Phase behaviour of a hard sphere colloidal system in the presence of an external laser field

Pinaki Chaudhuri, Ajay K. Sood, H. R. Krishnamurthy

Department of Physics
Indian Institute of Science
Bangalore 560012, India.

Abstract

We study the phase behaviour of a two-dimensionally confined hard sphere colloidal system in the presence of a periodic light field of two interfering laser beams using Monte Carlo simulations. For a given packing fraction of the particles, the colloidal system undergoes a transition from a modulated liquid to a modulated crystal as the light intensity is increased, corresponding to laser induced freezing. For certain packing fractions of the colloidal particles, the system again becomes a modulated liquid as the field strength crosses a threshold value, showing a re-entrant behaviour.
In recent times, there has been a renewed interest in laser induced freezing (LIF), i.e., the freezing of colloidal particles in the presence of an external modulating (laser) field. LIF was first demonstrated by Choudhury et al.\[1\]. A sample of 1µm diameter polystyrene particles was suspended in water placed between two optical flats. The highly charged particles, repelled by the walls, formed a two-dimensional monolayer structure. This two-dimensional system was subjected to a laser intensity pattern periodically modulated along one direction. It was found that when the wavevector of the stationary electric field is tuned to half the wave vector \( q_o \) where the liquid structure factor peaks, a triangular lattice with full two-dimensional symmetry results for light intensities above a threshold value.

A simple theoretical analysis in terms of the Landau-Alexander-Mctague\[1,2\] theory showed a rich phase diagram with a first order freezing transition turning to second order at higher field strengths via a tricritical point. In a density functional theory\[3\] analysis, Chakrabarti et al.\[4\] obtained a similar crossover and in addition deduced a symmetry criteria for obtaining the tricritical point in the phase diagram. Monte Carlo simulative studies of 1.1µm diameter colloidal particles interacting via a purely repulsive DLVO potential by Chakrabarti et al.\[5\] semed to confirm such a phase diagram, showing in addition an interesting reentrant transition to a liquid state for higher laser fields. Recently Wei et al.\[6\] reported an experimental study of LIF and from the real space density plots concluded that there is indeed such a re-entrant liquid phase. However, more recent Monte-Carlo simulations by Das et al.\[7,8\] of the same system as in \[5\] did not show any re-entrant phase. An even more recent theoretical work by Frey et al.\[9\], argues (by extending the KTHNY picture of unbinding of dislocation pairs during melting in two dimensions to the case when an external field is present) that for highly-screened short-range interactions, there should exist a re-entrant transition to a liquid-state.

In this paper, we study the phase behaviour of a system of hard sphere colloidal particles confined to a 2-d layer under the influence of a modulated laser field as a function of the light intensity. Using Monte Carlo simulations, we see that as the field intensity is increased, the system changes from a modulated liquid to a crystal, and finally back to a modulated liquid again, i.e, LIF in a hard-sphere colloid system does seem to show reentrant laser induced melting transition (LIM) unlike the 1.1µm DLVO colloidal system\[7,8\].

Hard sphere systems are interesting model systems in their own right \[10\] and should be a reasonable zeroth approximation for describing charge stabilised colloids which are highly screened. In such systems, where there is an exclusion of the interpenetration of the particles, the inter-particle potential is \( U(r) = \infty (r < R) \) and \( U(r) = 0 (r > R) \), where \( R \) is the hard sphere radius. The free energy is determined entirely by entropy, which is dependent on the fraction \( \phi \) of the total volume occupied by the spheres. At low volume fractions, the inter-particle collisions are rare. However when the packing fraction \( \phi \) increases, the motion of the particles is restricted because of more and more collisions with neighbouring particles. As \( \phi \) is increased from the liquid phase, it becomes entropically favourable for the system to form a periodic crystal rather than a random fluid structure. Thus, there is a purely entropy driven liquid-to-solid transition which is interesting \[10\]. The objective of this paper is to study the effect of the external field on this entropy driven phase transition.

