Laser-Induced Freezing

Aslam Chowdhury and Bruce J. Ackerson
Department of Physics, Oklahoma State University, Stillwater, Oklahoma 74078

and

Noel A. Clark
Department of Physics, University of Colorado, Boulder, Colorado 80309
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Laser beams are crossed in a two-dimensional colloidal liquid of strongly interacting spherical particles to produce an external periodic potential and stimulate a density modulation. If the modulation wave vector is at the peak in the static structure factor, a sufficiently large potential induces a phase transition to a structure which exhibits solidlike order having density modes other than those directly excited. A Landau theory is presented and discussed in terms of our results.

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Ashkin and co-workers have demonstrated and investigated radiation pressure and photophoretic effects in suspensions of noninteracting submicron plastic spheres.[1] In a recent experiment[2] particles were forced into rows aligned along the light-intensity interference fringes produced by two laser beams crossed in the sample. This forced number-density mode is detected by probing the sample with a third laser beam which scatters from the resulting induced diffraction grating. In this Letter we apply this forced-density-mode technique to a suspension of strongly interacting particles, demonstrating that in a two-dimensional (2D) colloidal liquid, coupling effects can produce a freezing transition (three-mode condensation) in response to a single driven mode.

Recently there has been interest in structure and phase transitions of aqueous suspensions of dilute but strongly interacting colloidal particles. Most investigations of these systems involve average intensity scattering to determine the static structure factor or dynamic light scattering to determine the mutual or collective diffusion constant.[3] However, cross-correlation intensity-fluctuation spectroscopy (CCIFS) has been used to examine the local structure in disordered "colloidal liquid" states.[4] In this technique a strongly focused laser beam illuminates a small portion of the sample and the light scattered through two wave vectors is collected and cross-correlated by separate detectors. Results of these experiments indicate that the colloidal-liquid local fluid order is predominantly hexagonal, similar to the 2D triangular lattice of the solid. Here we demonstrate the stimulated version of CCIFS by subjecting a 2D colloidal liquid to crossed laser beams and monitoring the self-scattered field in a full range of k space.

Figure 1 presents the intensity distribution of 4880-Å laser light scattered from a two-dimensional sample of 1-μm-diam polystyrene particles suspended in highly deionized water. The scattering area is typically 50 μm in diameter and the sample cell is made of two quartz optical flats separated by less than 30 μm. The highly charged particles are repelled by the walls and form a two-dimensional monolayer structure as evidenced by direct viewing in a microscope. In Fig. 1(a) the laser beam with wave vector $\mathbf{k}_i$ is incident at an angle of 4° with respect to a normal to the sample plane, and the scattered light produces a diffuse Debye-Scherrer ring concentric with the incident beam, indicating an amorphous or liquidlike order in the 2D sam-

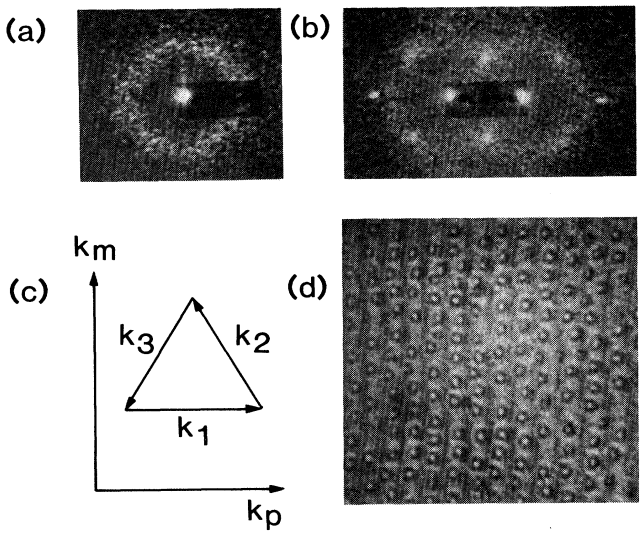

FIG. 1. (a) Intensity distribution of light scattered from a 2D colloidal liquid by a single laser beam. The diffuse Debye-Scherrer ring concentric with the incident beam indicates an amorphous order. (b) Self-scattering of light by two laser beams crossed in the 2D sample. (c) The crossed beams directly excite a density mode with wave vector k_1, and two other modes with wave vectors k_2 and k_3 are coupled to the k_1 mode by particle interactions. (d) Real-space image of particles aligned by the crossed laser beams.

