

## Phase Behavior of Two-Dimensional Colloidal Systems in the Presence of Periodic Light Fields

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We investigate the phase behavior of a two-dimensional suspension of charge stabilized polystyrene spheres in the presence of a one-dimensional periodic light field. With increasing light intensity we observe a liquid-solid followed by a solid-liquid transition which are known as laser-induced freezing and melting, respectively. Here we report on measurements where, in addition to the light intensity, the single particle density was also systematically varied. As a result, we obtain for the first time the full thermodynamic information about the system which allows comparison with numerical predictions of other authors.

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There has been considerable interest in the freezing and melting of colloidal particles during the recent years which has been largely motivated by the fact that colloidal particles provide ideal model systems for experimental studies of two-dimensional (2D) melting. Accordingly, such systems have been intensively investigated by several authors (see, e.g., [1,2]). While there exist numerous theoretical and experimental studies on 2D melting on homogeneous substrates [3–5], only little is known about 2D melting on corrugated surfaces, although the latter is much more relevant when modeling the substrate potential of a crystalline, i.e., atomically corrugated surface.

It was the experimental work of Chowdhury, Ackerson, and Clark which originally demonstrated that one-dimensional (1D) periodic substrate potentials can cause interesting effects on the phase behavior of colloidal particles [6,7]. When they investigated a charge-stabilized colloidal liquid of polystyrene (PS) particles being confined between two glass plates and additionally exposed to a standing laser field (with its wave vector  $q$  tuned to the first peak of the direct correlation function), they observed a phase transition from a liquid to a crystal upon increasing the laser intensity. This phenomenon which has been termed laser-induced freezing (LIF) has also been theoretically analyzed by several authors employing Monte Carlo (MC) studies [8] and density functional theory (DFT) [9]. LIF has been explained as an alignment of particles in the high intensity regions of the interference pattern which produces a directly stimulated density mode of particles, followed by a registration of particles between neighboring lines due to interparticle interactions.

When Chakrabarti *et al.* [10] theoretically investigated the phase behavior of such a system as a function of the laser intensity, in addition to LIF which takes place at relatively small laser intensities, at higher laser intensities they found a reentrant laser-induced melting (LIM) transition, where a remelting of the crystal back into the modulated liquid phase was observed. In order to understand this—at first glance very surprising—remelting process, the role of particle fluctuations perpendicular to the inter-

ference fringes has to be taken into account because they largely contribute to the registration of adjacent lines and thus to crystallization. Accordingly, upon reducing those fluctuations by increasing the laser intensity, the crystal remelts. This effect has also been demonstrated to be in agreement with experimental studies [11,12].

In previous measurements the phase behavior was investigated in a regime of fixed particle-particle interaction, i.e., constant particle number density and salt concentration, and only the laser intensity was varied. In this Letter we present for the first time a systematic study where in addition to the depth of the light potential the particle-particle interaction was also varied. Since it is the counterplay of those two interactions which is the physical origin of the unusual phase behavior in this situation, our data provide further insight in the nature of LIF and LIM and give the full thermodynamic information on the system. Our data clearly show that reentrant melting from the crystalline state to a modulated liquid is observed only if the crystalline state was formed by LIF (and not by spontaneous crystallization as has been theoretically suggested [10]). In addition, we observe LIF and LIM to take place at considerably higher laser fields than predicted [10] and only in a relatively small region of particle number densities and salt concentrations.

The experimental setup has been described elsewhere; therefore it will be discussed here only in brief. We used aqueous suspensions of sulfate PS particles of 3  $\mu\text{m}$  diameter and a polydispersity of 4% (Interfacial Dynamics Corporation). Because of sulfate-terminated surface groups which partially dissociate off when in contact with water, the suspended particles are negatively charged and experience a screened electrostatic repulsion which can be described by [13,14]

$$\Phi(r) = \frac{(Z^*e)^2}{4\pi\epsilon_r\epsilon_0} \left( \frac{\exp(\kappa R)}{1 + \kappa R} \right) \frac{\exp(-\kappa r)}{r}. \quad (1)$$

