Report

Determination of the Phase Diagram of Binary Mixtures in Two Dimensions

In recent years an alternative way to find the minimum energy configurations of one-component systems was devised: The optimisation of the lattice parameters with respect to the energy of the crystal structure, applying Genetic Algorithms [1]. Genetic Algorithms (GAs) were chosen for this task, because their combination of deterministic and non deterministic features makes them appropriate for problems with a complex and high-dimensional search-space. It is thus possible to perform a parameter-free and unbiased search in the *entire* search-space of possible crystal lattices, without the danger to preclude relevant lattices in a preselection process.
The search for equilibrium structures using optimisation techniques has already been applied to various one-component systems with much success [2, 3, 4].

The knowledge that soft binary mixtures can crystallise in very intricate patterns led to the idea of extending the GA-program to systems with two components. During my stay at the Heinrich-Heine-Universität in Düsseldorf, we completed and checked the computer code, so that we were able to start investigations of a two dimensional binary mixture of polystyrene particles. We are working publication to present our results on the structural behaviour of the chosen model system. Preliminary results are given in section 2.
Due to the variety of structures found, we decided to investigate the phonon spectra of the crystal lattices. There seems to be the possibility of finding phononic crystals in this system, the properties of which might be tuneable by the potential parameters. The first steps to include an algorithm that calculates the phonon spectra of the structures found were made at Düsseldorf as well.
Once the current investigations with optimisation techniques are complete, we will start Monte-Carlo-simulations for the chosen model system, using the simulation-package I was introduced in at Düsseldorf.

The collaboration with Federica LoVerso and Christos N. Likos on this topic will be continued by Federica LoVerso applying for a Marie-Curie-Grant in August 2007 to join our group in Vienna.

1 The Model System

Polystyrene particles of different size, trapped at an oil-water-interface are a good model for soft binary mixtures in two dimensions. The particles interact via an effective

dipole-dipole-potential, which depends on the particle radii, R_i and R_j:

$$\Phi_{ij}(r) = \frac{P_i P_j}{16\pi\epsilon R_i R_j}\frac{1}{r}\ \ln\left[\frac{r^2-(R_i-R_j)^2}{r^2-(R_i+R_j)^2}\right] \tag{1}$$

The overall dipole moment P_i of a particle has its origin in the vector sum of surface charge dipoles, formed by dissociated, hydrophilic headgroups on the particles surface (see figure 1) [5, 6].

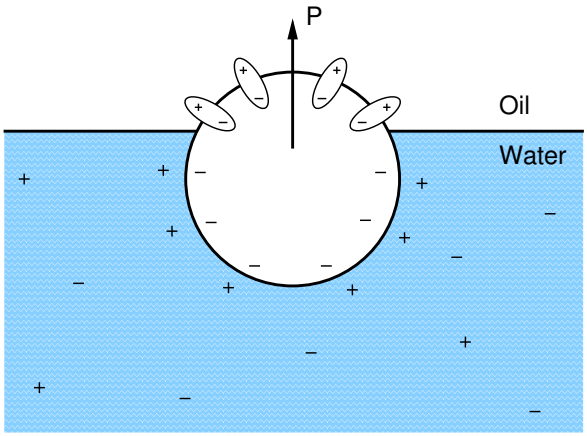

Figure 1: Schematic diagram of a polystyrene particle at the oil-water-interface.

The potential (1) can be simplified in the following way: First, we introduce a hard-core to the system. In addition we set the energy scale by fixing $\epsilon = 1$ and the length scale, by setting the diameter of the larger particle species, σ_A, to 1. Additionally, we introduce the ratio of the particle radii, $x = \frac{R_B}{R_A}$ and an exponent n to vary the interaction strength.
With these changes, we get

$$\Phi_{AA}(r) = \begin{cases} \infty & r \le \sigma_A \\ \frac{1}{4\pi r}\ln\left(\frac{r^2}{r^2-1}\right) & r > \sigma_A \end{cases} \tag{2}$$

for interactions between particles of species A,

$$\Phi_{BB}(r) = \begin{cases} \infty & r \le \sigma_B \\ \frac{x^n}{4\pi r}\ln\left(\frac{r^2}{r^2-x^2}\right) & r > \sigma_B \end{cases} \tag{3}$$

for interactions between particles of species B and

$$\Phi_{AB}(r) = \begin{cases} \infty & r \le (\sigma_A+\sigma_B)/2 \\ \frac{x^{n/2}}{4\pi r}\ln\left(\frac{r^2-\frac{1}{4}(1-x)^2}{r^2-\frac{1}{4}(1+x)^2}\right) & r > (\sigma_A+\sigma_B)/2 \end{cases} \tag{4}$$

for inter-species interactions. The form of the potential for different values of x and n is shown in figures 2 and 3.

