

## Re-entrant disordering of colloidal molecular crystals on two-dimensional periodic substrates

M Mikulis<sup>1,2</sup>, C J Olson Reichhardt<sup>1</sup>, C Reichhardt<sup>1</sup>, R T Scalettar<sup>2</sup> and G T Zimányi<sup>2</sup>

<sup>1</sup> Center for Nonlinear Studies and Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

<sup>2</sup> Department of Physics, University of California, Davis, CA 95616, USA

Received 23 April 2004, in final form 2 September 2004

Published 29 October 2004

Online at [stacks.iop.org/JPhysCM/16/7909](http://stacks.iop.org/JPhysCM/16/7909)

doi:10.1088/0953-8984/16/45/013

### Abstract

Using numerical simulations, we study colloidal ordering and disordering on two-dimensional periodic substrates where the number of colloids per substrate minima is two or three. The colloids form dimer or trimer states with orientational ordering, referred to as colloidal molecular crystals. At a fixed temperature such that, in the absence of a substrate, the colloids are in a triangular floating solid state, upon increasing the substrate strength we find a transition to an ordered colloidal molecular crystal state, *followed* by a transition to a disordered state where the colloids still form dimers or trimers but the orientational order is lost. These results are in agreement with recent experiments.

Colloidal particle assemblies in two dimensions (2D) are an ideal system in which to study ordering and melting, since quantities such as diffusion, dislocation dynamics, and local ordering can be directly observed, which is typically not the case for atomic and molecular systems [1]. Repulsively interacting colloids on a smooth substrate in 2D form triangular arrangements at high density or low temperatures, with hexatic or liquid states at lower densities [1], and have been used to explore two-dimensional melting [2–5] and structural transitions [6], both experimentally [7] and in simulations [8]. Optical techniques such as interfering laser arrays have created one-dimensional (1D) line-like potentials which attract the colloids. Experimental studies of periodic 1D potentials find a remarkable laser-induced freezing transition, where for zero substrate strength the colloids form a disordered liquid, but with increasing substrate or laser strength there is a transition to a frozen ordered state [9]. This laser-induced freezing was studied with density-functional theory [10] and simulations [11]. These theoretical works also found that for increased substrate strength, the frozen state can show a re-entrant disordering transition to a 1D modulated liquid. This re-entrance was similar to that subsequently observed in experiments [12, 13]. Further theoretical studies have mapped

additional properties of this system [14], including the presence of locked floating solids and smectic phases as well as the orientational dependence of the melting temperature, and some of these predictions, including the laser-induced melting transition into the re-entrant phase, have also been confirmed in experiment [15]. The re-entrant disordering occurs because, as the substrate strength is gradually increased, the system becomes effectively 1D. The fluctuations are enhanced for lower dimensionality and can lead to the formation of a 1D liquid.

More recently, colloidal assemblies interacting with 2D periodic substrates have been investigated [16–19]. Simulations of colloids on 2D periodic substrates have considered the case where the number of colloids is an integer multiple of the number of potential minima [16]. In this case, multiple colloids sit in each potential minimum and form dimer, trimer, or higher states depending on the filling. These colloidal states can have an additional orientational ordering and have been termed colloidal molecular crystals (CMCs) in analogy with molecules forming crystalline states with orientational ordering of the molecules. Three phases appear in the simulations: a high temperature liquid regime, a low temperature orientationally ordered CMC, and an intermediate disordered CMC phase where the orientational order is lost but the colloids remain trapped in each minimum, rotating freely but not diffusing. Experiments on 2D periodic optical traps with three colloids per potential minimum confirmed the existence of the three phases [17]. In these experiments, the temperature and density of the system were fixed and the intensity of the traps was increased by tuning the laser power. Here, as a function of increasing substrate strength, the initial state was a liquid, followed by a transition to an orientationally ordered CMC and, at higher strengths, a transition to a disordered CMC. This re-entrant disordering is similar to that found for 1D periodic modulated substrates. While some previous simulations [16] indicate re-entrance, it was not carefully explored.

