Entropy versus energy: The phase behavior of a hard-disk mixture in a periodic external potential

Kerstin Franzrahe* and Peter Nielaba
Department of Physics, University of Konstanz, Universitätsstrasse 10, 78457 Konstanz, Germany
(Received 22 September 2007; published 4 December 2007)

The phase behavior of a 50% binary hard-disk mixture with diameter ratio $\sigma_B/\sigma_A=0.414$, which is exposed to a one-dimensional periodic potential, is examined via Monte Carlo simulations. We find an induced structural crossover in the modulated liquid. At higher densities, depending on the strength of the external potential, the system exhibits a tunable demixing transition, followed by fluid-solid coexistence of an equimolar mixture with the $S_1(AB)$ square lattice. We find a decoupled melting of the sublattices of the $S_1(AB)$ lattice. The melting of the small-component sublattice perpendicular to the external potential minima leads to fissuring in the large-component sublattice.

DOI: 10.1103/PhysRevE.76.061503 PACS number(s): 64.75.+g, 61.20.Ja, 64.70.Dv, 82.70.Dd

Two-dimensional (2D) systems often differ significantly in their physical properties and phase transition behavior from corresponding three-dimensional systems. The need to understand these differences is obvious in the face of general minimization trends in physics and technology. In this context, monolayers and their interactions with a substrate have attracted a lot of interest. But also from a purely theoretical point of view the ongoing discussion on the nature of freezing and melting in two dimensions (Kosterlitz-Thouless-Halperin-Nelson-Young scenario [1–3] versus first-order transition) shows the importance of two-dimensional systems in general. Colloidal suspensions have proven to be ideal model systems for studies on such systems, their advantage being the direct accessibility to real space data via laser scanning microscopy, an excellent control over the colloidal interactions, and the tunability of the substrate potential in its shape and strength, as it is modeled, e.g., by the interference pattern of laser beams. Monodisperse 2D colloidal systems with and without a substrate potential have been studied extensively in experiments [4–6], computer simulations [7–12], and theory [13–15] over the last decades. But as in nature monolayers are often not necessarily monodisperse, our focus is on the question of how the addition of another length scale into the system will influence the intricate competition between adsorbate-adsorbate and adsorbate-substrate interactions. This question is addressed by studying a binary system under the influence of a 1D spatially periodic substrate potential. A variety of interesting phenomena are discovered that could be exploited in experimental techniques. The interaction with the substrate will completely change the miscibility of the binary mixture. As the change is induced by the external field, it is a means to directly control miscibility. In addition, such a system exhibits a field-induced ordering transition, which could be exploited for controlled structural growth. We show that these phenomena are to be found even in purely repulsive systems such as a 2D hard-disk mixture by means of Monte Carlo computer simulations. In experiments, sterically stabilized poly(methylmethacrylate) (PMMA) spheres are often used to model such repulsive particle interactions. In an experimental realization, a binary mixture of sterically stabilized PMMA colloids with the desired ratio of radii and a large difference in polarizabilities might be exposed to an interference pattern of laser beams. The polarizability of the larger component should tend to zero in order to approach the limit of no coupling to the external potential.

The choice of a purely repulsive interaction allows a direct comparison to the extensive studies on monodisperse systems in a 1D periodic light field [16]. These show a highly nontrivial phase behavior as the amplitude of the external field is raised: laser-induced freezing (LIF) [4] and laser-induced melting (LIM) [5,9]. The occurring stable phases depend crucially on the given commensurability ratio, i.e., the ratio of the wave vector of the external field to the corresponding parallel reciprocal lattice vector.

