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On the stability of Archimedean tilings formed by patchy particles

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Abstract

We have investigated the possibility of decorating, using a bottom-up strategy, patchy particles in such a way that they self-assemble in (two-dimensional) Archimedean tilings. Except for the trihexagonal tiling, we have identified conditions under which this is indeed possible. The more compact tilings, i.e., the elongated triangular and the snub square tilings (which are built up by triangles and squares only) are found to be stable up to intermediate pressure values in the vertex representation, i.e., where the tiling is decorated with particles at its vertices. The other tilings, which are built up by rather large hexagons, octagons and dodecagons, are stable over a relatively large pressure range in the centre representation where the particles occupy the centres of the polygonal units.

S Online supplementary data available from stacks.iop.org/JPhysCM/23/404206/mmedia

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Is it possible to design colloidal particles so that they self-assemble into a desired target structure? Recent experiments [1, 2] have impressively demonstrated that such a bottom-up strategy can indeed be successfully realized. To be more specific, Chen *et al* designed and fabricated so-called patchy colloidal particles, carrying hydrophobic caps on the two opposite poles, as reported in [1]. Under suitable external conditions, the colloids did indeed self-organize in the targeted two-dimensional kagome lattice. Simulations [3, 4] complemented these experimental observations and provided in addition exhaustive information about the phase behaviour of the system in terms of a temperature versus density phase diagram.

The term 'patchy particles' stands for a particular class of colloidal particles whose surfaces have been treated with suitable physical or chemical methods, creating thereby regions which differ in their interaction behaviour from the untreated, naked surface of the particle. Via those well-defined regions ('patches') the particles are able to establish bonds with other particles in a highly selective fashion. As a consequence of their strongly anisotropic interactions and their selectivity in the formation of bonds, patchy particles are considered to be very promising building blocks for larger entities on a mesoscopic scale [5]. Overviews of recent progress in experimental and theoretical investigations on patchy particles can be found in [6] and [7], respectively.

In the present contribution we deal with the question of whether—via a bottom-up strategy similar to the one mentioned above—patchy particles can be designed in such a way as to self-assemble in even more complex ordered two-dimensional particle arrangements. As target structures we have chosen Archimedean tilings. The eight Archimedean (or semiregular) tilings are presumably known and have been used since antiquity. They are characterized by an edge-to-edge tiling of the plane with at least two regular polygons such that all vertices are of the same type [8]. The polygons involved are the equilateral triangle, the square, the regular hexagon, the regular octagon, and the regular dodecagon. For completeness, we have also included the three related edge-to-edge tilings of the plane formed by a single regular polygon in our investigations; these tilings are

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Table 1. List of the three Platonic and eight Archimedean tilings (first column) and their vertex specifications (second column). In the two other columns parameters are collected that specify patchy particles for the vertex representation (see the text): N stands for the number of particles required per unit cell (cf figure 1). The last column specifies the patch positions along the circumference via the indicated angles. Note that in the vertex representation all particles have the same size; only for the truncated trihexagonal tiling are two particle species of equal size but different chirality in their decoration required.

Vertex representation			
Tiling	Vertices	N	Patch angles (deg)
Triangular	3^6	1	{0, 60, 120, 180, 240, 300}
Square	4^4	1	{0, 90, 180, 270}
Hexagonal	6^3	2	{0, 120, 240}
Elongated triangular	$3^3.4^2$	2	{0, 60, 120, 180, 270}
Snub square	$3^2.4.3.4$	4	{0, 60, 120, 210, 270}
Snub hexagonal	$3^4.6$	6	{0, 60, 120, 180, 240}
Trihexagonal	3.6.3.6	3	{0, 60, 180, 240}
Rhombitrihexagonal	3.4.6.4	6	{0, 60, 150, 270}
Truncated square	4.8^2	4	{0, 90, 225}
Truncated hexagonal	3.12^2	6	{0, 60, 210}
Truncated trihexagonal	4.6.12	6	{0, 90, 240}
	4.12.6	6	{0, 90, 210}

also known as regular or Platonic tilings [8]. In table 1 we have listed the resulting 11 tilings, introducing the commonly used nomenclature and specification via their vertices; further information compiled in this table will be discussed below. In figure 1 we have depicted these planar tilings; their decoration with particles will be addressed later and can therefore be ignored for the moment.