Although this model system has been investigated by Monte-Carlo-simulations [6], it seems that the identification of the minimum energy configurations is still incomplete. Experimental data on the system only exists for the one component case, where all particles have the same size [7].

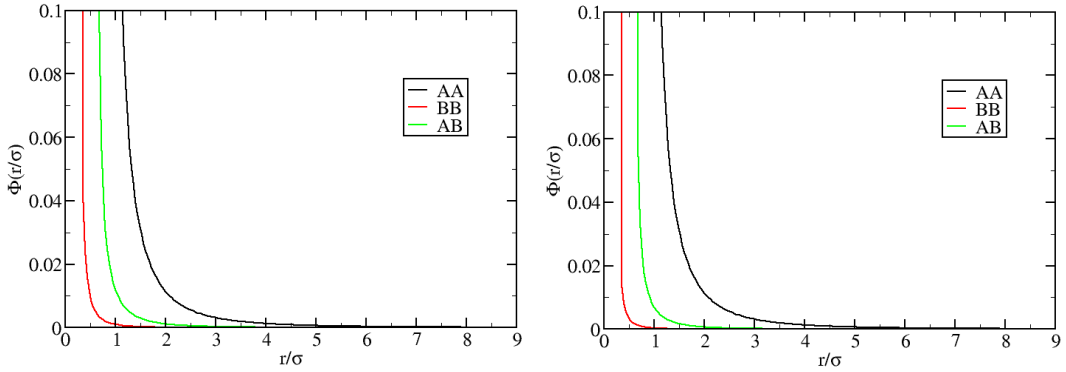

Figure 2: Simplified effective dipole-dipole-potential for $x = 0.3296$ $n = 2$ (left) and $x = 0.3296$ $n = 3$ (right).

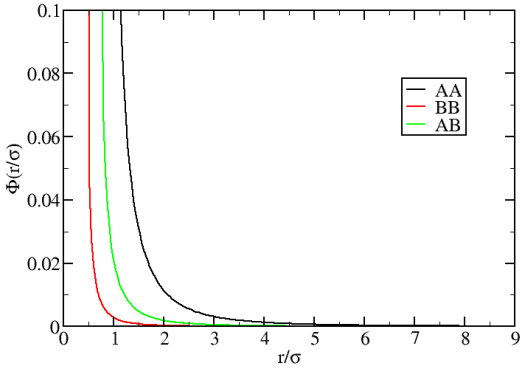

Figure 3: Simplified effective dipole-dipole-potential for $x = 0.5$ $n = 3$.

2 Results

The simplified potentials (2, 3, 4) have two parameters to vary its strength: x, which is the ratio of the particle diameters and the exponent n. During my stay at the Heinrich-

Heine-Universität in Düsseldorf, we collected data on the structural behaviour for three different relative interaction strengths and changing composition at zero temperature. We started with the parameter values used in previous MC-simulations by Stirner and Sun, namely ($x = 0.3296$, $n = 3$) and ($x = 0.3296$, $n = 2$) [6]. Additionally we investigated the influence of increasing the ratio of the particle diameters ($x = 0.5$, $n = 3$). For all invetigations, the particle density $\eta\sigma^2$ was in the range $0.1 - 0.8$.

x=0.3296, n=2 and **x=0.3296, n=3**
We investigated all compositions with up to eight particles per unit-cell (i.e. 1:1, 1:2,..., 1:7, 2:1,.., 2:6,...,7:1) and, additionally, 2:7. For certain compositions we encountered exotic structures with low symmetry (see figure 2 for examples).
Structural change was not observed as the density increases for any of the compositions.

x=0.5, n=3
Again we investigated all possible compositions with up to eight particles per unit-cell. With the small particles increased in size, we encounter structural changes by varying the particle density (see figure 2, bottom). Since the effective distance between the hard cores of the particles is smaller in this case than for $x = 0.3296$, we are now in a range where the potential deviates from the normal dipole potential.