ple. The scattered wave vector $k_{DS}=2k_1\sin(\theta/2)$ of the maximum of the ring is given by $k_{DS}=2\pi/a_{10}$, where $a_{10}=2.6$ μm is the maximum row spacing with Miller index 10 of the local hexagonal clusters which have been shown by CCIFS to exist in such a 2D colloidal liquid. Figure 1(b) displays the structure that results when a second laser beam crosses the first with an angle $\theta=8°$ in the sample to drive the density mode of wave vector $\mathbf{k}_1$, where $k_1=k_{DS}$. Here the local fluid clusters observed by CCIFS are aligned by the light fringe pattern to produce the scattering pattern displayed.

As in samples of noninteracting particles, the particles line up along the intensity fringe pattern to produce a diffraction grating which strongly scatters light to discrete positions $\pm\mathbf{k}_1$ along the $\mathbf{k}_p$ axis (in the plane of the incident laser beams and normal to the plane of the fringes). However, because the particles interact strongly on micron distance scales, there is a uniform separation between particles within a row and registration between rows. This results in the appearance of secondary intensity maxima indicating periodic structures not directly excited by the crossed laser beams. However, these modes are coupled to the laser-stimulated mode. The collodial liquid is "frozen," being two-dimensionally ordered by application of a one-dimensional external field which directly breaks the symmetry of the liquid state only along the $\mathbf{k}_p$ direction. This driven mode induces a spontaneous symmetry breaking in the $\mathbf{k}_n$ direction (in the sample plane and normal to $\mathbf{k}_p$) affecting the alignment of microscopic clusters over a macroscopic region.

The symmetry of the resulting scattered intensity pattern may be compared to that observed by CCIFS. In the CCIFS experiments the cross-correlation function $C(\mathbf{k},\mathbf{q})$ was measured as a function of ϕ, the angle between two scattered wave vectors, $\mathbf{k}$ and $\mathbf{q}$, for $k=q=k_{DS}$. The function $C(\mathbf{k},\mathbf{q})$ displayed strong correlation at $\phi=0°$ and 180° and weaker correlation at $\phi=60°$ and 120°. Anticorrelations were evident at $\phi=30°$, 90°, and 150°. The stimulated intensity variation observed in the present experiments is qualitatively similar for $k=k_{DS}$ if ϕ is measured with respect to one of the two incident beams. At $\phi=0$ we are positioned on the first Debye-Scherrer ring at the position of the second incident beam. This incident-beam–Debye-Scherrer-ring configuration insures that we have the fringe wavelength nearly equal to a_{10}. Then at $\phi=180°$ there is an intensity maximum due primarily to the first-order scattering of the primary incident beam from the particles aligned along the fringes. There are also intensity maxima at $\phi=60°$, 120°, 240°, and 300° which are of reduced intensity and result from the interrow registration of particles. As the interrow forces are weakened, there are large-amplitude shear waves which propagate parallel to $\mathbf{k}_p$ with displacement along $\mathbf{k}_n$. These shear modes result in a smearing of the intensity maxima parallel to $\mathbf{k}_p$ and produce reduced intensity maxima compared to those visible at $\phi=0°$ and 180°. Thus the cross-beam experiment is the stimulated analogue of CCIFS. Microscopically, however, the stimulated experiment in the weak-fringe limit is related to three-particle correlations in contrast to four-particle correlations for CCIFS.[4]

We now construct a Landau theory to account for this mode coupling. The free-energy functional to be minimized has the following form[5]:

$$F=2A\xi_1+B\sum_i\xi_i^2+2C\xi_1\xi_2\xi_3+D(\sum_i\xi_i^2)^2+E(\sum_i\xi_i^4)$$
$$=2A\xi_1+B\sum_i\xi_i^2+2C\xi_1\xi_2\xi_3+E\sum_{ij}(\xi_i^2-\xi_j^2)^2/6+(E/3+D)(\sum_i\xi_i^2)^2.$$