At this point one might argue that the formation of Archimedean tilings by patchy particles represents a rather academic problem. At least two examples can be put forward to refute these objections: (i) experiments on colloids, exposed to a force field induced by interfering laser beams, give evidence [9] of a self-assembly scenario of those particles into an Archimedean-like tiling; (ii) theoretical investigations [10] indicate that deformable spheres form Archimedean tilings in coexistence regions of the phase diagram. Finally, some of the more open Archimedean tilings might show some interesting features in their phonon spectra.

In an effort to demonstrate a successful bottom-up strategy for forming the desired target structures via suitably decorated patchy particles, Platonic and Archimedean tilings are ideal candidates: all vertices are of the same type and all the distances between two vertices are the same. These two features make an appropriate 'guess' for the decoration of the particles with patches rather easy.

In realizing our bottom-up strategy there are essentially two options for positioning the particles on the tilings: either at the vertices or at the centres of the polygons (to be denoted as vertex and centre representations, respectively). These two alternatives are visualized in figure 1. The former has the advantage that only one particle species per tiling is required (except for the truncated trihexagonal tiling, where the two enantiomers of a chiral particle are used), which might represent a particular advantage in a possible experimental realization. However, this representation has serious problems in minimizing the volume contribution to the thermodynamic potential. In particular one encounters problems for those tilings that are built up by polygonal units with six vertices or more. The centre representation, on the other hand, requires considerably more complex unit cells and at least two particle species, characterized by a large size disparity and a relatively large number of patches. These issues might represent a particular challenge in an experimental realization. This representation allows one, however, to stabilize tilings that are built up by hexagons, octagons, and dodecagons.

Based on these considerations we have addressed the following two questions. (i) Can patchy particles be suitably decorated to self-assemble in Archimedean tilings? (ii) How stable are these self-assembly scenarios as the pressure increases? Working in the *NPT* ensemble, by construction the desired target structures are stable at vanishing pressure. However, as the system is exposed even to a tiny pressure, the competition between the energy and the volume contributions to the thermodynamic potential sets in, leading possibly to structures other than the desired target structure. As will be discussed in detail in the body of the paper (in particular in section 3), all tilings, except for the trihexagonal tiling, can be stabilized at low, sometimes even at intermediate pressure values via either of the two representations. We emphasize at this point that we only consider the case of vanishing temperature, $T = 0$. Thus from the results presented in this contribution no conclusions can be drawn as regards which of the structures identified will survive at finite temperature.

The paper is organized as follows. In the next section we briefly summarize the characteristic features of our model for patchy particles and of our optimization strategy (referring the reader to the literature for more details in both cases). Section 3 is dedicated to a thorough discussion of the results. In the final section the results are summarized.

2. The model and theoretical tools

2.1. The model

In the present contribution we have used a model for patchy particles proposed by Doye *et al* [11], suitably adapted to the two-dimensional case. In this model the interaction between two particles is given by a pair potential $V(\mathbf{r}_{ij}, \mathbf{p}_{i\alpha}, \mathbf{p}_{j\beta})$, discussed below; here $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ is the vector between particles i and j and the patch vector, $\mathbf{p}_{i\alpha}$, specifies the patch α of particle i. The explicit expression for $V(\mathbf{r}_{ij}, \mathbf{p}_{i\alpha}, \mathbf{p}_{j\beta})$ consists of a spherically symmetric Lennard-Jones potential modulated by an angular factor taking into account the relative orientation of the two interacting particles. A parameter w specifies the extent of the patch along the circumference. The explicit expression for $V(\mathbf{r}_{ij}, \mathbf{p}_{i\alpha}, \mathbf{p}_{j\beta})$ can be found in [11, 12]. For our investigations the radial part of the potential has been truncated at $r_c = 1.9\sigma$ (σ being the Lennard-Jones diameter) and the patch width parameter w was chosen to be $w = 2\pi 0.025$.