Our simulations have been done in an ensemble where both the rectangular box size and the number of particles are fixed. In order to change the the area fraction occupied by the hard spheres, the diameter of the colloidal particles is changed. Temperature is
not a relevant quantity when the external field is absent; but in the presence of the field, the unit of energy chosen is the thermal energy $k_B T$. We consider the external laser field to be modulated along the y-direction and model its effects in terms of a potential of the form $V(r) = V_o \cos(q_o y)$, where $q_o$, equal to $2\pi/a_0 \sqrt{3}/2$, is the smallest reciprocal lattice vector corresponding to the triangular lattice of lattice constant $a$.

The particles are contained in a rectangular box where the ratio of the two sides $L_y$ and $L_x$ is $\sqrt{3} : 2$. This ensures that the simulation box is commensurate with a triangular lattice. $L_x (=L)$ is chosen as the square root of the number of particles. To avoid surface effects, we have chosen periodic boundary conditions using minimum image convention. The rectangular simulation box is replicated throughout space and in the course of the simulation, as a particle moves in the original box, so do the periodic images in exactly the same manner. In our simulations, we have considered a system of 900 particles. The typical number of configurations over which equilibration has been done is of the order of $5 \times 10^6$.

The thermodynamic quantity of our interest is the translational order parameter. The translational order parameters are defined by:

$$\rho_{\vec{q}_k} = \langle \frac{1}{N} \sum_i e^{i \vec{q}_k \cdot \vec{r}_i} \rangle \quad (1)$$

In the above equation, $\vec{r}_i$ is the real-space co-ordinate of the $i$-th particle, $\vec{q}_k$ is the $k$-th reciprocal lattice vector (rlv) belonging to the first shell of the rlvs. The averaging has been done over a canonical ensemble.

The value of $\rho_{\vec{q}_k}$ as defined in eqn (1) depends on the origin of co-ordinates. Therefore, in our simulations, we measure the translational order parameter as:

$$\rho_{\vec{q}_k} = \langle \frac{1}{N} | \sum_i e^{i \vec{q}_k \cdot \vec{r}_i} | \rangle \quad (2)$$

The order parameter so defined is of order unity in the crystalline state, while in the liquid state it goes to zero as $\frac{1}{\sqrt{N}}$ for a system of $N$ particles.

The primitive translation vectors of the direct triangular lattice can be chosen as: $a_1 = a(1,0), a_2 = a(\frac{1}{2}, \frac{\sqrt{3}}{2})$ and those for the reciprocal triangular lattice as $q_1 = \frac{2\pi}{a\sqrt{3}/2}(\frac{\sqrt{3}}{2}, \frac{1}{2}), q_2 = \frac{2\pi}{a\sqrt{3}/2}(0, 1)$. In our simulations, we have chosen $a$ to be unity. We denote by $\rho_l$ the order-parameters for the wavevectors $\pm \vec{q}_2$ parallel to the modulation wave-vector and $\rho_d$ denote the order parameter for the other four first-shell wave-vectors.

In Fig.1(a) we have plotted $\rho_d$ for the cases when there is no external field and when the field strength is infinite. In the case of zero field, entropy is the only mechanism that is forcing the density modes at the wave vectors $\vec{q}_k$ to develop, and this happens at a packing fraction of about 0.7. For the case of infinite strength, the external potential is so large that the freedom of the particles to move in a y-direction is totally suppressed and hence they can execute motion only in the x-direction. Now we find that $\rho_d$ becomes sizeable when the area fraction exceeds 0.68. This value of the area-fraction corresponds to the situation when there is vertical contact between the particles for the first time. For all area fractions less than 0.69, the system consists of $L$ uncoupled 1-dimensional chains of particles, with particles in the same line interacting through the hard-sphere repulsive potential. We know that
a disorder-to-order transition is not possible in a 1-dimensional system with short-ranged interactions. Hence there is no ordering before $\phi = 0.69$. Development of the density mode corresponding to the wave-vector $\mathbf{q}_2$ occurs only when a coupling between two neighbouring chains is established through vertical contact. To identify the threshold for the transition from the modulated liquid to modulated crystal phase, we have plotted $d\rho_d/d\phi$ as a function of $\phi$ in Fig. 1(b). It can be seen that $d\rho_d/d\phi$ has a pronounced peak at certain $\phi$ signifying sharp change in $\rho_d$ at that value of $\phi$. We identify the peak in $d\rho_d/d\phi$ as the onset of the freezing transition leading to a non-zero density mode $\rho_d$. These area fractions for the zero-field and infinite-field are 0.702 and 0.688, respectively.

