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Two-dimensional crystals of star polymers: a tale of tails

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The formation of non-hexagonal crystalline structures by the organisation of colloidal nanoparticles often involves the use of complex particles with anisotropic shape or interactions or the imposition of non-uniform external fields. Here we explore how unusual symmetries can be created using experimentally realistic particles that interact through isotropic and purely repulsive potentials. In particular, we use simulations to explore the phase behavior of two-dimensional systems of star polymers. We uncover how the tail of the pair potential has a large role in dictating the phase behavior. Star polymers interacting in the far field with a Gaussian potential only form hexagonal phases, while an exponential tail gives rise to stable primitive oblique and honeycomb lattices. We identify the ratio in strength between long and short range interactions and the nature of the transition between these regimes as crucial parameters to predict when non-hexagonal crystals of star polymers can be stable. This leads to experimental design rules for creating star polymers which should exhibit unusual lattice formation.

1 Introduction

The self-organisation of colloids and nanoparticles into ordered two-dimensional lattices offers the potential for the creation of new electronic and photonic metamaterials 1–5. The symmetry of the two-dimensional lattice, which governs the transport of electrons or photons through the structure, is dictated by the interactions between the particulate building blocks. For particles interaction through relatively 'simple' isotropic repulsive interactions, such as hard sphere-like or exponential potentials, a hexagonal crystal is found to be the only stable solid phase 6–9. Obtaining non-hexagonal crystal symmetries requires tailoring of the pair interactions. For example, breaking the isotropic symmetry of the interaction forces can result in stable non-hexagonal crystal monolayers; this can be achieved in a variety of ways, for example by introducing shape anisotropy 10, chemically-reactive facets 3, a patchy particle surface 11, directional attractions mediated by supramolecular motifs 12, the use of bidisperse particle populations 13 or the imposition of non-uniform fields 14.

In the past decade, extensive computer simulations have revealed that a plethora of non-hexagonal crystals and quasicrystals can also be formed by particles that interact through isotropic potentials. For example, square lattices can be stable in systems with a square softened single well 15, whereas a double well leads to the formation of decagonal and dodecagonal two-dimensional quasicrystals 16. More complex and designed potentials featuring multiple attractive minima and repulsive regions, can give rise to the sought-after honeycomb lattice 17, which exhibits unique electronic and photonic properties 3,18. Even with purely repulsive and isotropic potentials, non-hexagonal crystals have been predicted to occur. For example, introducing an inflection point in a core-softened repulsive potential can lead to string-like and Kagome phases 19.

It appears that the presence of two distinct length scales and interactions beyond a first nearest-neighbor shell are crucial to stabilise many of these uncommon crystals and quasicrystals 20,21. A well-studied example is the repulsive hard-core/square-shoulder potential. This potential is used as a simplified description of the interactions between particles with a hard and impenetrable core decorated with a soft corona. By varying the size and softness ratio of hard core and soft corona a variety of two-dimensional lattices can theoretically be obtained 20,22,23. Also for elastic spheres that interact by means of bounded Hertzian potentials a rich phase behavior has been predicted, including square, honeycomb, Kagome and snub square tilings 24, despite the fact that these potentials only have one length scale.

Despite the overwhelming choice of potentials to create non-hexagonal two-dimensional crystals in computer simulations, most of these potentials are impossible to create experimentally, given only a few exceptions 23,24. To make the translation from...
the in-silico results to systems that could be achieved in experiments, it is necessary to explore what realistic potentials can yield the same rich phase behavior in order to establish experimental design rules. Moreover, if the stability of the crystalline phase depends very sensitively on the exact shape of the potential, its success in experiments will be largely hampered by the inherent dispersity in the particle size, shape, conformation and softness during particle synthesis. Finding experimentally-realistic, isotropic and purely-repulsive potentials capable of stabilising non-hexagonal two-dimensional lattices in a robust manner thus remains an open challenge.