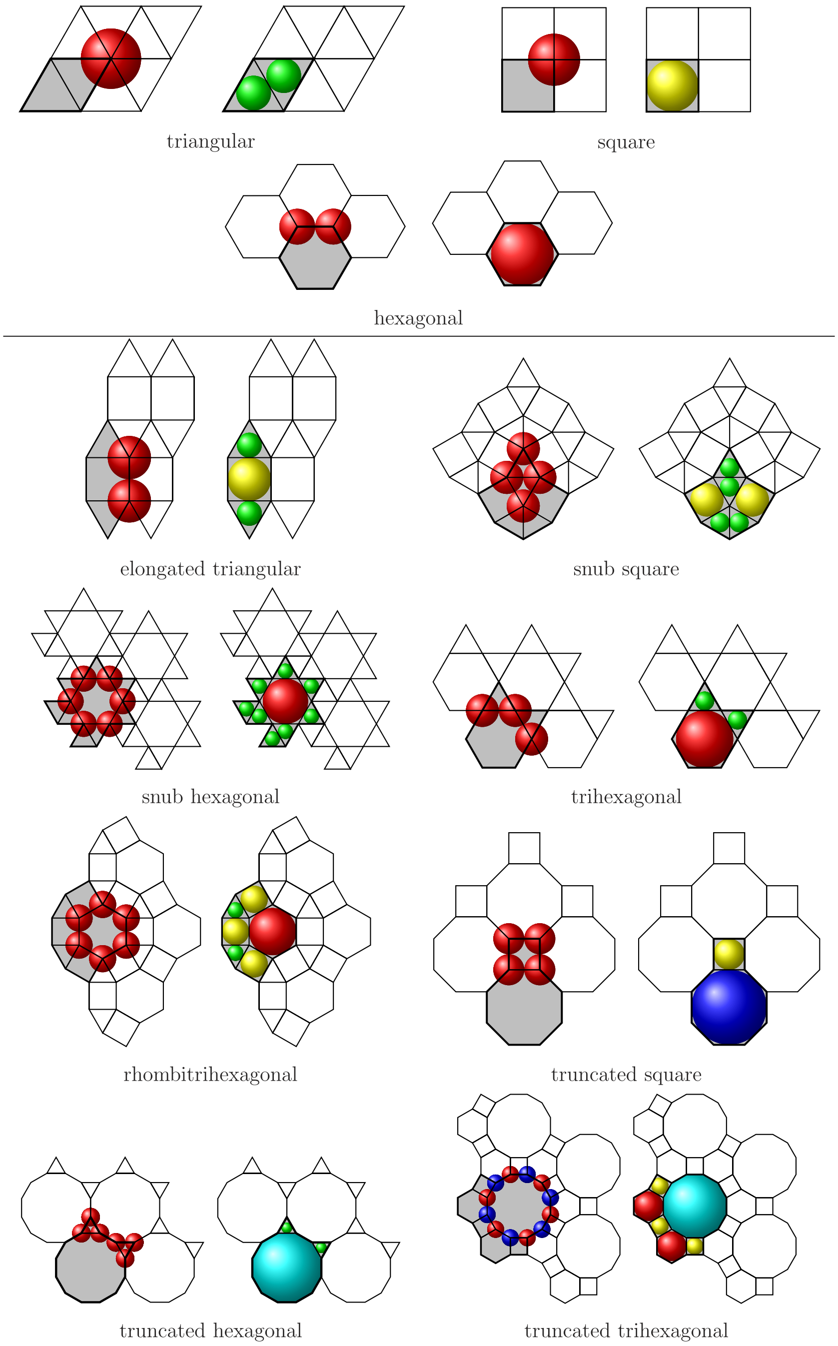

Figure 1. Representative sections of the three Platonic and the eight Archimedean tilings (as labelled)—thin lines. The left (right) panels show the vertex (centre) representations. The grey-shaded areas delimited by thick lines represent the respective unit cells. Different particle species (either distinguished via their patch decoration or via their size) are displayed in different colours.

2.2. Theoretical tools

The ordered equilibrium configurations into which the patchy particles self-organize have been obtained by an optimization tool that is based on ideas of genetic algorithms (GAs). This approach has turned out to be a highly reliable, efficient and robust optimization tool that copes extremely well with rugged energy landscapes and high dimensional search spaces in numerous applications in soft matter physics (see, for instance, [13–17] and references therein). For the basic ideas behind this technique we refer the reader to [18, 19].

In this contribution we have used a phenotype algorithm [20–22] as detailed in [12]. With respect to this implementation the following changes have been made for the present contribution.

(i) The code has been extended to allow for multiple different particle species, offering for each of them an individual patch decoration with up to 12 patches, enabling the algorithm to form rather complex unit cells, which are necessary for realizing Archimedean tilings (especially in the centre representation).

Table 2. List of the three Platonic and eight Archimedean tilings and parameters that specify patchy particles for the centre representation (see the text): N stands for the number of particles required per unit cell (cf figure 1). For all tilings at least two particle species with different sizes are required; their respective sizes (in units of σ_0) are given in the third column. The last column specifies the patch positions along the circumference via the indicated angles for each tiling and each particle species.