Employing a 1D spatially periodic external potential mimics the situation of a stripe patterned substrate. Such patterns are used as templates in colloidal epitaxy [17] for growing, e.g., photonic colloidal crystals [18,19]. Structure formation of monodisperse systems on such patterns has been investigated e.g., by Harreis *et al.* [20], who predict a variety of possible lattice structures depending on the width and periodicity of the stripes. Nevertheless, for a direct comparison with the reentrant LIF and LIM scenarios, we focus on the effect the periodicity has on the mixture, and set the external potential $V(\vec{r})$ to

$$V(\vec{r}) = V_0 \sin(\vec{K}\cdot\vec{r}), \quad \vec{K} = \frac{4\pi}{a}(1,0).$$

As for the equimolar binary mixture of interest (diameter ratio $\sigma_B/\sigma_A=0.414$), the $S_1(AB)$ [21] lattice structure allows for the densest packing, the periodicity of the potential $\lambda=2\pi/|\vec{K}|$ is chosen to be commensurate to the lattice planes of the $S_1(AB)$ crystal with a commensurability ratio

$$p = \frac{|\vec{K}|}{|\vec{G}_0|} = \left(\frac{4\pi}{a}\right) \Big/ \left(\frac{2\pi}{a}\right) = 2,$$

with a the lattice parameter of the square lattice. All lengths are measured in units of σ_A; therefore the dimensionless

*Kerstin.Franzrahe@uni-konstanz.de

number density is $\varrho=(N/A)\sigma_A^2$. Whether in the field-free case the $S_1(AB)$ lattice, which is predicted [21] to exist in equimolar mixtures for $\sigma_B/\sigma_A \in [0.392, \sqrt{2}-1]$, is a thermodynamic phase is still an open question. Watanabe *et al.* [22] observe a metastable state for the closest packing situation ($\sigma_B/\sigma_A=\sqrt{2}-1$ and $\varrho=2.0$). In this light the realization that a modulation of the dense fluid in 1D will induce an ordering transition in 2D is important as it opens up a pathway to grow defect-free square lattice structures. We perform Monte Carlo simulations in the *NVT* ensemble ($N=1848$). In order to facilitate equilibration we employ, besides the standard Metropolis Monte Carlo algorithm, an additional nonlocal cluster move by Lue and Woodcock [23]. Periodic boundary conditions are employed in all simulations. In contrast to the studies of monodisperse systems, in the case of a binary system one has to distinguish three cases: (a) only the smaller component interacts with the external potential, (b) both components interact with the external potential, or (c) only the larger component interacts with the external potential. This choice has an impact on the occurring underlying ordering mechanisms. We will concentrate on case (a).

Even in the field-free case, the addition of another length scale to a 2D system leads to interesting phenomena. As has been recently observed experimentally [24], introducing small particles into a system of large particles breaks the spanning network of large particles. The resulting competition between free volume and configurational entropy leads to clustering [25] and structural crossover [24,26]. Nevertheless, in a purely repulsive system the effect is too weak to drive phase separation. The equimolar binary mixture of interest to us ($\sigma_B/\sigma_A=0.414$) belongs to the regime of a spanning large-particle network. The dominating wavelength in the oscillations in the pair correlation function $g(r)$ is therefore set by the radius of the large particles. At low strengths of the external potential, we observe a modulated liquid phase. There is no spontaneous symmetry breaking, but the induced symmetry breaking leads to a translational order with periodicity λ in the component interacting with the substrate potential. This is visible in the stripe pattern of the pair correlation function $g_{BB}(\vec{r})$ [inset in Fig. 1(b)]. In contrast, the pair correlation function $g_{AA}(\vec{r})$ shows the characteristic concentric rings of an isotropic fluid [inset in Fig. 1(a)]. The system exhibits an induced structural crossover. The wavelength of the exponentially damped oscillations in the pair correlation functions changes from approximately $\sigma_A/2$ in the field-free case to $\lambda/2$ in the modulated liquid. Figure 1 shows the total correlation functions $h_{BB}(r)$ and $h_{AA}(r)$. It is remarkable that this crossover occurs also in $h_{AA}(r)$, as its short-range behavior is not affected by the substrate potential.