In this paper, we attempt to further bridge the gap between simulations and experiments in the quest for self-organised particle-based metamaterials. We explore the phase behavior of two-dimensional systems of star polymers strongly adsorbed to a planar interface, parameterised by previously developed potentials for surface-adsorbed star polymers. In three dimensions, star polymers and star-like micelles are known to exhibit a rich phase behavior, exhibiting body-centered orthogonal and diamond crystalline structures. Experiments have even revealed a stable quasicrystalline phase. Here we explore if these same star polymer particles can be used for the creation of non-hexagonal crystalline lattices in two dimensions. In particular, we explore the effect of the weak and long-ranged tail of the interactions, which we show to have a drastic effect on the phase behavior and the stability of non-hexagonal phases.

Both for the two- and three-dimensional case, the short-ranged interactions between star polymer cores can be analytically derived, whereas the exact shape of interactions at longer distances, beyond the diameter of the star, remains unknown. In some cases, the tail of the potential is presumed to decay exponentially, in the form of a Yukawa potential, with a decay length set by the blob size at the periphery of the star-shaped polymer, depending on the number of arms and the effective star diameter. In other cases, the tail of the potential is presumed to have a Gaussian shape. This is based on the observation that for 3D linear chains the interaction potential is Gaussian. This Gaussian tail approximation for star polymers is expected to work best for stars with low arm numbers, since this approaches the case of linear polymers which can be considered as star polymer with two arms. In the limit of very large arm numbers, the Gaussian tail assumption loses its validity as shown by unreasonably large interactions energies at distances far beyond the star diameter. However, there exists a region of arm numbers for three-dimensional stars where both Yukawa and Gaussian long-ranged forces give good agreement with the forces obtained from computer simulations of stars. The same overlap might occur in the two-dimensional case, where for stars up to at least twelve arms good agreement was found between the forces predicted by a Gaussian tail star potential and computer simulations.

Here we show how the shape of the tail has a drastic effect on the phase behavior; while only hexagonal crystals are stable for Gaussian tails, a much richer phase behavior with multiple crystalline states is found for the exponential tail. Moreover, we also explore what happens if we assume there is no long-ranged tail in the star-star interactions. Our results shed light on the importance of the tail in the interaction potential for the realisation of non-hexagonal two-dimensional solids and provides clues how these structures can be realised experimentally.

2 Methods

Since the phase behavior of three-dimensional star polymer solutions is well studied, we choose a form of the two-dimensional potential for star polymers that matches the three-dimensional formulation more closely. As compared to the original Gaussian-tail potential for adsorbed star polymers, we choose the star diameter $\sigma$ as the separation distance where the transition between the short-range and long-range sections of the interactions occur, in accord with the formulation for three-dimensional stars. In addition, we have shifted the potential and adjusted the prefactor of the tail interaction to ensure its derivative is continuous at the transition point $r = \sigma$:

$$
V(r) = \begin{cases} 
2 + 9 f^2 / 24 \left( -\ln(r/\sigma) + \frac{9}{2} \right), & r \leq \sigma \\
\frac{1}{2} \exp \left[ -\frac{1}{2} (r/\sigma - 1)^2 \right], & r > \sigma 
\end{cases}$$

(1)

Here, $r$ is the centre-to-centre distance between the stars and $f$ its number of arms.

To construct a two-dimensional star potential with an exponential tail, we use the outer blob diameter as the characteristic decay length in a Yukawa potential. The potential, again shifted and adjusted to ensure continuity in force at $r = \sigma$, reads:

$$
V(r) = \begin{cases} 
2 + 9 f^2 / 24 \left( -\ln(r/\sigma) + \frac{8}{\pi} \right), & r \leq \sigma \\
\frac{8}{\pi} \exp \left[ -\frac{4}{\pi} (r/\sigma - 1)^2 \right], & r > \sigma
\end{cases}$$

(2)