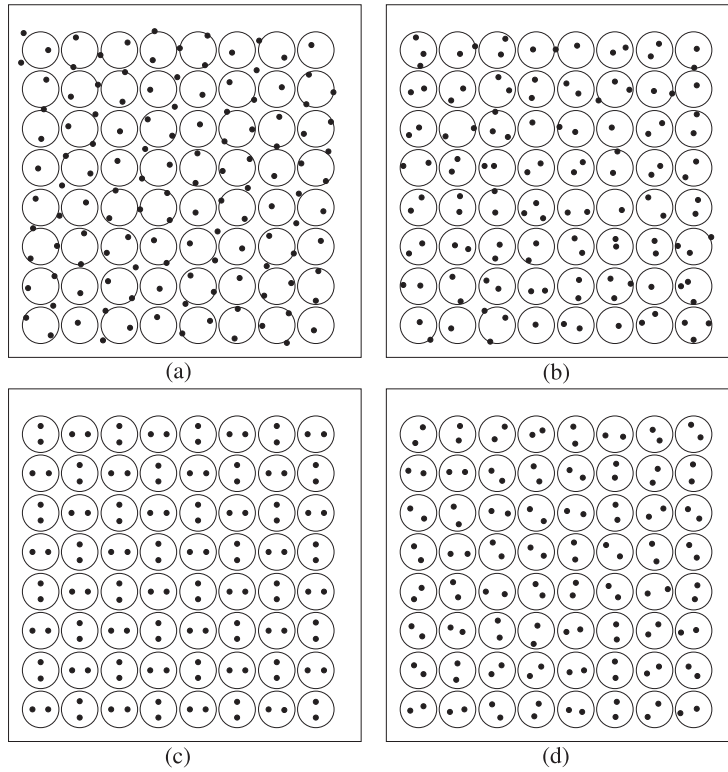
In this work we measure the diffusion of colloids from their traps and also the degree of rotational order between molecules in adjacent wells. We then numerically map the phase diagram as a function of substrate strength. We observe four phases, floating (triangular) solid, rotationally ordered and disordered colloidal molecular crystal, and liquid. The transition to the liquid state rises monotonically in temperature with the substrate potential strength, but the transition from the ordered to the disordered CMC phase first increases and then decreases in temperature with increasing substrate strength. This leads to a striking feature of the phase diagram: clear evidence for a re-entrant disordered CMC as a function of substrate strength.

As we shall describe, the phase diagram presented in this work, in addition to having higher resolution than in previous studies, also extends previous work by clearly indicating the region of phase space in which a floating solid occurs. That is, we identify the regime at weak and zero substrate potential where the colloids order into a triangular lattice. We also present a phase diagram for the case when the colloid number is three times the number of substrate minima, thereby quantifying the behaviour of the system at this filling.

We perform a Langevin simulation of a 2D system with periodic boundary conditions in the  $x$  and  $y$  directions, as in previous work [16]. There are  $N$  colloids interacting with a 2D periodic substrate which has  $M$  minima. We focus on the two cases  $N/M = 2$  and 3. The overdamped equation of motion for a single colloid  $i$  is

$$\frac{d\mathbf{r}_i}{dt} = \mathbf{f}_i + \mathbf{f}_s + \mathbf{f}_T, \quad (1)$$

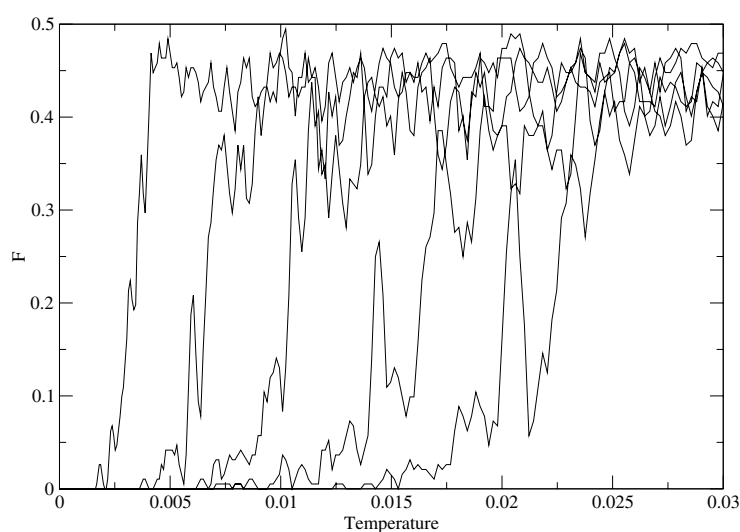
where  $\mathbf{f}_i = \sum_{j \neq i}^N -\nabla_i V(r_{ij})$  is the interaction force from the other colloids, which we take to be a Yukawa or screened Coulomb form,  $V(r_{ij}) = (Q^2/|\mathbf{r}_i - \mathbf{r}_j|) \exp(-\kappa|\mathbf{r}_i - \mathbf{r}_j|)$ . Here  $Q$  is the charge of the particles, which we set to 1.0,  $1/\kappa$  is the screening length, and  $\mathbf{r}_i$  is the position of particle  $i$ . We consider a square substrate with lattice constant  $a$  and force  $\mathbf{f}_s = A \sin(2\pi x/a)\hat{\mathbf{x}} + A \sin(2\pi y/a)\hat{\mathbf{y}}$ . The screening length  $1/\kappa$  is set to  $1.5a$ ; a larger