The LIF scenario differs from the monodisperse LIF scenario in the fact that there exists a regime of laser-induced demixing, i.e., the coexistence of a monodisperse lattice of the larger component with a small-component enriched fluid. This demixing does not occur in the field-free case. A heuristic argument by Buhot *et al.* [27] yields a diameter ratio of $\sigma_B/\sigma_A=1/100$ as the upper limit for possible phase separation in binary hard-disk mixtures. Nevertheless, exposing an equimolar binary mixture with diameter ratio $\sigma_B/\sigma_A=0.414$

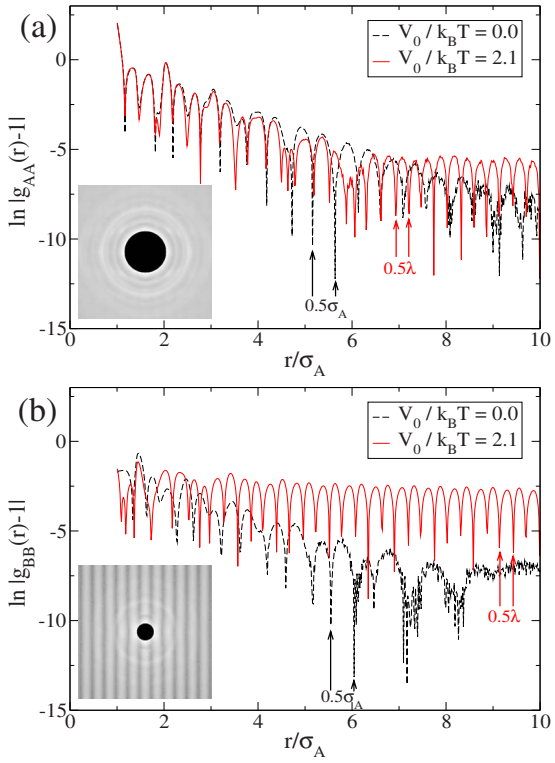

FIG. 1. (Color online) Comparison of the total pair correlation functions (a) $h_{AA}(\vec{r})$ and (b) $h_{BB}(\vec{r})$ for the dimensionless number density $\varrho=1.6$. Insets show the corresponding 2D pair correlation functions at $V_0/k_BT=2.1$.

to an external field interferes with the competition of free volume and configurational entropy in a controlled way by introducing the constraint of energy minimization. Phase separation is induced. The insets in Fig. 2 show overlays of the positions of the larger component during a simulation run (corrected for the motion of the center of mass). The left inset was taken in the demixing regime. The system mini-

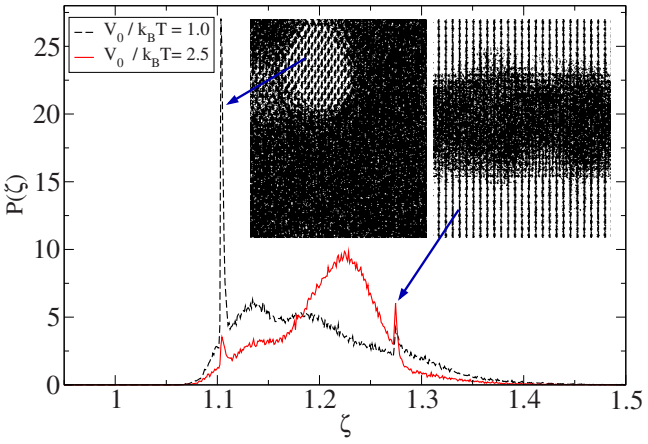

FIG. 2. (Color online) Probability distribution of the shape factor ζ in the demixing regime at $V_0/k_BT=1.0$ and in the coexistence region at $V_0/k_BT=2.5$ at a dimensionless number density of $\varrho=1.68$. The insets show overlays of the positions of the larger component in the two regimes.