Finally, we also explore a potential in which the star polymers do not interact at separation distances beyond their diameter, thus assuming the absence of chains that protrude beyond $\sigma$. In this case, the force is discontinuous at the star boundary:

$$
V(r) = \begin{cases} 
2 + 9 f^2 / 24 \left( -\ln(r/\sigma) \right), & r \leq \sigma \\
0, & r > \sigma
\end{cases}$$

(3)

We perform Monte Carlo (MC) simulations in the canonical ensemble by placing $N = 400$ stars in a square periodic box of length $L$. The maximum distance up to which star-star interactions is calculated thus equals $\sqrt{0.5L}$. The area fraction $\eta$ is defined as $\eta = N \pi \sigma^2 / (4L^2)$. We initialise the simulation with a low density fluid configuration, which is compressed to the desired area fraction after which the structure is equilibrated.

To make sure that the structure formation is not dictated by the box size or box shape, we have compared the results of simulations with $N = 400$ in a square box to MC simulations with a larger box size or with a rectangular box shape. Neither affected the structure formation. Examples of pair correlation function comparisons between different box sizes and box shapes are included in the supplementary information.

To construct the ground state diagram, we slowly quench the simulations until a zero-temperature configuration was found. For low arm numbers, $f = 6$ and $f = 8$, on occasion we observed quenched structures that differed strongly from the surrounding
ground states. In these cases, we computed the lattice sum of the interaction energy of the observed and surrounding symmetries to find the lattice of lowest energy, from which the complete ground-state diagram was constructed.

3 Results & Discussion

The exact functional form of the tail of the interactions between adsorbed star polymers, confined to a two-dimensional interface, remains unclear; whereas some studies predict a Gaussian shape of the interactions between dangling chains that extend beyond the average star diameter, others have suggested an exponential form is more appropriate. Interestingly, we find that the exact choice has a very strong effect on the observed phase behavior. This could provide clues to the appropriate experimental design of star polymers for the two-dimensional templating of non-hexagonal symmetries in creating novel electronic or photonic materials.

For star polymers interacting beyond their diameter with a Gaussian potential, the phase diagram only exhibits a stable solid phase with a hexagonal symmetry for \( f > 12 \) (Fig.1). This liquid-solid transition also leads to the emergence of distinct Bragg peaks in the computed two-dimensional structure factor as shown in Figure 2a-b. Interestingly, compressing a stable hexagonal phase of these stars leads to a re-entrance of the fluid phase. The same fluid re-entrance is observed in simulations of particles that interact by means of a Gaussian potential only. By contrast, star polymers with an exponential Yukawa tail in their interaction potential, show, in addition to the hexagonal phase and the re-entrant fluid, two additional non-hexagonal crystal states. At intermediate densities we find a primitive oblique phase, which has a parallelogram-shaped unit cell (Fig.2c), and at high packing densities we find the sought-after honeycomb symmetry (Fig.1 and Fig.2d). Compressing the primitive oblique structure first gives rise to a strained honeycomb (Fig.2e), whose strain axis is set by that of the parent primitive oblique lattice, before the symmetric honeycomb lattice is formed at higher densities. In all cases, a minimum arm number of \( \approx 12 \) is required to find ordered solid phases. Lower arm numbers result in interactions that are too soft to give rise to an distinct liquid-solid transition; this is in direct agreement with theoretical predictions and experimental data for three-dimensional phases of star polymers.