Here  $Z^*e$  is the renormalized charge of the particles which has been roughly determined to be  $Z^* \approx 20\,000$  [15],  $\epsilon_r$

is the dielectric constant of water,  $\kappa$  is the inverse Debye screening length, and  $r$  is the distance between particle centers. The experiments are performed in a closed circuit which is composed of the sample cell, a vessel of ion exchange resin, and an electrical conductivity probe to control the ionic strength of the suspension [16]. A peristaltic pump is used to pump the highly deionized suspension through the circuit. The Debye screening length was estimated from the interparticle distribution of the colloids to be on the order of  $\kappa^{-1} \approx 400$  nm. The sample cell consists of two horizontally aligned parallel glass surfaces with a distance of 1 mm. In the course of our experiments we tested several cells with different spacings between 20  $\mu\text{m}$  and 1 mm and observed no differences. We first deionized the circuit almost completely as confirmed by the value of the ionic conductivity  $\sigma = 0.07 \mu\text{S/cm}$ . Then the sample cell was disconnected from the circuit to allow stable conditions during several hours. This was determined by measurements of the mean particle distance which was observed to change only by about 3% during 5 h. The laser potential was created by two slightly crossed laser beams of a linearly polarized Nd:YVO<sub>4</sub> laser ( $\lambda = 532$  nm,  $P_{\text{max}} = 2$  W) which overlapped in the sample plane, thus forming an interference pattern. Because of the polarizability of the PS spheres this provides a periodic, one-dimensional potential for the particles. The periodicity could be adjusted by variation of the crossing angle. Because of the almost vertical incidence of the laser beams onto the sample the particles experienced additionally a vertical light pressure which pushed them towards the negatively charged bottom silica plate of our cell. This vertical force is estimated to be in the range of  $p\text{N}$  and largely reduces vertical fluctuations of the particles, thus confining the system effectively to two dimensions. The sample, which was in addition illuminated with white light from the top, was imaged with a microscope objective onto a CCD camera chip connected to a computer for further analysis. The intense Nd:YVO<sub>4</sub> laser light was blocked with an optical filter.

In order to compare our experimental measurements quantitatively to theoretical predictions, one must experimentally determine the depth of the laser potential as a function of the intensity of the interference fringes. This was achieved by exposing the above-mentioned light pattern to a highly diluted colloidal suspension. From the probability distribution of the particles perpendicular to the laser lines, we obtained the laser potential acting on the particles by employing the Boltzmann statistics. The shape of the laser potential in the central region of the overlapping laser beams is found to be

$$V(x) = -V_0 \left[ 1 + \cos\left(\frac{2\pi x}{d}\right) \right] \quad (2)$$

with  $V_0$  being the potential amplitude and  $d$  the period of the fringe spacing. The amplitude  $V_0$  as obtained from our experiments increases linearly as a function of

the laser intensity  $I$  (symbols in Fig. 1). According to Loudiyi *et al.* the colloid-light interaction  $V_0$  can be calculated by integration over the potential contributions for each infinitesimal volume element of the colloidal sphere [17]

$$V_0 = 6n_w^2 \sigma_0^3 \frac{P}{cr_0^2} \left( \frac{n^2 - 1}{n^2 + 2} \right) \left( \frac{j_1\left(\frac{\pi\sigma_0}{d}\right)}{\frac{2\pi\sigma_0}{d}} \right). \quad (3)$$

Here,  $P$  is the laser power,  $c$  is the velocity of light in vacuum,  $n$  is the ratio of the refraction indices of polystyrene  $n_P$  and water  $n_W$ ,  $\sigma_0$  is the colloidal particle diameter,  $j_1$  the first-order spherical Bessel function, and  $r_0$  is the waist radius of the Gaussian laser beam. When comparing the slope of a linear fit through our data points (as indicated by the dotted line in Fig. 1) with the result of Eq. (3) after inserting the corresponding values of our experiment ( $r_0 = 220 \mu\text{m}$ ,  $n_W = 1.33$ ,  $n_P = 1.59$  [18]), we found agreement within 10% which is within our experimental errors.

In order to keep the total light intensity independent of  $V_0$  in the following experiments, one of the laser beams was directed through a  $\lambda/2$  plate to rotate its polarization with respect to the other. Accordingly, the variation of  $V_0$  was achieved by adjusting the angle of the  $\lambda/2$  plate while keeping the total laser intensity constant.

To distinguish the different thermodynamic phases we first determined the particle center coordinates by means of a particle-recognition algorithm. From those data the time averaged single particle density  $\rho(x, y)$  and the pair correlation function  $g(x, y)$  were calculated, the latter being particularly useful for differentiating the modulated liquid from the crystalline phase. Here,  $x$  and  $y$  denote the direction perpendicular and along the interference fringes,