mizes its energy by aligning the smaller component with the potential minima. This leads to chain formation of the small particles in the y direction. By this ordering mechanism the accessible space for the larger component diminishes. As the monodisperse triangular lattice yields the highest packing fraction of the large component, the formation of triangular lattice droplets is induced. Their orientation with respect to the external field is arbitrary. Demixing has been observed for $1.64 < \varrho \leq 1.725$ and $0.1 \leq V_0/k_BT \leq 1.5$. For higher external field amplitudes, this intricate competition between entropy maximization and energy minimization induces coexistence of a commensurate square lattice and a 50% binary fluid (see right inset Fig. 2). The coexisting lattice is nearly defect-free. The solid is a "locked floating solid" (LFS) [15], as it is pinned to the substrate with respect to movement perpendicular to the potential minima, but can float freely along them.

The entrance into the coexistence region is visible as a change in the probability distribution of the shape factor $\zeta = C^2/(4\pi S)$ (C is the circumference and S the surface area of the Voronoi cell), which was introduced in [28] for the detection and characterization of structural changes in hard-disk fluids. The perfect square lattice has square Voronoi cells, which yield $\zeta = 1.273$. Fluctuations of the particles around their equilibrium positions lead to a broad distribution of irregular hexagons and pentagons as Voronoi cells with a shape factor close to $\zeta = 1.273$. In the coexistence regime, this broad peak in the probability distribution of the shape factor shifts to lower values and the height of the peak at $\zeta = 1.273$ diminishes (see Fig. 2). In contrast, the demixing regime can be discerned by a peak at $\zeta = 1.103$ due to the regular hexagonal Voronoi cells of the triangular lattice droplet (see Fig. 2).

We also addressed the question of whether a LIM scenario in analogy to the monodisperse LIM can occur in the binary system. In the monodisperse LIM scenario, melting at high external field amplitudes is mediated via a decoupling of the particle fluctuations in adjacent potential minima. This melting scenario is geometrically blocked in the analyzed binary mixture due to the chosen combination of diameter ratio and wavelength of the external field. Instead, we found a decoupled melting of the sublattices or fissuring in which the sublattice of the smaller component melts *perpendicular* to the potential minima, while the sublattice of the larger component persists. Strong fluctuations along the potential minima of the larger components enable this mechanism. Characteristic for the clustering of the smaller component in the fissuring regime is the formation of dimer structures, which align with the minima of the external field (see inset in Fig. 3). In order to quantify this, we adapt the orientational order parameter used for the analysis of nematic liquid crystals to our needs. We define

$$S_B = \begin{cases} 0 & \text{for } Z_B = 0, \\ \dfrac{1}{N_B}\displaystyle\sum_{j=1}^{N_B} \dfrac{1}{Z_B}\sum_{k=1}^{Z_B} \dfrac{3(\cos\,\theta_{jk})^2 - 1}{2} & \text{for } Z_B \neq 0, \end{cases}$$

with N_B the number of small particles with $Z_B \neq 0$, Z_B the number of small particles within a cutoff radius $r_c = \lambda$ of a small particle j, and θ_{jk} the angle between the connecting line of the dimer and the orientation of the potential minima. Detection of small particles within the cutoff radius signifies the onset of fissuring. Figure 3 shows the probability distributions of S_B for various number densities. At high number densities, no dimers can form, which leads to a δ peak at $S_B = 0$. At the onset of fissuring, peaks at $S_B = -0.5$ and/or $S_B = 1.0$ occur. Dimers in the fissure that are aligned with the potential troughs yield $S_B = 1.0$, while those perpendicular (this corresponds to small particles occupying adjacent minima) yield $S_B = -0.5$. For lower number densities the fissures get broader and other orientations of the dimers occur. This leads to a broad peak in $P(S_B)$ that converges to a distribution centered around $S_B = 0.5$ in the modulated liquid ($\varrho = 1.51$ in Fig. 3).