Centre representation			
Tiling	N	Size (σ_0)	Patch angles (deg)
Triangular	2	0.577	{0, 120, 240}
Square	1	1.000	{0, 90, 180, 270}
Hexagonal	1	1.732	{0, 60, 120, 180, 240, 300}
Elongated triangular	1	1.000	{0, 90, 180, 270}
	2	0.577	{0, 120, 240}
Snub square	2	1.000	{0, 90, 180, 270}
	4	0.577	{0, 120, 240}
Snub hexagonal	1	1.732	{0, 60, 120, 180, 240, 300}
	8	0.577	{0, 120, 240}
Trihexagonal	1	1.732	{0, 60, 120, 180, 240, 300}
	2	0.577	{0, 120, 240}
Rhombitrihexagonal	1	1.732	{0, 60, 120, 180, 240, 300}
	3	1.000	{0, 90, 180, 270}
	2	0.577	{0, 120, 240}
Truncated square	1	2.414	{0, 45, 90, 135, 180, 225, 270, 315}
	1	1.000	{0, 90, 180, 270}
Truncated hexagonal	1	3.732	{0, 30, 60, 90, 120, 150, 180, 210, 240, 270, 300, 330}
	2	0.577	{0, 120, 240}
Truncated trihexagonal	1	3.732	{0, 30, 60, 90, 120, 150, 180, 210, 240, 270, 300, 330}
	2	1.732	{0, 60, 120, 180, 240, 300}
	3	1.000	{0, 90, 180, 270}

(ii) An additional mutation operation was introduced which rotates with some pre-set probability, $\mathcal{P}_{\rm rot}$, a randomly selected particle of the unit cell; the rotation angle is either chosen at random or taken as one of the angles between two neighbouring patches (or a combination of these two options). This modification turned out to be very supportive in forming highly complex structures. $\mathcal{P}_{\rm rot}$ was set to 0.05.

(iii) For systems with more than one particle species, a permutation operation was introduced: with a pre-set probability, $\mathcal{P}_{\rm perm}$, the identity of two different particles can be swapped, leaving the orientation of the particles involved unchanged. $\mathcal{P}_{\rm perm}$ was set to 0.02.

(iv) Instead of fixing the number of generations in the evolution of the structure *a priori*, the search runs are terminated if, after a given number of generations, no further improvement in the resulting structure is achieved.

Like in our previous contribution [12] we identify the ordered equilibrium structures at constant pressure P and at vanishing temperature T. In this *NPT* ensemble, particles self-organize such that the Gibbs free energy, G, is minimized. At $T = 0$, G reduces to the enthalpy $H = U + PA$, U being the internal energy (i.e., the lattice sum) and A being the area of the system. The following reduced, dimensionless units are used: $G^\star = G/N\epsilon$, $U^\star = U/N\epsilon$, and $P^\star = P\sigma_0^2/\epsilon$, where N is the number of particles, ϵ is the usual energy pre-factor of the spherical Lennard-Jones potential and σ_0 is set to the Lennard-Jones diameter of a reference particle (in our calculations we set $\sigma_0 = 1.0$; cf table 2). Thus, $G^\star = U^\star + P^\star/(\eta\sigma_0^2)$, $\eta = N/A$ being the area number density.

3. Results

3.1. Vertex representation

In our efforts to realize the Platonic and Archimedean tilings in the vertex representation we have chosen patchy particles decorated according to the parameters listed in table 1. The patch decoration is imposed by the requirement that the resulting bonds are realized along the edges of the tilings. In this table we have compiled the number of required particles per unit cell and the decoration of the particles for each tiling, expressed via the angles that define the positions of the patches. For all tilings, except the truncated trihexagonal one (where the vertex configuration requires the use of two particle types with different chirality), a single particle species was assumed. In our investigations we have started from pressure values close to zero and have identified with our search algorithm the stable ordered structures formed by the particles as the pressure is increased. For obvious reasons at sufficiently high pressure all particles will arrange—irrespective of their decoration—in a triangular (i.e., close-packed) lattice.

Visualizations of some exemplary structures can be found in this contribution; for images depicting further configurations we refer the reader to the supplementary material (available at stacks.iop.org/JPhysCM/23/404206/mmedia; Archimedean tilings) and [12] (Platonic tilings).