Clearly, despite the softness of the tail interactions, the exact shape of this tail has a drastic effect on the phase behavior of the two-dimensional system. The transition from fluid to hexagonal solid followed by re-entrant melting, which is observed for stars with a Gaussian tail, is typical for purely Gaussian particles. The initial phase behavior of the stars with an exponential tail also corresponds to the behavior known for two-dimensional phases of Yukawa particles. Thus, as expected, at low densities, only the tail of the pair potential is important. The logarithmic interactions of the star polymer core begin to contribute when the stars begin to overlap. Assuming a hexagonal symmetry, star overlap begins to contribute significantly when the packing fraction exceeds the close packing limit for hard spheres \( \eta = \pi/(2\sqrt{3}) \approx 0.9. \) For both potentials, the stars behave as a fluid from this point, even when they crystallized at lower packing fractions. This re-entrant melting at intermediate densities is a property of certain bounded repulsive potentials whose Fourier transform is positive definite. The logarithmic interaction of the core belongs to this class of potentials, and the re-entrant fluid phase is found both in two (Fig. 1) and in three dimensions. This suggests that at intermediate densities the phase behavior of these adsorbed star polymers is determined in part by the core potential. Since the Gaussian potential also belongs to this class of bounded repulsive potentials, the re-entrant melting in this case occurs already at lower packing fractions.

Interestingly, the largest difference between the Yukawa and Gaussian-tailed stars occurs at the highest packing fractions, where one might have assumed that only core interactions contribute significantly to the phase behavior. Clearly, even at densities well above the overlap concentration, the tail interactions play a significant role in governing the behavior of the two-dimensional system.

To further elucidate these effects, we also determined the ground state diagrams, in which fluid phases and hence the re-entrance are suppressed. Here, we approach the ground state by quenching an equilibrated particle configuration by gradually increasing the interaction strength. Since this may lead to kinetically trapped states, we also computed the total potential energy of the structures we observed using a lattice sum of the interaction energies. However, we cannot rule out that there are other, more exotic structures that we have not observed with a lower overall energy. It is not necessary to quench all the configurations of the finite-temperature phase diagram. At the lowest packing fractions only the Gaussian or Yukawa tail contributes to the ground state symmetry, which have been established to lead to hexagonal solids. Moreover, for the stars with a Gaussian tail, the number of arms \( f \) only appears in the prefactor of the potential and thus has no influence on the shape of the potential; as a result, changing the arm number has no effect on the ground state. Thus, for the star potential with a Gaussian tail, the entire ground state diagram shows only a hexagonal symmetry. By contrast, for the Yukawa tail, we find stable ground states with the same primitive oblique and honeycomb structures also observed in the phase diagrams (Fig. 3).

To explain the difference between the behaviour of stars with a Yukawa versus Gaussian tail, we must understand what occurs at the transition from a hexagonal symmetry to the other crystalline structures. At this transition, a few neighbors move in to a closer star-star distance, while others move further away to a separation distance inbetween the original first and second neighbours distances, as can be seen in the distance scaled pair correlation functions (Fig. 4a). For a transition away from the high-symmetry hexagonal phase to be favorable, the combination of moving some neighbors closer while increasing the separation with others should result in a net decrease of the potential energy of interaction. In other words, this is most likely to occur when the increase in energy of the new nearest-neighbour is weak while the decrease in energy for moving some neighbors slightly further away significantly reduces their interactions with a central test particle.

To satisfy the first constraint, softness in the potential is a cru-
cial requirement. If the potential increases too steeply upon decreasing \( r \), the energy cost of bringing only a few closer is already larger than the energy of the sum of the energy of the original first row of neighbours in the hexagonal crystal. For star polymers, the short range interaction is logarithmic in form and thus provides the required softness. The second requirement explains why the shape of the tail interactions plays such a large role in governing the phase behavior. Transforming the hexagonal phase to a different symmetry creates a new second row of neighbors at distances \( r > \sigma \); these thus interact through the long range regime of the potential. By normalizing these two types of potentials to the energy at the transition \( r = \sigma \) (Fig. 4b), we observe how the long range interaction is weak for a Yukawa tailed interaction, as compared to the core-core repulsion, especially for larger arm numbers. On the other hand, for stars with a Gaussian tail, the long ranged interaction is relatively strong. Thus, for the Yukawa stars, the energy gain of moving some nearest-neighbors to a second shell significantly reduces the energy; by contrast, for the Gaussian stars this energetic gain is very limited. Since it is this energy gain that balances against the energy cost of the closer contact between the nearest neighbors to determine if lower energy states exist beyond the hexagonal symmetry, this explains why only the exponential tail gives rise to lower symmetry lattices.