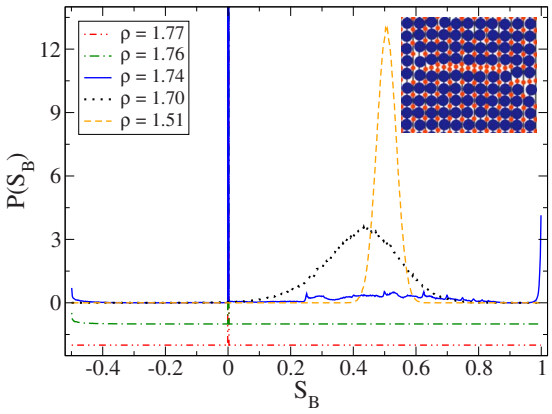

FIG. 3. (Color online) Probability distribution of the order parameter S_B at $V_0/k_BT = 20.0$. For clarity the plots for the dimensionless number densities $\varrho = 1.77$ and 1.76 are shifted. The inset shows a typical fissure at $\varrho = 1.74$.

We define an analogous order parameter S_A for the larger component. The cutoff radius is $r_c = 1.3\sigma_A$ and an additional constraint on the distance $|x_{ij}| < 1.3\lambda$ is used. The alignment of the large particles is only indirectly induced through the interaction with the small particles. At high number densities the probability distribution $P(S_A)$ is strongly peaked close to 1. Its broadening and shift to lower values signifies the entrance in the coexisting regime, as the alignment gets partially destroyed as soon as the sublattice of large particles melts. S_A is therefore used to calculate the upper boundary of the coexistence region. Its lower boundary can be determined by studying the probability distributions of the shape factor ζ, in which the peak due to the square lattice structure vanishes in the modulated liquid. From this analysis we obtain the phase diagram shown in Fig. 4. It was calculated by lowering the number density ϱ and taking a commensurate path through phase space [i.e., a change in ϱ is accompanied by a change in the wavelength of the external field $\lambda = 1/(\sqrt{2\varrho})$] and also by raising the potential strength V_0 at constant number density ϱ. Simulations carried out in an incommensurate setting, i.e., λ is kept constant independent of the number density ϱ, intersect the phase diagram consistently.

In conclusion, we have shown via Monte Carlo simulations that the miscibility of a binary hard-disk mixture can be

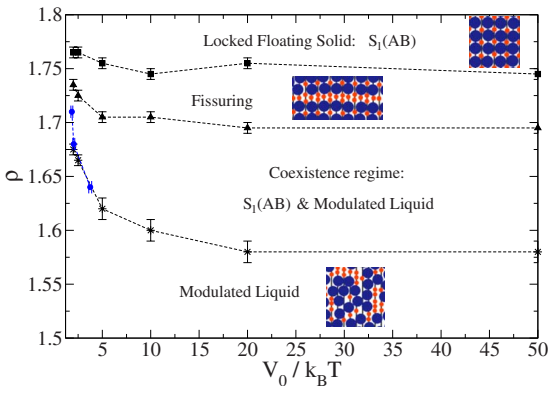

FIG. 4. (Color online) ϱ-V_0 plane of the phase diagram as obtained from the analysis of the order parameters S_B and S_A and the shape factor ζ. Lines are a guide to the eye.

tuned in a controlled way by exposing the mixture to a one-dimensional spatially periodic potential. Weak external fields induce a phase separation into an ordered monodisperse phase of the larger component and a disordered fluid phase, while increasing the strength of the substrate potential leads to a phase coexistence of a $S_1(AB)$ lattice and an equimolar binary mixture. This result opens up another experimental pathway to grow defect-free square lattice structures. At low number densities, the resulting modulated liquid exhibits interesting structural properties. It is modulated only in the component interacting with the external field, while the other component shows signatures of an isotropic liquid. At the same time, an induced structural crossover is observed in the asymptotic behavior of both total correlation functions. The decoupled behavior of the components is in particular palpable in the fissuring regime, where, in contrast to the monodisperse LIM scenario, a decoupled melting of the sublattice of the smaller component perpendicular to the minima of the substrate potential occurs. Our results visualize nicely the competition between entropy maximization and energy minimization in one of the important model systems for statistical mechanics, the hard-disk system.