**Figure 1.** The colloidal configurations for a square periodic substrate in 2D. The circles indicate the location of the potential wells. (a) For a sufficiently weak substrate potential, at low temperatures (here  $A = 0.0$ ,  $T = 0.0$ ) the colloids form a floating triangular lattice, which has some mild distortion (see the text). (b) At high enough temperature, for any substrate potential (here  $A = 1.0$ ,  $T = 0.125$ ) the colloids form a liquid. (c) For all but the smallest potentials, at low temperatures (here  $A = 1.0$ ,  $T = 0.0$ ) the colloids form a rotationally ordered solid. (d) For large enough substrate potentials (here  $A = 1.0$ ,  $T = 0.026$ ) an intermediate disordered CMC phase exists between the rotationally ordered solid phase and the liquid phase.

screening length (such as that used in [16]) would shift the phase boundaries to higher substrate strengths. In this work we keep  $a$  fixed and vary  $A$ . The thermal force  $f_T$  comes from Langevin kicks with the properties  $\langle f_T \rangle = 0$  and  $\langle f_T^i(t) f_T^j(t') \rangle = 2k_B T \delta_{ij} \delta(t - t')$ . The dimensionless temperature can be expressed in units of  $Q^2 / ak_B$ . The initial colloidal positions are obtained by annealing from a high temperature  $T = 0.5$  where the colloids are diffusing freely, and gradually cooling to zero in increments of  $T = 1.25 \times 10^{-5}$ . We equilibrated the sample for 20 000 molecular dynamics steps at each increment. We checked our results by both decreasing the temperature increment and increasing the number of time steps spent at each increment, and found that our results are robust.

We first concentrate on the case  $N/M = 2$ . As a function of  $T$  and  $A$ , we find the four phases illustrated in figure 1. For very low  $A$  and  $T$ , we find a floating triangular lattice as shown in figure 1(a), where the substrate is weak enough that the elastic interaction of the colloids dominates and they form a triangular lattice. At high enough  $T$ , for all  $A$  we find a modulated liquid where the colloids are disordered and have a large diffusion constant, as shown in figure 1(b). For low  $T$  and large enough  $A$ , the orientationally ordered CMC of figure 1(c) forms. Each potential minimum captures two colloids and the colloid dimer



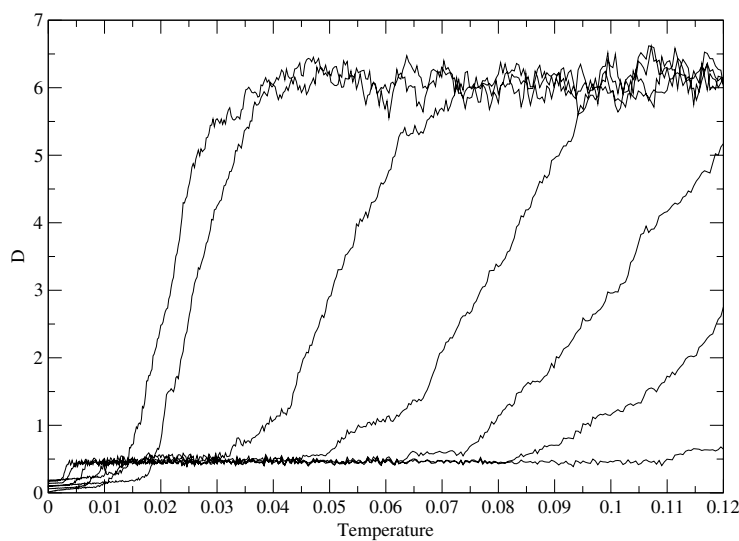
**Figure 2.** Rotational disorder fraction versus temperature, for (from left to right)  $A = 3.0, 2.0, 1.50, 0.25,$  and  $0.50$ . The phase transition from the ordered CMC to the disordered CMC state is defined as the temperature at which  $F = 0.4$ . The transition temperature first increases from  $A = 0.25$  to  $0.50$ , but then decreases for larger  $A$ .