In Fig. 2, we have plotted the variation of $\rho_d$ and $d\rho_d/d\phi$ with changing area fractions for some typical values of field strength ($\beta V_o = 0.1, 1.0, 10.0, 2000.0$, where $\beta = 1/k_BT$). From the plots we have identified, for each value of $\beta V_o$, the corresponding value of $\phi$ where the onset of freezing occurs. Using these values, we have thus constructed the phase diagram of the hard-sphere colloidal system in the presence of an external laser field, which is plotted in Fig. 3.

As noted above, in the absence of the laser field, the onset of freezing takes place at an area fraction value of 0.702. When the field is switched on, the density modes ($\rho_l$) corresponding to the modulating wave-vector become nonzero, and this facilitates the development of the the other density modes ($\rho_d$) causing the freezing transition to happen at a smaller $\phi$. As we can see from the phase diagram, the value of $\phi$ required for freezing continues to decrease till a $\beta V_o$ value of 2.0, where it is down to 0.667. Then it increases again to reach the infinite-field limit of about 0.69. A possible explanation for this latter increase could be the following. As $\beta V_o$ gets increased to values much larger than unity, the motion of the particles become more and more restricted to be around the lines $q_0y = (2n + 1)\pi$. Thus, beyond a threshold value of the field strength, the influence of particles of neighbouring lines on the motion of particles on a particular line decreases. This manifests in the fact that the condensation of the density mode $\rho_d$ takes place at a higher area fraction compared to the values corresponding to field strengths below that threshold. With increasing field strength, the value of the critical $\phi$ goes on increasing until it reaches the limiting value of 0.688.

If we examine the phase diagram in Fig. 3, we can see that for any fixed value of $\phi$ less than 0.66, the colloidal system continues to be in modulated liquid state for all values of $\beta V_o$. For values larger than 0.7, the system remains in crystalline form throughout the entire range of field strengths. The intermediate region is interesting. For example, consider a $\phi$ value of 0.675. For low field strength, at this volume fraction, the system behaves like a modulated liquid. If one exceeds a certain field strength ($\beta V_o = 1.4$), the system undergoes a transition to a modulated crystalline state. But beyond $\beta V_o = 31$, the hard sphere system again becomes a modulated liquid. Thus, from the measurement of the translational order parameter in Monte Carlo simulations, we find a possibility of re-entrant behaviour in the two-dimensional hard sphere system in the presence of an external modulation potential.

To examine the three phases at $\phi = 0.675$, we have measured in our simulations the equilibrium real-space particle density $\langle \rho(x,y) \rangle$ for three different field strengths, as shown in Fig. 4(a)-(c). After equilibrating for $10^5$ configurations, $\langle \rho(x,y) \rangle$ was measured by averaging over $1.5 \times 10^5$ configurations. From the plots, we can see that for $\beta V_o$ equal to 0.1, the system is in a liquid state, the modulations not being very prominent. When $\beta V_o$ is equal to 2.0, the system is nearly crystalline and for $\beta V_o = 1000$, the system loses its
crystalline structure and again becomes a modulated liquid. This confirms the occurrence of a re-entrant melting as a function of the strength of the modulating potential. This is consistent with the recent prediction by Frey et al. [9], but it remains to be shown that the melting here is a continuous transition and is mediated by the unbinding of dislocations. More extensive simulations are needed to demonstrate the latter. Meanwhile, it would be interesting to carry out experiments involving hard sphere colloidal particles and observe whether such a reentrant melting occurs as the strength of the laser field is increased.