Apart from explaining the difference between Gaussian and Yukawa stars, the normalized potentials also disclose the origin of the different behavior for different arm numbers for Yukawa stars. For larger arm numbers, the interaction potential has a steeper increase around \( r = \sigma \). As a result, around the overlapping area fraction, the stars will rearrange themselves to minimize the number of stars within the star diameter distance. This is reflected in the pair correlation functions where for larger arm numbers the area under the curve up to \( r = \sigma \) decreases (see the ESI). Increasing the arm number even further in the end results in the formation of a hexagonal-like pattern with a few stars dislocated to allow the hexagonal nearest neighbors to be at a star diameter distance. However, this phase will not be observed experimentally because the interaction energy for these arm numbers is so strong that (part of) the star will desorb from the interface.

The normalized potentials also shed light on the reason that the honeycomb lattice becomes stable at lower densities for stars with fewer arms, as can be seen in the ground state diagram in Fig. 3. In the strand-like primitive oblique phase that the stars form, the neighboring stars within the same strand are closer than the stars from the neighboring strands (see Fig. 2c). In this primitive oblique phase a star thus has 2 nearest-neighbors. The transition to the honeycomb phase that a star thus has 3 nearest-neighbors. The transition to the honeycomb phase increases the number of nearest neighbors to 3 (Fig. 2d). Simultaneously, the second row of neighbors move further away, as can be clearly seen when comparing the scaled pair correlation functions (Fig. 4). This shows how the mechanisms for the primitive oblique to honeycomb transition lies in the fact that further compression of the primitive phase leads to such a high energy cost for second nearest neighbors, that energy can be gained by adding an additional nearest neighbor allowing the second row to move further away. It is exactly the same mechanism that causes a transition from the body-centered orthogonal to a diamond symmetry in three dimensional star polymer phases. The normalized potentials show how the relative strength of the tail interactions decreases with \( f \), such that the transition occurs at lower packing fractions as \( f \) is decreased.

These arguments give us a qualitative explanation for the phase changes we observe in our simulations. To support this line of thought, we can make an analytical lattice sum of the potential energy to compare the ground state energies of hexagonal and honeycomb configurations. We choose the symmetrical (6)
honeycomb and (6) hexagonal symmetries for this comparison as their lattice coordinates are well-defined and subject only to isotropic compression as the density is increased. By contrast, the ratio of side lengths of the less symmetric primitive oblique varies with density such that an analytical comparison is more cumbersome. In our analytical calculation of the lattice energy we sum interactions over the 6 nearest-neighbors for the hexagonal lattice and 3 first nearest- and 6 second-nearest neighbors for the honeycomb, along the lines of our qualitative arguments described above. Interaction energies beyond these neighbors are sufficiently small at relevant densities that they contribute marginally to the ground state energy and are thus ignored for the purposes of this comparison. At a given packing fraction, the first nearest-neighbor distances for the hexagonal and honeycomb lattice follow from the lattice geometry (Fig. 5) as

$$r_{\text{hex}} = \sigma \sqrt{\frac{\phi_{\text{hex}}}{\eta}}$$

and

$$r_{\text{hc}} = \sigma \sqrt{\frac{\phi_{\text{hc}}}{\eta}} = \sqrt{\frac{2}{3}} r_{\text{hex}},$$

with \(\phi_{\text{hex}}\) and \(\phi_{\text{hc}}\) the maximum hard-sphere packing fractions of the two lattices, respectively, and the second nearest-neighbour distance for the honeycomb pattern is