orientation alternates from vertical to horizontal. For larger  $A$  and  $T$ , a disordered CMC phase occurs in which the colloids are still fixed to the potential minima but long range orientational ordering is lost, as seen in figure 1(d).

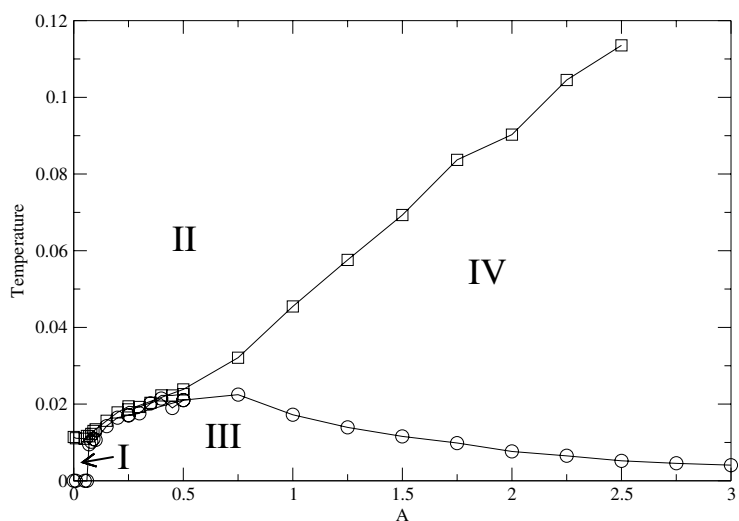
We use various measures to identify the different phases in the  $T$  versus  $A$  phase diagram. In order to locate the ordered to disordered CMC transition, we measure the rotational disorder fraction  $F$  of the particles. To determine  $F$ , we define each dimer to be horizontally or vertically oriented depending on whether the  $x$  or  $y$  component of the vector joining the two colloids is larger.  $F$  is then defined as the fraction of the dimers which differ from the ordered CMC configuration of alternating vertical and horizontal orientations. This quantity is zero in the ordered solid phase and saturates to a higher value when the orientational ordering is lost. In figure 2 we plot  $F$  versus  $T$  for different values of  $A$ . The transition temperature first increases from  $A = 0.25$  to  $0.50$ , but then decreases for larger values of  $A$ .

To distinguish between the CMC phases and the liquid phase, we measure the diffusion  $D$  of the particles by calculating the average of the square of the distance travelled by the particles from their initial positions after a large, fixed number of time steps. In figure 3, we plot  $D$  as a function of temperature  $T$  for different potential depths  $A$ . The first low temperature step-like increase in  $D$  corresponds to the ordered/disordered CMC phase transition (since the particles are now rotating freely) and the second much larger increase indicates the transition into a liquid state. The melting temperature is defined as the point at which  $D$  first increases sharply, when the particles are no longer bound in the potential wells. This temperature rises monotonically with  $A$ . For high values of  $A$ , the colloid dimers are no longer in a rotationally ordered configuration before they leave the wells, showing the existence of the disordered CMC. We measured the transitions for several different initial starting configurations of the colloids and found that the results were unchanged.

