First publ. in: Progress in Colloid and Polymer Science 110 (1998), pp. 46-49

Qi-huo Wei
C. Bechinger
D. Rudhardt
P. Leiderer

Structure of two-dimensional colloidal systems under the influence of an external modulated light field

Qi-huo Wei · Dr. C. Bechinger (✉)
D. Rudhardt · P. Leiderer
Fakultät für Physik
Lehrstuhl Prof. Dr. P. Leiderer
University of Konstanz
D-78434 Konstanz
Germany
E-mail: Clemens.Bechinger@uni-konstanz.de

Abstract The presence of a modulated laser field can induce crystallization of a colloidal liquid where the particles interact via screened Coulomb repulsion. This phenomenon is called laser-induced freezing (LIF). In this paper, we present experimental results on LIF which were performed under controlled particle interaction potentials. This was achieved by defined ion concentration conditions during our experiments. We observed distorted and almost perfect hexagonal structures as well as a modulated liquid as a function of the periodicity of the modulated laser field.

Key words Laser-induced freezing and melting · colloidal dispersion

Introduction

Since the pioneering work by Ashkin and co-workers on optical forces acting on small dielectric particles [1], there has been an enormous interest in the field of particle manipulation with light fields. One example are optical tweezers which allow to trap and manipulate single or several particles with one or more intense laser beams. Light forces can also be used to measure interaction forces between colloidal particles and motor molecules [2–5], to probe the elasticity of single polymer like DNA [6], or to investigate properties of membranes [7, 8].

It has been also demonstrated, that by creating an extended light intensity pattern, e.g. by interfering two or more laser beams, the structure of many colloidal particles can be manipulated [9, 10]. For colloids with effectively hard sphere interaction, one can organize the particles to form any structure, even a two-dimensional fivefold symmetrical and three-dimensional ones, according to the structure of intensity antinodes where the particles are trapped [9, 10]. For strongly interacting charge-stabilized colloidal particles where the interparticle interaction is a screened Coulomb potential, it has been shown experimentally by Chowdhury et al. [9] that a two-dimensional colloidal liquids starts to crystallize when exposed to a periodic light pattern created by two interfering laser beams. When the wave vector of the modulation potential is chosen to coincide the location of the first peak of the structure factor of colloidal liquids (or the periodicity $d = \sqrt{3}a/2$, with the mean interparticle separation), a dominantly hexagonal order is observed. This effect is called laser-induced freezing (LIF) [9, 11].

Later, density functional theory and Monte-Carlo simulations confirmed the existence of LIF and also predicted that this freezing transition changes from a first order to second order one via a tricritical point. Furthermore, it is expected that a colloidal crystal can re-melt (LIM) when the external field exceeds some critical value [12, 13]. This, however, has not been proven experimentally, yet.

LIF is anyway a result of many-body effects, although one can understand it in the following way, that the external potential induces the alignment of the particles along rows, whereas the interparticle-screened Coulomb repulsion leads to an equal distribution of particles within a single row (see Fig. 2c) and to the registration of particles

in neighboring rows. As shown by density functional theory [12], LIF is, in fact, the excitation of the density modulation modes in colloidal liquids with one specific external modulation potential. In this paper we perform experiments to study the structure when the periodicity (or the wave vector) of the external modulation potential deviates from the above value ($\sqrt{3}a/2$). To control the ion concetration we exployed a continuous deionization technique [14] which allows us to adjust different salt concentrations. In the following we present the results on LIF and the induced structures.

Experimental

The sample cell is composed of two microscopic cover glasses whose spacing can be adjusted from several mm to about 20 μm. After assembling the cell, it was connected to a closed circuit which contained the colloidal suspension. We used charge-stabilized surfactant-free polystyrene sulfate particles from IDC with a diameter of 3 μm. The particle concentration was about 1.5×10^7/ml, but due to sedimentation the actual particle concentration in the cell is assumed to be somewhat higher. The suspension was then pumped through this circuit which also contained a vessel of ion exchanger and an electrical conductivity probe to control the ionic strength in the suspension. This method allowed us to perform measurements at different ionic strengths [14].