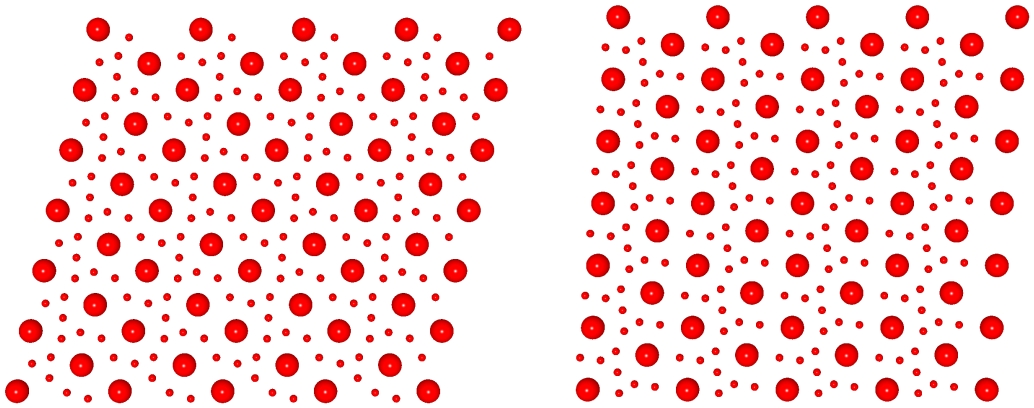

Figure 4: Exotic structures found for a composition of $2:7$, $x = 0.3296$, $n = 2$ (left) and $n = 3$ (right)

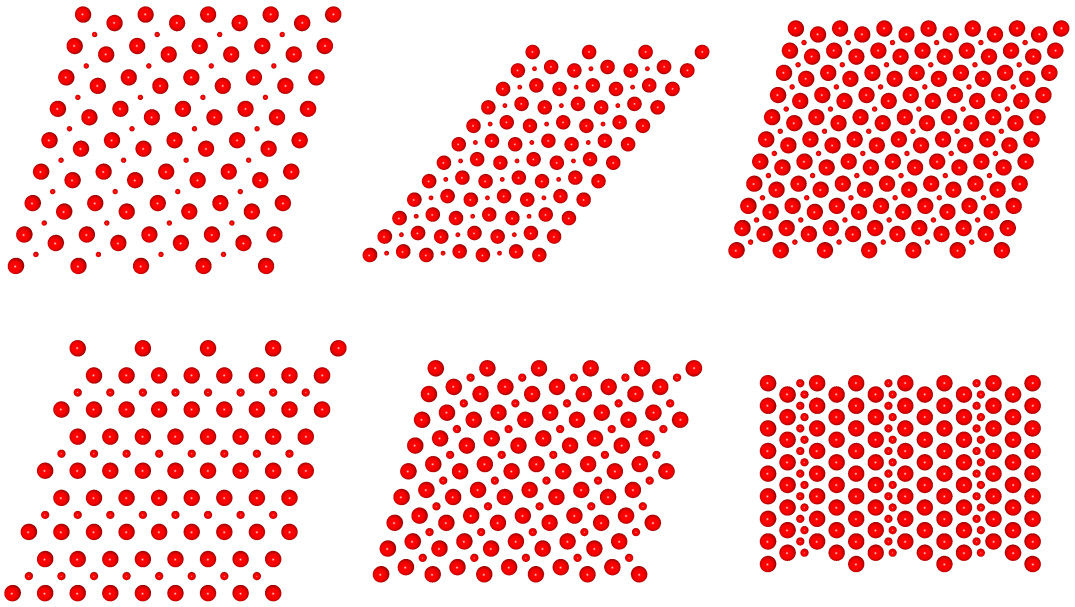

Figure 5: Sequence of structures found for increasing density ($\eta\sigma^2 = 0.4$, 0.6 and 0.8 from left to right), composition $2:1$, $n = 3$.
Top row: $x = 0.3296$, no structural change visible in chosen density range.
Bottom row: x=0.5, structural change between $\eta\sigma^2 = 0.6$ and 0.8.

References

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