In figure 4 we plot the transition lines from the ordered CMC to the liquid, floating solid, and disordered CMC states, obtained using the measures illustrated in figures 2 and 3. Here, the range of temperature over which the ordered CMC phase exists increases in extent as  $A$

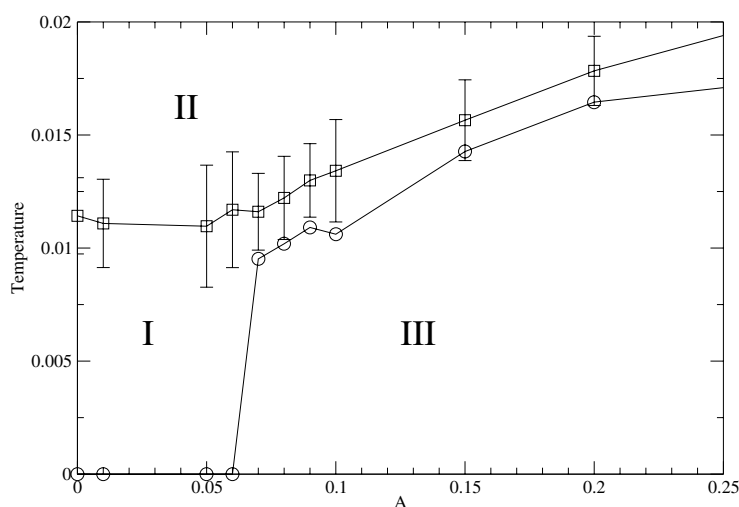


**Figure 3.** Diffusion versus temperature for (from left to right)  $A = 0.25, 0.5, 1.0, 1.5, 2.0, 2.5,$  and  $3.0$ . The melting temperature is defined as the point at which  $D$  first increases sharply, when the particles are no longer bound in the potential wells.



**Figure 4.** The phase diagram of temperature versus potential strength  $A$ . In region **I** the colloids form a floating solid triangular lattice. In region **II** the colloids are in a liquid state. Region **III** contains a rotationally ordered solid. Finally, in region **IV** the colloids are in a solid state which has no rotational ordering. Circles indicate the transition to the ordered CMC as determined by the rotational disorder fraction  $F$ . Squares indicate the melting transition measured from the diffusion  $D$ .

increases from the CMC onset at  $A = 0.06$ , reaching a maximum width at  $A = 0.75$ . As  $A$  is further increased above  $A = 0.75$ , the width in  $T$  of the ordered CMC phase decreases, showing a slight nonlinearity. The transition line between the disordered CMC and the liquid moves to higher temperatures roughly linearly as  $A$  increases, as expected, since it represents a



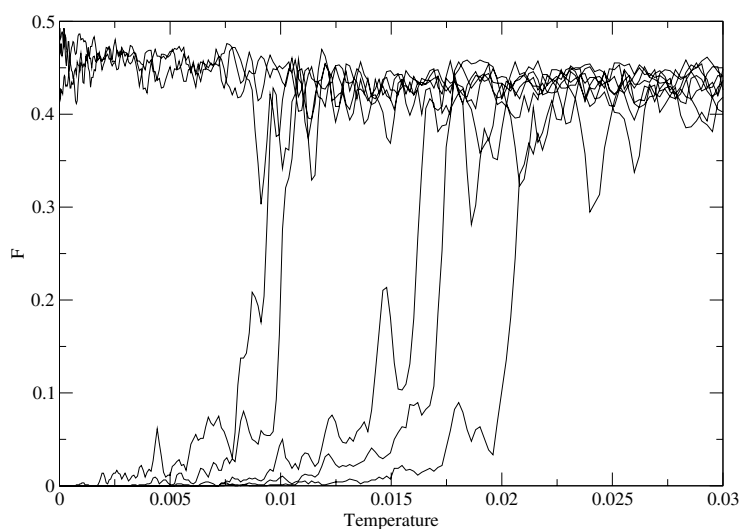
**Figure 5.** The phase diagram of temperature versus  $A$  at small  $A$ , highlighting the floating solid region.

first-order phase transition. For values of  $A < 0.5$ , the two transition lines converge, indicating that the ordered solid melts directly into the liquid phase without passing through a disordered solid phase. Figure 4 shows a clear disordering re-entrance. For a fixed  $T = 0.016$ , the colloids are in a liquid state at  $A = 0$ . A transition to the ordered CMC state occurs at  $A \approx 0.19$ , while a transition to the disordered CMC state occurs at  $A \approx 1.07$ . This sequence of transitions for increasing substrate strength is exactly what is seen in experiment [17].