For the three Platonic tilings our investigations confirmed expected results: the triangular tiling represents the high pressure structure; it is thus stable for all pressure values, guaranteeing throughout saturation of all bonds. With the self-evident four-patch decoration, the square tiling is stable

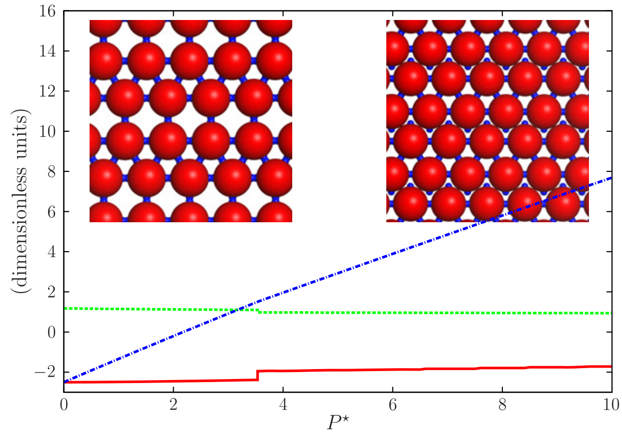

Figure 2. Gibbs free energy ($G^\star = U^\star + P^\star/(\eta\sigma_0^2)$, dash–dotted blue line), lattice sum ($U^\star$, solid red line) and area ($1/(\eta\sigma_0^2)$, dashed green line) of the energetically most favourable structures formed by the elongated triangular system in the vertex representation, as functions of pressure $P^\star$. Insets: low pressure configuration (elongated triangular tiling, left) and high pressure configuration (distorted triangular lattice, right).

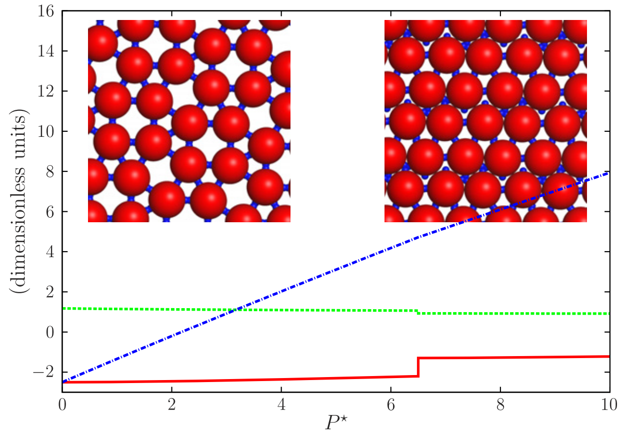

Figure 3. Gibbs free energy, lattice sum and area of the energetically most favourable structures formed by the snub square system in the vertex representation, as functions of the pressure. Insets: low pressure configuration (snub square tiling, left) and high pressure configuration (distorted triangular lattice, right). The line styles are as in figure 2.

with full bond saturation for pressure up to $P^\star \simeq 2.9$. As the pressure increases, the system transforms into the triangular high pressure configuration. Finally, the rather open hexagonal honeycomb structure, induced again by an obvious three-patch decoration, is stable for pressure values up to $P^\star \simeq 0.8$; this rather small threshold value is due to the relatively large area required for this tiling and to the comparably small number of possible bonds. Beyond this value of $P^\star$, the lattice transforms into the close-packed triangular structure.

The situation is more complex for the Archimedean tilings. Anticipating results that will be discussed later in more detail we have found out that in the vertex representation only the elongated triangular and the snub square tilings can be kept stable at low and intermediate pressure values; all target structures resembling other Archimedean tilings are even at low pressure unstable with respect to configurations with similar binding energies, but smaller areas. For the elongated triangular tiling the obviously suitable decoration is realized with five patches (see table 1). The tiling remains stable up to $P^\star \simeq 3.5$. In this pressure range the structure can be viewed as parallel zigzag lanes, characterized internally by a strong bonding (involving four of the five patches); the fifth patch of each particle is used to connect to the neighbouring zigzag lanes (cf figure 2, left inset). As one passes the threshold value for the pressure, the fourfold bonding is able to resist while the inter-lane bonds are broken. In an effort to decrease the area, the now disconnected neighbouring zigzag lanes are shifted relative to each other (lowering thereby the thermodynamic potential), leading to a structure which closely resembles a triangular configuration, with a small deviation in order to retain bonds (cf figure 2, right inset). This deviation continuously becomes smaller with increasing pressure. For the snub square tiling the pressure dependence of the emerging structures is even more complex (cf figure 3). Five patch particles are used with the decoration as specified in table 1. Again, the full saturation of all bonds of this tiling combined with a comparatively small area guarantees that the configuration is able to resist up to relatively high pressure values (i.e., $P^\star \simeq 6.5$). Only then is a more close-packed arrangement with approximately half of the maximum binding energy energetically more favourable. This configuration resembles the triangular high pressure arrangement, like in the elongated triangular case, but has a more complicated bonding scheme.