Figure 1 shows schematically the setup used in our experiments. The beam of an argon ion laser (TM_{00} mode, $\lambda = 514$ nm, $I_{max} = 2.6$ W) is split into two parallel beams of equal intensity by means of two beam splitters (BS1, BS2) and two mirrors (M1, M2). The distances s of the parallel beams can be adjusted by the position of the mirror M2 which is mounted on a motor controlled translation stage. After passing the lens L, the two beams are overlapped inside the sample cell where they produce interference fringes. The spacing of the interference fringes d is controlled by beam spacing s through

$$d = \lambda/2 \sin(\theta/2) = f\lambda/s\,, \tag{1}$$

where θ is the angle between the laser beams and f the focus length of the lens L. The sample cell with the colloidal suspension is illuminated with white light (not shown in Fig. 1) and imaged with a microscope objective (magnification 40) on a CCD camera. In order to prevent the camera to be damaged by the intense laser light, the transmitted and scattered laser light is blocked by a filter. The obtained data were recorded on tapes through a video system which was connected to a computer for further analysis.

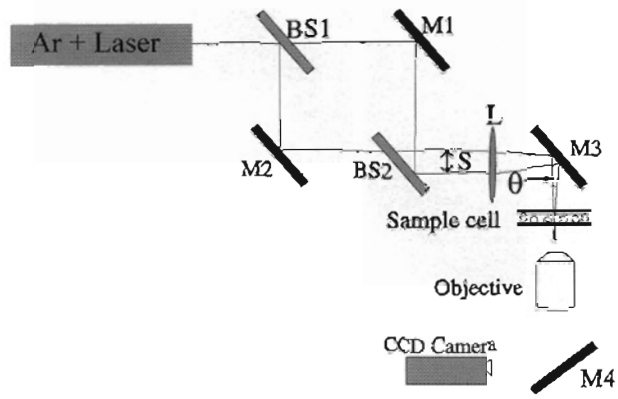


Fig. 1 The optical setup used during the experiments. M1, M2, M3, M4 are mirrors, BS1, BS2 beam splitters, L is a lens. The position of mirror M2 which can be changed by a motor-controlled translation stage determines the fringe spacing d

Results

When the laser is switched on and the colloidal suspension is subjected to an intererence pattern, the radiation pressure causes the particles to be pushed towards the bottom glass plate and a two-dimensional system is produced. Since glass surfaces are known to be negatively charged when immersed in water, the particles are prevented from sticking to the glass surface by electrostatic repulsion [15]. Due to the difference in the refraction indices of PS ($n_p = 1.59$) and water ($n_w = 1.33$) the particles are drawn into the intensity maximum of the interference grid which can be considered as an external periodic potential). The form of this potential $V(x)$ can be written as [11]

$$V(x) = V_0 \cos(2\pi x/d)\,, \tag{2}$$

where $V_0 = [3n_w \mathrm{Pr}^3(n^2 - 1)/c\sigma_0^2(n^2 + 2)][j_1(\pi r/d)/2\pi r]$, with P being the laser power, c the light velocity in vacuum, $n = n_p/n_w$, j_1 the first-order spherical Bessel function, r the particle diameter, and σ_0 the waist radius of the laser beam in the sample. Due to the Gaussian shape of the interfering laser beams, V_0 has also an Gaussian envelope. To minimize this effect [9] which would complicate the analysis we expanded the interference region to an area of about 300 μm in diameter.