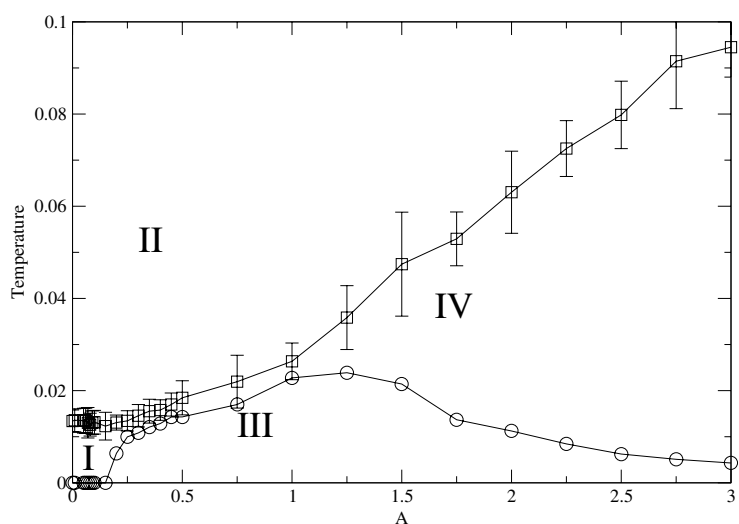
The initial increase in the disordering temperature with substrate strength occurs due to the fact that some finite substrate strength is required to confine the colloids, which are either in a floating solid or liquid state for a very weak substrate. When the potential is just strong enough to trap the colloids, the size of each dimer (the distance between the two colloids composing the dimer) is at its maximum, and the colloids are close to jumping out of the confining well. At a somewhat higher temperature, the colloids begin to diffuse; thus, as the potential strength increases, the temperature at which diffusion begins also increases. We note that the cause of the orientational ordering of the dimers is their effective quadrupole moment. The energy of interaction between these moments is minimized when the dimers are oriented as in figure 1(c). The strength of the quadrupole moment is proportional to the square of the distance between the two colloids in a single potential minimum. As  $A$  is increased, this distance decreases. If we approximate the well confining the colloids as a parabola, then the distance between the colloids in the dimer decreases by  $\delta r \propto A$ . As the strength of the quadrupole moment drops, thermal effects dominate the orientational ordering and the colloidal dimer begins to rotate, destroying the orientational ordering.

In figure 5 we show a blow-up of the phase diagram from figure 4 for the region with small  $A$ . Here, we find that at low temperatures the elastic interactions between the colloids dominate over the substrate, and an almost triangular lattice forms. We call this a floating solid since the system is effectively frozen with no diffusion. In figure 6 we show the rotational disorder fraction plot for small values for  $A$ , which was used to identify the floating solid phase.

In order to show that the re-entrant disordering is a general feature for CMC states we have considered other integer fillings as well. In figure 7 we plot the phase diagram using



**Figure 6.** Rotational disorder fraction  $F$  versus temperature for (from left to right)  $A = 0, 0.05, 0.06, 0.07, 0.10, 0.20, 0.30,$  and  $0.50$ . For  $A \leq 0.07$ , the colloids are initially ( $T = 0$ ) in a floating solid state. The rotational disorder fraction exceeds 0.4 for these values of  $A$  at all temperatures.



**Figure 7.** The phase diagram of temperature versus  $A$  for trimer states. The same four phases occur as in the dimer states, namely: **I**—floating solid, **II**—liquid, **III**—ordered CMC (colloid molecular crystal), and **IV**—disordered CMC.

the same measures as in figure 4 for the case of  $N/M = 3$  on a square substrate. This is the filling fraction used in recent experiments [17]. Here the ordered CMC is the same as found in earlier simulations [16]. The phase diagram has the same basic features as in figure 4, where  $M/N = 2$  and dimers form in the wells. However, the critical temperatures are a bit lower, as is reasonable, and while the non-monotonic (re-entrant) behaviour of the rotational melting line is still clearly evident, the liquid at small  $A$  does not extend as deeply below the peak in the rotationally ordered phase.

In conclusion, we have shown clear numerical evidence for re-entrant disordering of colloidal molecular crystals on 2D periodic substrates for increasing substrate strength and fixed temperature, in agreement with recent experiments. We map out the temperature versus substrate phase diagram and show that four phases can occur: a high temperature liquid, a triangular floating solid, an orientationally ordered colloidal molecular crystal state, and a disordered colloidal molecular crystal state.

## Acknowledgments

We thank C Bechinger for useful discussions. This work was supported by the US DoE under Contract No W-7405-ENG-36, by the LANL/UC CARE and CLE programmes, and by NSF-DMR-0312261.