This work was funded by the Deutsche Forschungsgesellschaft (SFB TR6/C4). The granting of computer time from HLRS, NIC, and SSP is gratefully acknowledged.

[1] J. Kosterlitz and D. Thouless, J. Phys C **6**, 1181 (1973).
[2] A. P. Young, Phys. Rev. B **19**, 1855 (1979).
[3] B. I. Halperin and D. R. Nelson, Phys. Rev. Lett. **41**, 121 (1978).
[4] A. Chowdhury, B. J. Ackerson, and N. A. Clark, Phys. Rev. Lett. **55**, 833 (1985).
[5] Q.-H. Wei, C. Bechinger, D. Rudhardt, and P. Leiderer, Phys. Rev. Lett. **81**, 2606 (1998).
[6] K. Zahn, A. Wille, G. Maret, S. Sengupta, and P. Nielaba, Phys. Rev. Lett. **90**, 155506 (2003).
[7] K. Binder, S. Sengupta, and P. Nielaba, J. Phys.: Condens. Matter **14**, 2323 (2002).
[8] C. H. Mak, Phys. Rev. E **73**, 065104(R) (2006).
[9] J. Chakrabarti, H. R. Krishnamurthy, A. K. Sood, and S. Sengupta, Phys. Rev. Lett. **75**, 2232 (1995).
[10] W. Strepp, S. Sengupta, and P. Nielaba, Phys. Rev. E **66**, 056109 (2002).
[11] D. Chaudhuri and S. Sengupta, Phys. Rev. E **73**, 011507 (2006).
[12] P. Chaudhuri, C. Das, C. Dasgupta, H. R. Kirshnamurthy, and A. K. Sood, Phys. Rev. E **72**, 061404 (2005).
[13] J. Chakrabarti, H. R. Krishnamurthy, and A. K. Sood, Phys. Rev. Lett. **73**, 2923 (1994).
[14] E. Frey, D. R. Nelson, and L. Radzihovsky, Phys. Rev. Lett. **83**, 2977 (1999).
[15] L. Radzihovsky, E. Frey, and D. R. Nelson, Phys. Rev. E **63**, 031503 (2001).
[16] W. Strepp, S. Sengupta, and P. Nielaba, Phys. Rev. E **63**, 046106 (2001).
[17] A. van Blaaderen, R. Ruel, and P. Wiltzius, Nature (London) **385**, 321 (1997).
[18] K. H. Lin, J. C. Crocker, V. Prasad, A. Schofield, D. A. Weitz, T. C. Lubensky, and A. G. Yodh, Phys. Rev. Lett. **85**, 1770 (2000).
[19] M. Allard, E. H. Sargent, P. Lewis, and E. Kumacheva, Adv. Mater. (Weinheim, Ger.) **16**, 1360 (2004).
[20] H. M. Harreis, M. Schmidt, and H. Löwen, Phys. Rev. E **65**, 041602 (2002).
[21] C. Likos and C. Henley, Philos. Mag. B **68**, 85 (1993).
[22] H. Watanabe, S. Yukawa, and N. Ito, Phys. Rev. E **71**, 016702 (2005).
[23] L. Lue and L. Woodcock, Mol. Phys. **96**, 1435 (1999).
[24] J. Baumgartl, R. P. A. Dullens, M. Dijkstra, R. Roth, and C. Bechinger, Phys. Rev. Lett. **98**, 198303 (2007).
[25] N. Hoffmann, F. Ebert, C. N. Likos, H. Löwen, and G. Maret, Phys. Rev. Lett. **97**, 078301 (2006).
[26] C. Grodon, M. Dijkstra, R. Evans, and R. Roth, Mol. Phys. **103**, 3009 (2005).
[27] A. Buhot and W. Krauth, Phys. Rev. E **59**, 2939 (1999).
[28] F. Moucka and I. Nezbeda, Phys. Rev. Lett. **94**, 040601 (2005).