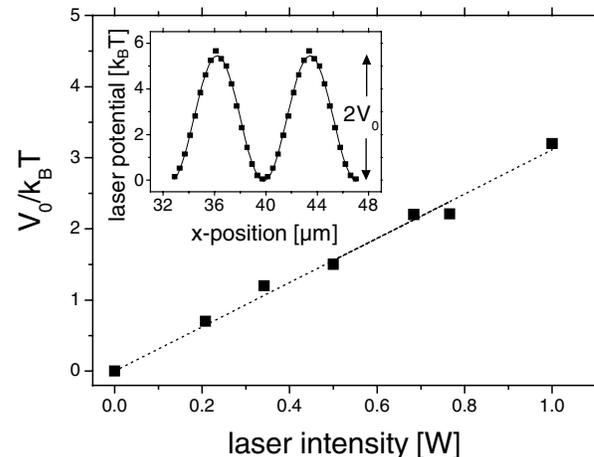


FIG. 1. Amplitude of light potential acting on colloidal particles of 3  $\mu\text{m}$  diameter as a function of the incident laser intensity. The symbols correspond to measured data and the dashed line corresponds to a theoretical prediction. The inset shows the spatially modulated laser potential experienced by the particles at the center region of the periodic light field (symbols). The line corresponds to a cosine function.

respectively. Since in the modulated liquid phase no registration between adjacent lines occurs, no correlations among particles in neighboring lines are observed. This leads to a  $g(x, y)$  plot with smeared-out lines along the interference fringes. In contrast, adjacent lines in the crystalline phase are interlocked due to particle excursions perpendicular to the laser lines which leads to well-defined, nonoverlapping patches in the vicinity of the reference point in  $g(x, y)$  [11]. In addition, when fitting the decays  $g(y)$  of the different phases, we find that the modulated liquid phases always have short range order and an exponential decay, whereas the decay in the crystal extends over a much longer range and can be described with an algebraic function  $g(y) - 1 \propto y^{-\eta}$ . It has been mentioned that unlike conventional 2D melting, in the presence of a modulated light field,  $\eta$  is universal at the melting transition and should be equal to 1 at the melting temperature [19]. This is also consistent with our previous experiments [11].

In contrast to earlier measurements, where the particle number density was held constant, here we measured systematically the phase behavior for different particle number densities as a function of the light potential amplitude  $V_0$ . Particular attention was paid to the fact that the periodicity of the laser potential  $d$  was adjusted properly to obtain a hexagonal crystal, i.e.,  $d = \frac{\sqrt{3}}{2} a$ . Otherwise a distorted lattice would have been observed. The range of  $d$  was between 6 and 8  $\mu\text{m}$ . Only the central region of the interference pattern (corresponding to about 400 particles) was used for the data analysis to ensure  $V_0$  to be constant within about 5%. To obtain sufficient statistics,  $g(x, y)$  was averaged over more than one thousand pictures with a time interval of one second each. The result of more than one hundred single measurements is shown in Fig. 2. We plotted the vertical axis in units of  $(\kappa a)^{-1}$  with  $a$  being

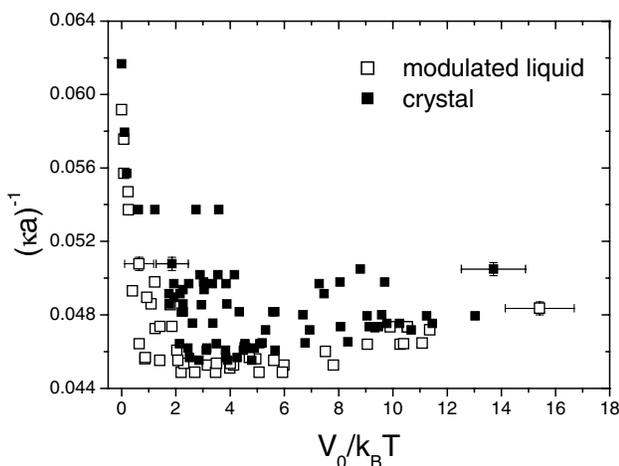


FIG. 2. Experimentally determined phase diagram as a function of  $(\kappa a)^{-1}$  vs  $\frac{V_0}{k_B T}$ . The open symbols denote the modulated liquid and the closed symbols denote the crystalline phase, respectively. For clarity, error bars are plotted only for a few data points.

the mean distance of next neighbor particles which was measured for each particle concentration in the absence of the laser field. As can be seen, the value of  $(\kappa a)^{-1}$  where the transition towards the crystal occurs decreases at small laser intensities as a function of  $V_0$ . This is the characteristic feature of LIF and is in agreement with numerical calculations [9]. For larger values of  $V_0$ , however, the separation line between the crystalline and the modulated liquid region is shifted back to higher  $(\kappa a)^{-1}$  values and starts to saturate at the highest values which could be obtained with our setup. It is this up bending which gives rise to the LIM phenomenon. If  $(\kappa a)^{-1}$  is in a range between 0.045 and 0.048, with increasing  $V_0$  one observes the following sequence of states: isotropic liquid—modulated liquid—crystal—modulated liquid, which is in agreement with earlier results [11,12].