Figure 2a shows a typical configuration of particles in the sampe cell when no interference pattern is present. The particles are arranged as expected for a colloidal liquid and interact only via a screened Coulomb potential. The corresponding Fourier transformation which is plotted in Fig. 2b consists of two ring-shaped areas, the larger one being due to an illustration artefact, whereas the smaller (and darker) one confirms – due to the absence on any

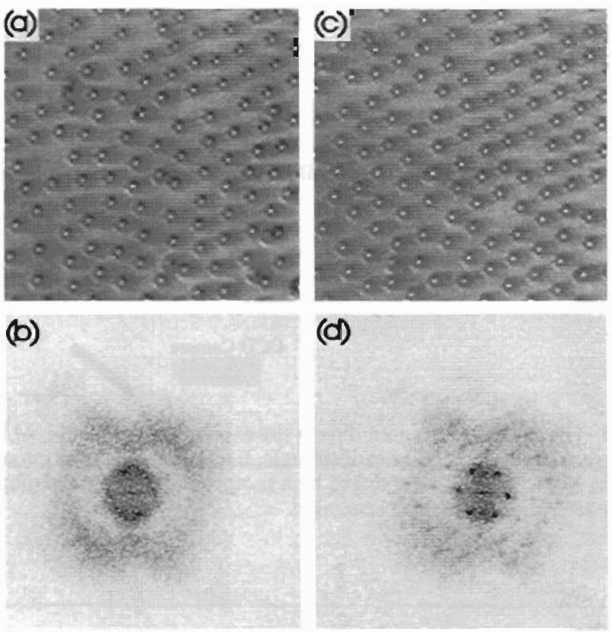
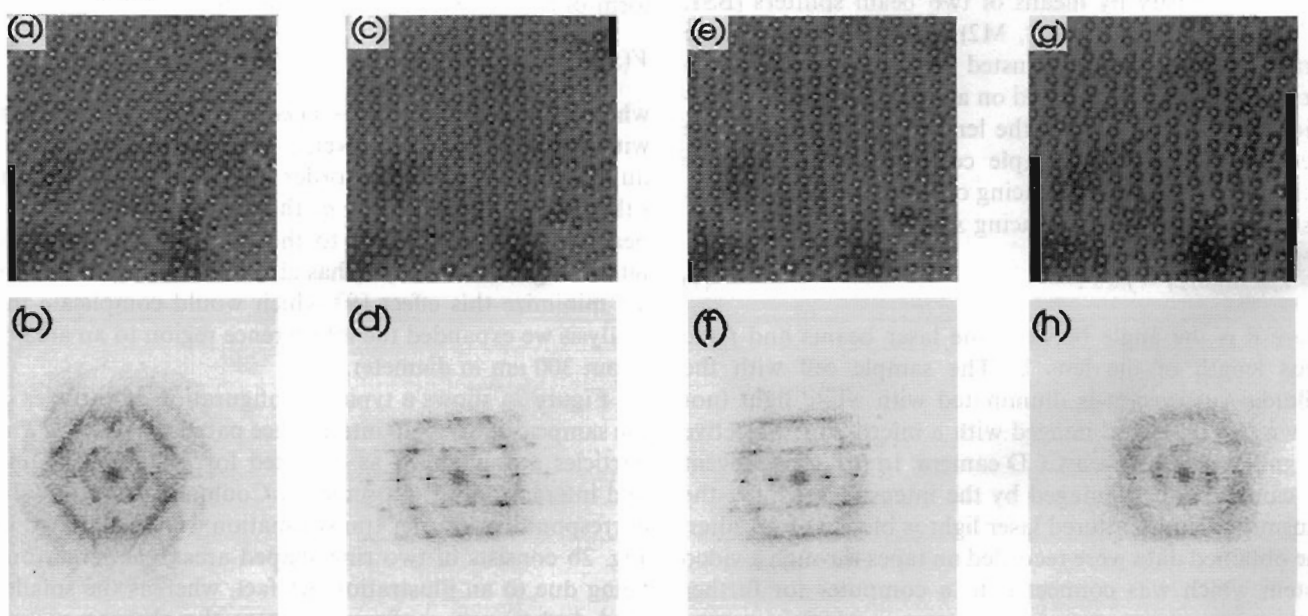