$$r_{\text{hc2}} = \sqrt{3} r_{\text{hc}}.$$

A phase change does not only alter the interaction free energy between the stars, it changes their translational entropy as well. Translational entropy changes are essential in various phase transitions\textsuperscript{40}, with the freezing of hard spheres as the most well known example. Here, a phase transition from disordered to ordered structures occurs because the local translational entropy gain that can be obtained by crystallizing becomes larger than global translational entropy loss. The local translational entropy is proportional to the number of available positions that a particle has on its lattice site. For the hexagonal and honeycomb lattice, this number scales in a first approximation with the ‘hard sphere area’ indicated with the striped lines in Fig. 5. This means that the hexagonal phase and honeycomb phase have a different local translational entropy and that this difference can be approximated with

$$S_{\text{trans}} - S_{\text{trans,hex}} \approx k_B \ln \left( \frac{2}{3} \right).$$

The total free energy difference is thus given by

$$\frac{F_{\text{hc}} - F_{\text{hex}}}{k_B T} \approx - \ln \left( \frac{2}{3} \right) + \frac{V_{\text{hc},\text{tot}}}{k_B T} - \frac{V_{\text{hex},\text{tot}}}{k_B T}.$$

When \(F_{\text{hc}} - F_{\text{hex}} < 0\), the honeycomb phase is favored over hexagonal phase (note that this requirement is equivalent to \(F_{\text{hc}} / F_{\text{hex}} < 1\), which is plotted in Fig. 5 (without taking the local translational entropy into account)). For large area fractions \(V_{\text{hc}}/k_B T - V_{\text{hex}}/k_B T \gg \ln(2/3)\). We can thus neglect the effect of the local translational entropy change and directly compare the lattice sums of the potential energies.

The analytical calculation echoes the findings in our simulation.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2}
\caption{Fig. 2 Representative examples of two-dimensional phases formed in star polymer systems with a Yukawa tail in their interactions (top) and the corresponding two dimensional structure factors \(S(q_x, q_y)\) (bottom). The top images are zoomed in to a quarter of the simulation box. Grey spheres indicate the diameter \(\sigma\) of the star polymers to indicate the degree of star-star interpenetration, while blue dots are drawn for the sake of clarity. Unit cell structures are indicated with red lines. For the calculation of the structure factors with sufficient resolution, we simulated structures with \(N = 3600\) for \(2 \times 10^9\) MC steps.}
\end{figure}
Fig. 4 (a) Two-dimensional pair correlation functions for a hexagonal (black), primitive oblique (blue) and honeycomb lattice (red) obtained by quenching the configurations of two-dimensional Yukawa stars with $f = 14$ at $\eta = 0.9$, $\eta = 1.2$ and $\eta = 1.4$, respectively. For a direct comparison, the distance axis is scaled to the relative degree of compression, taking $\eta = 1.2$ as the reference state: $r_{\text{scaled}} = rL(\eta = 1.2)/L(\eta)$. (b) Interaction potentials normalized to the interaction energy at the transition point $r = \sigma$, for a Gaussian-tailed potential (red) and a Yukawa-tailed potential with $f = 8$ (black), $f = 12$ (grey), $f = 16$ (blue) and $f = 20$ (light blue).

Fig. 5 Analytical comparison of the ground-state energy of hexagonal and honeycomb lattices. Top: example structures of hexagonal pattern and honeycomb pattern, both with the same star packing fraction $\eta$. Top left: stars (grey spheres) are positioned in a hexagonal pattern of hard spheres (indicated with striped lines). The diameter of the hard spheres and thus the first neighbour distance is $r_{\text{hex}}$. Top right: stars are positioned in honeycomb pattern at a distance $r_{\text{hc}}$ from each other. Bottom: comparison of the hexagonal and honeycomb energy as function of packing fraction.