## References

- [1] Murray C A and Winkle D H V 1987 *Phys. Rev. Lett.* **58** 1200  
Zahn K, Lenke R and Maret G 1999 *Phys. Rev. Lett.* **82** 2721  
Pertsinidis A and Ling X S 2001 *Nature* **413** 147
- [2] Kosterlitz J M and Thouless D J 1973 *J. Phys. C: Solid State Phys.* **6** 1181
- [3] Halperin B I and Nelson D R 1978 *Phys. Rev. Lett.* **41** 121  
Nelson D R and Halperin B I 1979 *Phys. Rev. B* **19** 2457
- [4] Young A P 1979 *Phys. Rev. B* **19** 1855
- [5] For a review, see Strandburg K J 1988 *Rev. Mod. Phys.* **60** 161
- [6] Sun J and Stirner T 2003 *Phys. Rev. E* **67** 051107
- [7] Pieranski P 1980 *Phys. Rev. Lett.* **45** 569  
Murray C A and Van Winkle D H 1987 *Phys. Rev. Lett.* **58** 1200  
Murray C A and Wenk R A 1989 *Phys. Rev. Lett.* **62** 1643  
Tang Y, Armstrong A J, Mockler R C and O'Sullivan W J 1989 *Phys. Rev. Lett.* **62** 2401  
Armstrong A J, Mockler R C and O'Sullivan W J 1989 *J. Phys.: Condens. Matter* **1** 1707  
Kusner R E, Mann J A, Kerins J and Dahm A J 1994 *Phys. Rev. Lett.* **73** 3113  
Kusner R E, Mann J A and Dahm A J 1995 *Phys. Rev. B* **51** 5746  
Marcus A H and Rice S A 1996 *Phys. Rev. Lett.* **77** 2577  
Marcus A H and Rice S A 1997 *Phys. Rev. E* **55** 637  
Zahn K, Lenke R and Maret G 1999 *Phys. Rev. Lett.* **82** 2721
- [8] Frenkel D and McTague J P 1979 *Phys. Rev. Lett.* **42** 1632  
Toxvaerd S 1980 *Phys. Rev. Lett.* **44** 1002  
Kalia R K and Vashishta P 1981 *J. Phys. C: Solid State Phys.* **14** L643  
Naidoo K J and Schnitker J 1994 *J. Chem. Phys.* **100** 3114  
Bagchi K, Anderson H C and Swope W 1996 *Phys. Rev. Lett.* **76** 255  
Zangi R and Rice S A 1998 *Phys. Rev. E* **58** 7529  
Terao T and Nakayama T 1999 *Phys. Rev. E* **60** 7157
- [9] Chowdhury A, Ackerson B J and Clark N A 1985 *Phys. Rev. Lett.* **55** 833
- [10] Chakrabarti J, Krishnamurthy H R and Sood A K 1994 *Phys. Rev. Lett.* **73** 2923
- [11] Chakrabarti J, Krishnamurthy H R, Sood A K and Sengupta S 1995 *Phys. Rev. Lett.* **75** 2232
- [12] Wei Q-H, Bechinger C, Rudhardt D and Leiderer P 1998 *Phys. Rev. Lett.* **81** 2606
- [13] Bechinger C, Brunner M and Leiderer P 2001 *Phys. Rev. Lett.* **86** 930
- [14] Frey E, Nelson D R and Radzihovsky L 1998 *Phys. Rev. Lett.* **83** 2977  
Radzihovsky L, Frey E and Nelson D R 2001 *Phys. Rev. E* **63** 031503
- [15] Bechinger C and Frey E 2001 *J. Phys.: Condens. Matter* **13** R321
- [16] Reichhardt C and Olson C J 2002 *Phys. Rev. Lett.* **88** 248301
- [17] Brunner M and Bechinger C 2002 *Phys. Rev. Lett.* **88** 248302
- [18] Mangold K, Leiderer P and Bechinger C 2003 *Phys. Rev. Lett.* **90** 158302
- [19] Korda P T, Spalding G C and Grier D G 2002 *Phys. Rev. B* **66** 024504  
Korda P T, Taylor M B and Grier D G 2002 *Phys. Rev. Lett.* **89** 128301