Fig. 2 Microscopic pictures and corresponding Fourier transformation of colloidal structure (a), (b) in absence of laser field, and (c), (d) when exposed to an interference pattern (laser intensity 200 mW). The direction of the interfering fringes is vertical

distinct features – the liquid structure of Fig. 2a. When the laser is turned on and the interference pattern (the fringes are aligned vertically) interacts with the particles, the structure changes and starts to crystallize. This can be seen in Fig. 2c, where the laser light intensity is 200 mW, corresponding to a potential depth of 1.9 $k_B T$, and the fringe spacing $d = \sqrt{3}a/2$, with $a = 10\ \mu m$ being the average particle distance determined from Fig. 2a. Under these conditions the interference fringes are commensurate with a hexagonal lattice which can be also seen in the Fourier transformation in Fig. 2c.

However, when the modulation periodicity $d \neq \sqrt{3}a/2$, deviation from a hexagonal symmetry are expected. Figure 3 shows several structures formed under different fringe spacing conditions, the laser light intensity was kept constant at a value of 200 mW as above. The ion concentration, i.e. the ionic conductivity during the experiments was kept contants at a value of 0.5 μS/cm. When d is increased (from the left to the right) the corresponding Fourier transformations clearly indicate that a change of the induced structure from a crystalline (Fig. 3a and b) into a liquid-like structure (Fig. 3g and h) occurs. With a_1 being the mean distance of particles along a row (parallel to the interference fringes) we can define the parameter $k = d/a_1$. As mentioned above, the close packed hexagonal lattice corresponds to $k = \sqrt{3}/2 = 0.866$. When k is smaller than that value, as being the case in Fig. 3a and b, where k was chosen to be 0.55, the particles in adjacent rows are so close that a crystal with almost quadratic symmetry (which can be also considered as a hexagonal lattice distorted in the vertical direction) is observed. In fact, for $k = 0.5$ we

Fig. 3 Microscopic pictures and corresponding Fourier transformation for different fringe spacing. The ratio of the fringe spacing to the mean particle separation a_1 is 0.55 in (a) and (b), 0.91 in (c) and (d), 1.0 in (e) and (f), and 1.2 in (g) and (h). The laser intensity is 200 mw, the direction of the fringes is vertical



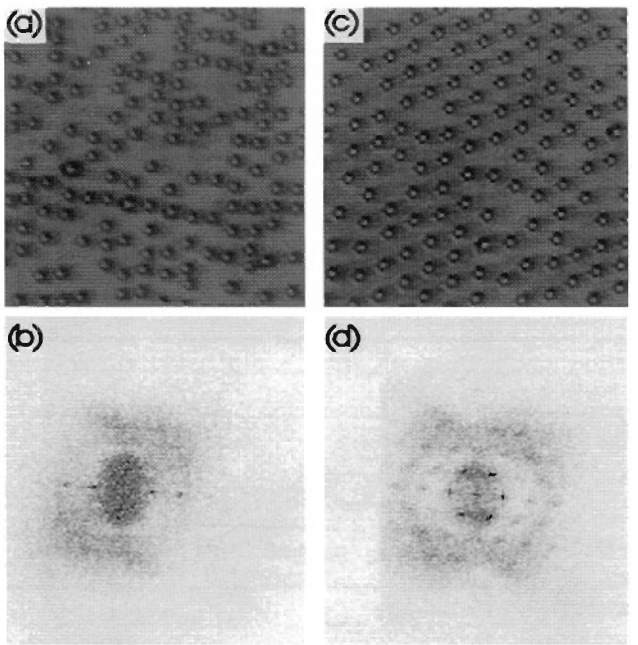


Fig. 4 Microscopic pictures and corresponding Fourier transformation of colloids for two different ion concentrations. The conductivity of the colloidal suspension is 2.6 and 0.5 μS/cm respectively, in (a) and (b) and (c) and (d). The laser intensity is 200 mW in both cases