Here the ξ_i ($i=1$–3) represent the amplitudes of fluid density modes with the wave vectors $\mathbf{k}_1$, $\mathbf{k}_2$, and $\mathbf{k}_3$ as indicated in Fig. 1(c). These are the three (six complex) lowest-order modes needed to represent the local liquid and quasi-long-range crystalline 2D-hcp structure of the solid state. Only those terms up to fourth order in ξ_i are kept which are not zero after integration of the free-energy functional over all space.[5] In the first term we have assumed that the external field couples only to the k_1 mode and only to first order in ξ_1. The second term stabilizes the fluid state ($\xi_i=0$) for sufficiently large values of B, while the third term couples the modes together and induces the observed[4] first-order freezing transition in the absence of external fields. The last two terms equalize the mode amplitudes and stabilize the overall free energy. If a single mode ξ_1 is stimulated by an external field as in our experiments, we expect ξ_1 to differ from the degenerate modes ξ_2,ξ_3. Results of minimization of F are shown in Fig. 2 for ξ_1 and ξ_2 (assumed equal to ξ_3) as a function of A and B for $C=-1$, $D=\frac{1}{2}$, and $E=\frac{3}{2}$. At $A=0$ all the ξ_i are equal and undergo a first-order transition from a solid to a liquid as B increases. At finite A the ξ_1 mode is larger than ξ_2, in general. For sufficiently large B the transition from liquid to solid becomes second order with $\xi_2=\xi_3\sim(A-A_0)^{1/2}$. Such a symmetry-changing transition can be second order because the external field reduces the symmetry of the fluid before freezing occurs. Thus it should be possible to take a fluid system to a solid by a second-order process which involves externally applied fields, as indicated by the continuous growth of structure in our experiments.

Figure 3 presents data for the intensity maxima at $k_p=2\pi/a_{10}$, $k_n=0$ ($\phi=180°$) and $k_p=\pi/a_{10}$, k_n

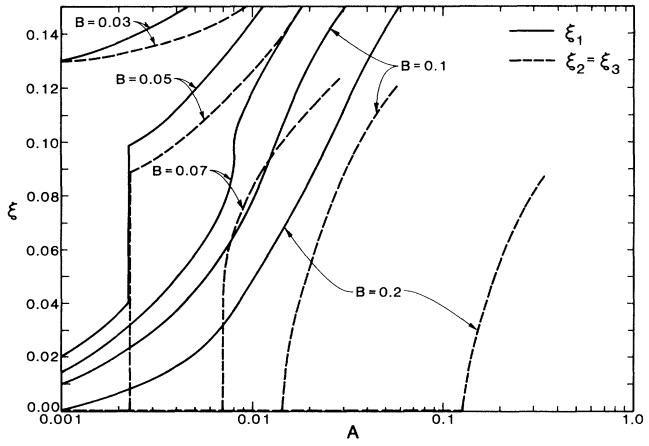

FIG. 2. Landau theory for the order parameter ξ_1 (solid curves) and $\xi_2=\xi_3$ (dashed curves) for $C=-1$, $D=\frac{1}{2}$, and $E=\frac{3}{2}$ as a function of A and parametrized by B. A first-order transition is evident as $A\rightarrow 0$ (no external field). This transition becomes second order for sufficiently strong external fields.

$=\sqrt{3}\pi/a_{10}$ ($\phi=120°$) as a function of the input power of the crossed laser beams. Also shown is the variation of the intensity maximum of the first-order diffraction peak for a noninteracting particle sample of the same-size particles. For the noninteracting sample the output intensity is proportional to the third power of the input power: The induced density modulation amplitude increases in proportion to the applied external power; the scattering probability is proportional to the square of the modulation amplitude; and this amplitude is self-probed by one of the input beams which has an intensity proportional to the input power. For the interacting sample the dependence of the first-order scattering peak at $k_p=2\pi/a_{10}$, $k_n=0$ also displays a nearly cubic-power-law dependence. The secondary intensity maximum at $k_p=\pi/a_{10}$, $k_n=\sqrt{3}\pi/a_{10}$ displays a $\frac{3}{2}$-power-law dependence. We present raw data with no correction for the intensity of the Debye-Scherrer ring, which is a function of input power. Data normalized by the input power will extrapolate to the Debye-Scherrer ring intensity at zero input power.

We have not observed the secondary maxima "turn on" as indicated by the Landau theory for $\xi_2=\xi_3$ modes. However, the inclusion of fluctuations in this theory[6] will produce strong diffuse scattering before true long-range order sets in. The asymptotic form for $\xi_2(A\rightarrow\infty)\sim A^{1/3}$ is in contrast with our observed dependence on input power. If we are not probing the asymptotic limit experimentally, then the theory forces us to conclude that the secondary maxima must be dominated by fluctuations. On the other hand, the experiments may provide a strict test for Landau theories. Higher-order terms or couplings to the external field may be required.