In conclusion, we have studied the effect of the external laser field modulation on a two-dimensional system of colloidal particles interacting via a hard sphere potential. By identifying the maxima in the rate of variation of the order-parameter $\rho_d$ (as a function of the packing fraction) as the onset of condensation of the density mode, we have constructed the phase diagram for the system. For a certain range of packing fractions, re-entrant melting occurs in the system as the strength of the field increases. Measurement of real-space density for $\phi = 0.675$ confirms that the system first freezes into crystalline form but later on becomes a modulated liquid on increase of the field strength. A method has been proposed recently to calculate isothermal elastic constants for the hard disk triangular solids in two dimensions using Monte Carlo simulations [11]. It would be of interest to check (using this method) whether these elastic constants soften when the field strength is increased beyond a certain value in our systems.

After our work was completed, we learnt of an independent and more extensive Monte Carlo simulational study on the same system by Strepp et al. [12]. Using the cumulant intersection method, they have obtained a phase diagram has been obtained which is qualitatively and quantitatively similar to the one obtained by us. This further strengthens the case for the existence of the re-entrant modulated liquid phase in a hard-sphere colloidal system subject to an external laser field modulation.

I. ACKNOWLEDGEMENTS

We are grateful to Chinmay Das for helpful discussions.
REFERENCES

[1] A. Chowdhury, B. Ackerson and N. A. Clark, Phys. Rev. Lett. 55, 833 (1985).
[2] S. Alexander and J. McTague, Phys. Rev. Lett. 41, 702 (1984).
[3] T. V. Ramakrishnan and M. Yussoff, Phys. Rev. B 19, 2775 (1979).
[4] J. Chakrabarti, H. R. Krishnamurthy, and A. K. Sood, Phys. Rev. Lett. 73, 2923 (1994).
[5] J. Chakrabarti, H. R. Krishnamurthy, A. K. Sood, and S. Sengupta Phys. Rev. Lett. 75, 2232 (1995).
[6] Q. H. Wei, C. Bechinger, D. Rudhart and P. Leiderer, Phys. Rev. Lett. 81, 2606 (1998).
[7] Chinmay Das, A. K. Sood, H. R. Krishnamurthy, condmat(9902006).
[8] Chinmay Das, A. K. Sood, H. R. Krishnamurthy, Physica A 270, 237 (1999).
[9] E. Frey, D. R. Nelson, L. Radzihovsky, Phys. Rev. Lett. 83, 2977 (1999).
[10] T. C. Lubensky , Solid State Communications 102, N2-3:187-197 (1997).
[11] S. Sengupta, P.Nielaba, M.Rao, K. Binder, condmat(9906063).
[12] W. Strepp, S. Sengupta, P. Nielaba, preprint.
FIGURES

FIG. 1. Variation of $\rho_d$ and $d\rho_d/d\phi$ for $\beta V_o = 0$ and for infinite field.

FIG. 2. Plots of $\rho_d$ and $d\rho_d/d\phi$ for some typical values of field strength, $\beta V_o = 0.1, 1.0, 10.0, 2000.0$.

FIG. 3. Phase diagram of the colloidal system for 900 particles in an external laser field.

FIG. 4. Contour plots of average density for $\phi = 0.675$ in presence of external field. (a), (b) and (c) correspond to $\beta V_o = 0.1, 2.0, 1000.0$ respectively.
Fig. 1
Fig. 2
area fraction ($\phi$)

modulated crystal

modulated liquid

$\beta V_0$

Fig. 3
\( \langle \rho(x,y) \rangle \) for \( \beta V_0 = 0.1 \)
$\langle \rho(x,y) \rangle$ for $\beta V_0 = 1000$

Fig. 4c