that the Gaussian-tailed stars can only form hexagonal solids, as the ratio of lattice energies of the honeycomb $V_{\text{hc, tot}}$ to that for the hexagonal lattice at equal density $V_{\text{hex, tot}}$ never goes below unity irrespective of density of arm number $f$ (Fig. 5). Indeed, for the exponential tail, the honeycomb lattice gains a lower energy than the hexagonal phase, giving rise to a hexagonal-to-honeycomb transformation. In reality, this transition occurs through the primitive oblique phase as an intermediary, which continuously transforms into a stretched honeycomb until the symmetrical honeycomb becomes stable. We note however that the phase boundary predicted analytically is not exactly matched with what we observe in the simulations. According to the analytical description, for $f = 8$ the hexagonal patterns are always favored as the energy ratio remains $> 1$, while the simulated ground state diagram shows a stable honeycomb phase for $f = 8$ and even for $f = 6$. Apparently, taking into account the interactions up to only the second-nearest neighbor shell cannot capture the behavior exactly. In experimental realisations of this system however, one can wonder how relevant such long ranged interactions are, since this would require the stars to interpenetrate to such an extent that chains extend to well beyond the first row. Obviously, also non-additive effects that are ignored in these simulations and calculations may come into play at these densities in real star polymer phases.

An experimental effect that is not captured by the simulations or the analytical description is the response of the material to shear. This response is important because phases with lower shear moduli can be more easily distorted and therefore can be more difficult to obtain experimentally. The simulations and analytical comparison focus on the equilibrium structures of the stars in the absence of external forces and therefore do not provide us with the shear response. However, the unit cell symmetry can give us some indications on the expected shear response of the different phases. The stars in a primitive oblique and hexago-
that there is no tail interaction and truncate the interaction potential at the star diameter such phases. This raises the question what would occur if we shift effects on the phase behavior of two-dimensional star polymer particles have can understand by inspecting the pair correlation function. These symmetry structures in the overlap regime (Fig. 6b), which we via particles interacting by placing as many particles possible at a distance of exactly truncation point was not observed for Hertz potentials, \( r = \sigma \). However, for the Hertzian case, the force is continuous at \( r = \sigma \), while this is not possible for the logarithmic form of the star polymer potential. Even this subtle effect of continuity versus discontinuity in the force at the transition point has a large effect on the phase behavior. While Hertzian spheres exhibit a variety of ordered structures, the truncated star potential behaves hard-sphere like up to a critical density beyond which we find the unusual phases with a large number of particles position at exactly \( r = \sigma \). In experimental system a discontinuity is not likely to occur since the transition between core and corona is not a sharp wall but defined by a internal density gradient that remains smooth.

4 Conclusions

We have shown how the possibility of star polymers to form non-hexagonal lattices in two dimensions depends strongly on the exact details of the tail of their interaction potential. Since it remains unclear how these interactions take shape for existing experimental star polymer systems it is impossible to predict the viability of star polymers as an experimental platform to template for example honeycomb lattices. Therefore, the most promising approach would be to design chemical routes to prepare star polymers whose tail interactions can be tuned, taking advantage of the recent developments in polymer synthesis.\(^{47-49}\) For example, synthetic routes exist to functionalise the end group at each of the \( f \) arms attached to the star core.\(^{50,51}\) To approach the Yukawa-tailed pair potential, functionalisation of the arm ends with a charged group may give rise to an exponential tail whose range can be tailored by means of ionic strength. Interestingly, if the star arm interpenetrate during compression, the electrostatic repulsion emerging from these charged end groups would be maximum at contact \( r = \sigma \), while further compression reduces the electrostatic repulsion as the charged ends of the two opposing stars move further apart either by backfolding or interpenetration of the arms. This could hypothetically result in a shoulder in the potential, which has been shown to greatly increase the complexity of the phase diagram.\(^{15,19}\) A second strategy to tune the tail interactions, is the use of special miktoarm stars, whose arms are identical in chemical composition but bidisperse in length. In this case, a dense core of short arms will set the range and strength of the core repulsion while a dilute corona of longer arms governs the interactions beyond the star diameter. This system would offer excellent tuneability through arm number and ratio, and length ratio of the short and long arms.

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References