstrong, R. Mockler, R. J. O'Sullivan, Phase Transitions **21**, 75 (1990). Invited.

[8] A. Armstrong, Y. Tang, R. Mockler, and W. J. O'Sullivan, 63rd Colloidal and Surface Science Symposium, June 18-21, 1989, Seattle WA. Invited Talk.

[9] Allen Armstrong, *Defect Mediated Melting in a Colloidal Monolayer*, Dept. of Physics, University of Colorado (1988), Unpublished Thesis.

[10] Y. Tang, A. Armstrong, R. Mockler, and W. J. O'Sullivan, Bul. Am. Phys. Soc. **33**, 436 (1988).

[11] Y. Tang, A. Armstrong, R. Mockler, W. J. O'Sullivan, Phys. Rev. Lett. **62**, 2401 (1989).

[12] Yeke Tang, *Study of Two-Dimensional Melting in Colloidal Monolayers*, Dept. of Physics, University of Colorado (1989). Unpublished Thesis.

[13] B. Pouligny, R. Malzbender, and N. A. Clark, Bull. Am. Phys. Soc. **33**, 436 (1988).

[14] M. Glas~~s~~er, R. Malzbender, and N. A. Clark, Bull. Am. Phys. Soc. **33**, 678, (1988).

[15] B. Pouligny, R. Malzbender, P. Ryan, and N. A. Clark, *Analog Simulation of Melting in Two Dimensions*, to appear in Phys. Rev. B (July 1990).

[16] Y. Tang, R. Malzbender, R. Mockler, and W. J. O'Sullivan, J. Phys. A: Math. Gen. **20**, L189 (1987).

[17] D. A. Cohen, R. Mockler, and W. J. O'Sullivan, Bull. Am. Phys. Soc. **33**, 668 (1988).

[18] A. Hurd, N. A. Clark, R. Mockler, and W. J. O'Sullivan. Phys. Rev. A **26**, 2869 (1982).

[19] E. Chang and D. Hone, J. Phys. (Paris) **49**, 25 (1988).

[20] A. Hurd, J. Phys. A **18**, L1055 (1985).

[21] David A. Cohen, *Light-Scattering Measurements and Hydrodynamics of 2D Interfacial Colloidal Crystals*, Dept. of Physics, University of Colorado (1989). Unpublished Thesis.

[22] D. Cohen, R. Mockler, and W. J. O'Sullivan, Bull. Am. Phys. Soc. **31**, 281 (1986).

[23] C. Sohl, K. Miyano, and J Ketterson. Rev. Sci. Instr. **49**, 1464 (1978).

[24] M. A. Glaser, N. A. Clark, A. J. Armstrong, and P. Beale, Bul. Am. Phys. Soc. **35**, 389 (1990).

[25] M. Glaser, A. Armstrong, N. A. Clark, and P. Beale, *Geometrical Quasiparticle Condensation Model of Melting in Two Dimensions*, Proceedings of the 4th Nishinomiya–Yukawa Memorial Symposium (1989), Dynamics and Patterns in Complex Fluids — New Aspects of Physics- Chemistry Interface. Springer-Verlag, in press.

[26] P. Phillipson and A. Armstrong, Phys. Lett. A **146**, 401 (June 11, 1990).

[27] R. Crandall and R. Williams, Science, **198**, 293 (1977).

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