Figure 3 shows the phase diagram as obtained by means of MC simulations from Chakrabarti *et al.* [9]. The phase separation line has a pronounced minimum at nonzero laser potentials which is in agreement with our data. Besides this qualitative agreement, however, there are several important differences between Figs. 2 and 3. The experimental data suggest that LIF and LIM occur at considerably higher  $V_0$  than in the MC simulations. Possibly some deviations between theory and experiment stem from the fact that the latter were performed in finite size systems, whereas the simulation results were obtained by extrapolation to the thermodynamic limit. We believe, however, that this is not sufficient to explain such a large difference because our values for LIF are consistent with experimental and numerical results of other authors [6,8,17]. The second, and even more significant, difference between Figs. 2 and 3 is the qualitative behavior of the phase separation line at high  $V_0$ . The MC simulations suggest that  $(\kappa a)^{-1}$  at  $V_0 = 0$  is below the corresponding value at very high  $V_0$ . This implies that LIM is not restricted to crystals formed by LIF but may also appear in systems where the particle concentration is above that for spontaneous crystallization. This is in contrast to our experiments, where LIM was only observed for light-induced crystals. The latter is also supported by a recent theoretical work by Frey *et al.* where the qualitative phase behavior of a 2D system of charged colloids in the presence of a periodic light potential was reinvestigated [19]. By using the same concepts developed in the context of dislocation mediated melting theory, their data also support the existence of LIF and LIM. In contrast to Ref. [9], however, the melting temperature of the reentrant modulated liquid is found to be higher than that of the modulated liquid at small  $V_0$ . This directly corresponds to our finding that reentrant melting is only possible in a range of  $(\kappa a)^{-1}$  values which allows for LIF and thus demonstrates the unique properties of the light-induced crystalline phase. Therefore, this result is more than a quantitative correction to the above-mentioned MC simulations since our data provide strong evidence for

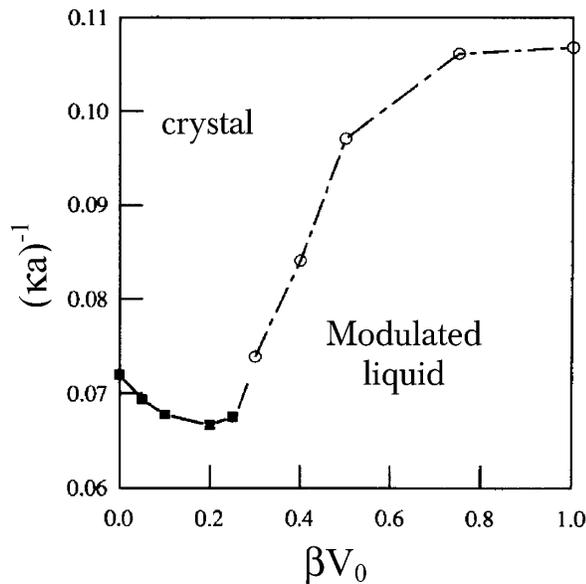


FIG. 3. Phase diagram in the same parameter space as Fig. 2 as obtained by MC simulations. Filled squares denote first-order transition points, whereas open circles correspond to continuous transition points. The data are taken from Ref. [10].

the fluctuation-induced nature of the LIM transition. In addition, because the region of  $(\kappa a)^{-1}$  values where reentrance occurs is rather small, this might explain why such an effect has experimentally not been observed before although such behavior should also be found in other 2D systems with periodic 1D potentials.

From our experiments, it is difficult to resolve the controversially discussed nature of LIF and LIM phase transitions conclusively at this point. When investigating the region near the LIF and LIM transition in detail, we never observed any hysteresis effects within our experimental errors. This observation is consistent with a continuous phase transition for LIF and LIM as predicted by Frey *et al.* [19], but at this point not sufficient to make any final statements yet.

So far, we have investigated only the influence of periodic 1D potentials on the phase behavior of colloidal particles. By interfering more than two laser beams, however, we can also produce 2D potentials of hexagonal, quadratic, or rhombic geometry which would then mimic a more realistic surface potential compared to the case studied here. Since the surface potential depth can be continuously varied by the laser intensity, investigations on colloidal model systems might help to understand the details of the phase behavior of atomic adsorbates on crystalline surfaces. Experiments are in progress to study the phase behavior under such conditions.

In summary, we have studied the phase behavior of a 2D colloidal suspension subjected to a periodic 1D light potential. We have varied both the mean particle distance as well as the light potential amplitude. As a result we obtained the phase diagram which shows a minimum in the  $(\kappa a)^{-1}$  vs  $V_0$  plane which is the characteristic feature of the LIF and LIM transitions. While at the present moment theoretical results obtained by different techniques are not yet consistent, our data show good agreement with recent calculations of Frey *et al.* [19].

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