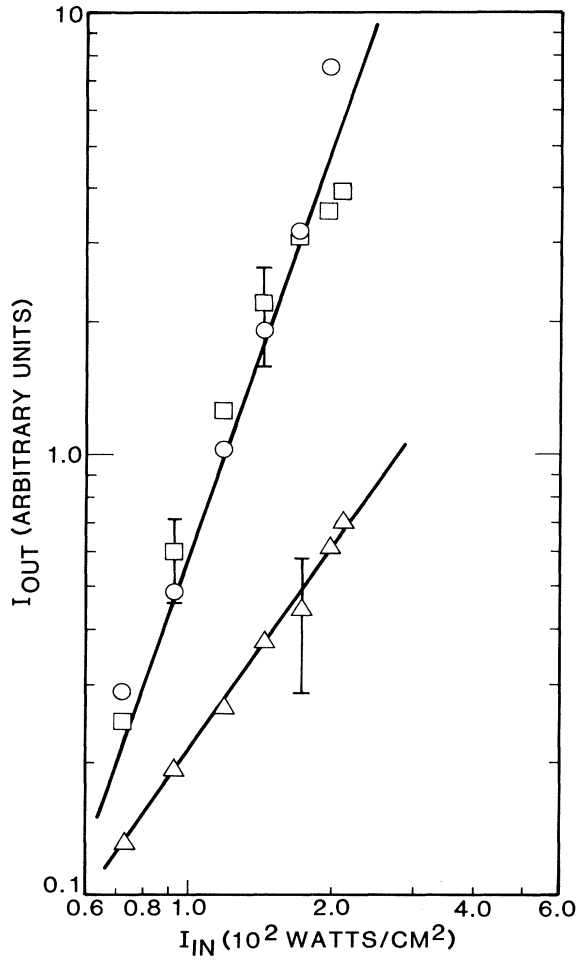

FIG. 3. Data for the measured intensity of self-scattered light as a function of the input intensity. The intensity of scattering at $k_p=2\pi/a_{10}$, $k_n=0$ by the directly stimulated mode is given by circles for weakly interacting particles at high solution ionic strength and by squares for more strongly interacting particles at low solution ionic strength. The upper solid curve represents a cubic-power-law dependence on input power. The intensity of the scattering at $k_p=\pi/a_{10}$, $k_n=\sqrt{3}\pi/a_{10}$ is given by triangles for the more strongly interacting sample. The lower solid curve represents a $\frac{3}{2}$-power-law dependence.

We have made studies of the structures produced when the intensity-figure-pattern wavelength is different from the average particle separation a_{10}. When the stimulating mode is not commensurate with the average particle separation, the first-order diffraction maxima are not as intense for the same external input power. We have also made some preliminary studies of the time decay of the intensity maxima when the secondary probe beam is extinguished. The first-order diffraction maximum decays similarly to that measured by Berne and Pecora[7] and the secondary spots similarly

to that measured by dynamic CCIFS techniques.[8] The results of these studies will be reported elsewhere. This experiment shows that laser light can be an effective way of applying a spatially varying external potential to a colloidal particle suspension. A particularly interesting possibility would be to use multiple cross beams or a modulated scanned laser to produce quasiperiodic structures.

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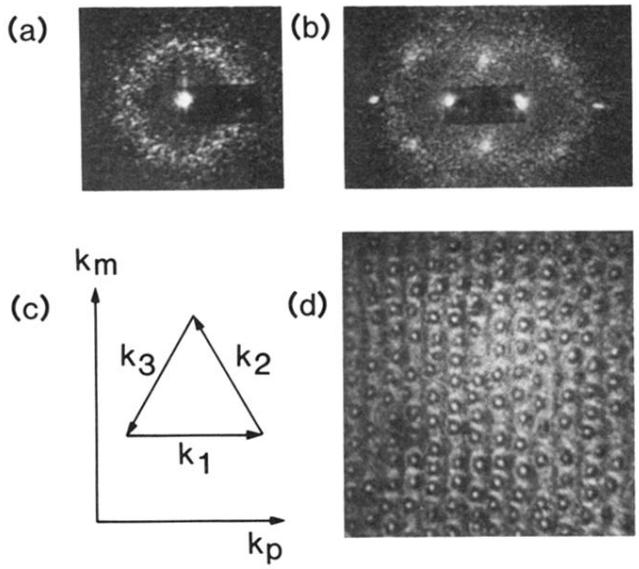

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