observed a structure with exact quadratic symmetry. The structure in Fig. 3c and f with $k = 0.91$, being very close to 0.866, is nearly a hexagonal lattice. With k increased further to 1.0, we obtain the structure shown in Fig. 3e and g which is still a hexagonal lattice but now distorted in the horizontal direction. However, as can be seen from the spots in the corresponding Fourier transformation (Fig. 3f), registration between neighboring rows (i.e. repulsive interaction between particles of adjacent rows) still occurs. Figure 3g and h finally, show the structure for $k = 1.2$. The spots in Fig. 3h only correspond to a particle density modulation along vertical direction, but the registration between neighboring rows is lost because their interaction is smaller than the thermal energy. The obtained structure is a modulated liquid.

Finally, we want to demonstrate the effect on the light-induced structures when changing the ionic concentration in the system. We found that for low particle density or high ion concentration where the system is far from the freezing condition, the colloidal liquids never freeze to a crystalline phase, even at very high light intensities. This can be seen from Fig. 4, where the particle concentrations are nearly the same (about 9% higher in Fig. 4a), but the ion concentration is changed. The measured conductivity is 2.6 and 0.5 μS/cm, respectively, for Fig. 4a and c. In Fig. 4a we only observe the alignment of particles along the interference fringes, however, no order within rows and no registration between them are found. This can be also seen in the corresponding Fourier transformation in Fig. 4b, which is characteristic of a modulated liquid. In contrast to this, after the ionic concentration was decreased, the colloidal suspension is crystallized under the influence of the same periodic light potential (Fig. 4c and d). This is in agreement to theoretical calculations [13].

In summary, we have studied the phase transitions of colloids under the influence of a periodic light field. We observed the light-induced freezing transition of the system when the fringe spacing and the particle concentration is chosen properly. Additionally, we also observed strong deviations of the induced crystal structure from a perfect hexagonal symmetry when the fringe spacing is veried. Finally, we demonstrated the influence of the salt concentration on LIF.

Acknowledgments Financial support by the Deutsche Forschungsgemeischaft, Sonderforschunggsbereich 513 is gratefully acknowledged. One of the authors (Q.H.W.) would like to acknowledge the research fellowship support from the Alexander von Humboldt Foundation.

References

1. Ashkin A (1970) Phys Rev Lett 24:156; Ashkin A, Dziedzic JM (1975) Science 187:1073
2. Kepler GM, Fraden S (1994) Phys Rev Lett 73:356
3. Crocker JC, Grier DG (1996) Phys Rev Lett 73:352
4. Ashkin A, Schütze K, Dziedzic JM, Euteneuer U, Schliwa M (1990) Nature 348:346
5. Block SM, Goldstein LSB, Schnapp BJ (1990) Nature 348:348
6. Austin RH, Brody JP, Cox EC, Duke T, Volkmuth W (1997) Phys Today 33 and reference therein
7. Bariv R, Moses E (1994) Phys Rev Lett 73:1392
8. For a review, see Annu Rev Biophys Biomol Struct (1994) 23:247
9. Chowdhury A, Ackerson BJ, Clark NA (1985) Phys Rev Lett 60:833; Ackerson BJ, Chowdhury AH (1987) Faraday Discuss Chem Soc 83:309
10. Burns MM, Fournier J-M, Golovchenko JA (1990) Science 249:749
11. Loudiyi K, Ackerson BJ (1992) Physica 184A:1; 26
12. Chakrabati J, Krishnamurthy HR, Sood AK (1994) Phys Rev Lett 73:2923
13. Chakrabati J, Krishnamurthy HR, Sood AK, Sengupta S (1995) Phys Rev Lett 75:2233
14. Palberg T, Härtl W, Wittig U, Versmold H, Würth M (1992) J Phys Chem 96:8081
15. Prieve DC, Luo F, Lanni F (1987) Faraday Discus Chem Soc 83:297