Using the self-evident patch decorations (which are suggested by the lines forming the vertices of the respective tilings), the desired structure cannot be stabilized for the remaining six Archimedean tilings even at $P^\star \simeq 0$. The snub hexagonal and the trihexagonal tilings arrange at the lowest accessible pressure values in a distorted triangular lattice due to the large area required for these tilings. The particles designed for the rhombitrihexagonal lattice arrange at vanishingly small pressure values in a snub square lattice, which remains stable for pressure values up to $P^\star \simeq 5.3$ and then collapses into a triangular-like structure. Note that the particles have one patch less than the particles designed for the snub square lattice, which explains the lower threshold value in the pressure. Particles designed to self-assemble in a truncated square tiling assemble, instead, at vanishingly small pressure in a distorted hexagonal lattice: again, the full bond saturation combined with a smaller area than the tiling makes this structure energetically more attractive. This structure transforms at a relatively low pressure value ($P^\star \simeq 0.5$) into a configuration consisting of square four-particle arrangements. From $P^\star \simeq 2.8$, we identified a double-lane structure, where particles arrange in a zigzag pattern, stabilized by strong internal bonds as the most favourable one; the double lanes themselves are connected via single bonds: a loss in bond saturation is compensated by a relatively close-packed structure. Eventually, at $P^\star \simeq 5.0$ the system collapses to the triangular structure. Patchy particles designed to form the truncated hexagonal tiling form at low pressure a distorted hexagonal lattice, where the distortion is induced by the patch decoration (this configuration can also be seen as an elongated triangular tiling with a smaller number of bonds). At $P^\star \simeq 4.4$ the system transforms into a triangular structure. Finally, the vertex structure of the truncated trihexagonal tiling suggests using the two different enantiomers of a chiral patchy particle (six of each in the unit cell) to realize this ordered particle arrangement. Due to the large number of parameters that have to be optimized, it is difficult to give conclusive results on this system. However, we found evidence that the desired tiling is disfavoured against competing structures at all pressure values.

3.2. Centre representation

The parameters that specify the size and the decoration of the patchy particles designed to self-assemble in the Platonic and Archimedean tilings within the centre representation are summarized in table 2. Here, the particles are defined as inscribed circles of the polygonal building units of the respective tiling; their obvious patch decoration is imposed by the requirement that the bond between two patches bisects the edge of the polygonal units (cf table 1). Additional parameters listed in table 2 provide information about the number of particles required for the unit cells and the size ratio of the particles involved. Attempting to realize the desired target structures in the centre representation, at least two particle species of different size and decoration have to be introduced; we point out that, compared to the vertex representation, a relatively large number of patches is required. Again, we start our investigation at pressure values close to zero; we then gradually increase the pressure up to $P^\star = 10$. Note that due to the fact that at least two particle species are involved, the high pressure phase is no longer the (monodisperse) triangular lattice.

Again we point out that only a few exemplary structures are displayed in the following; the remaining configurations are summarized in the supplementary material (available at stacks.iop.org/JPhysCM/23/404206/mmedia).

Summarizing results that will be discussed later in more detail we find that now—and in striking contrast to the vertex representation case—all Archimedean tilings except for the elongated triangular, the snub square and the trihexagonal tiling are found to be stable at least for low pressure values. A discussion of possible reasons for these two different scenarios will be given in the subsequent subsection. All Platonic tilings are found to be stable for low and intermediate pressure values within the centre representation and therefore will not be discussed in the following.

Particles designed for the elongated triangular tiling show a size disparity of 0.577. Even at vanishingly low pressure values the target structure is not realized; instead, lanes form: the larger particles populate a square lattice, while the smaller ones self-assemble in hexagons. As the pressure becomes greater, the remaining particles form lanes as well, positioning themselves, however, in increasingly more compact arrangements. Since these lanes (consisting of alternating particle types) get broader as the number of particles in the unit cell is increased, we suspect that this

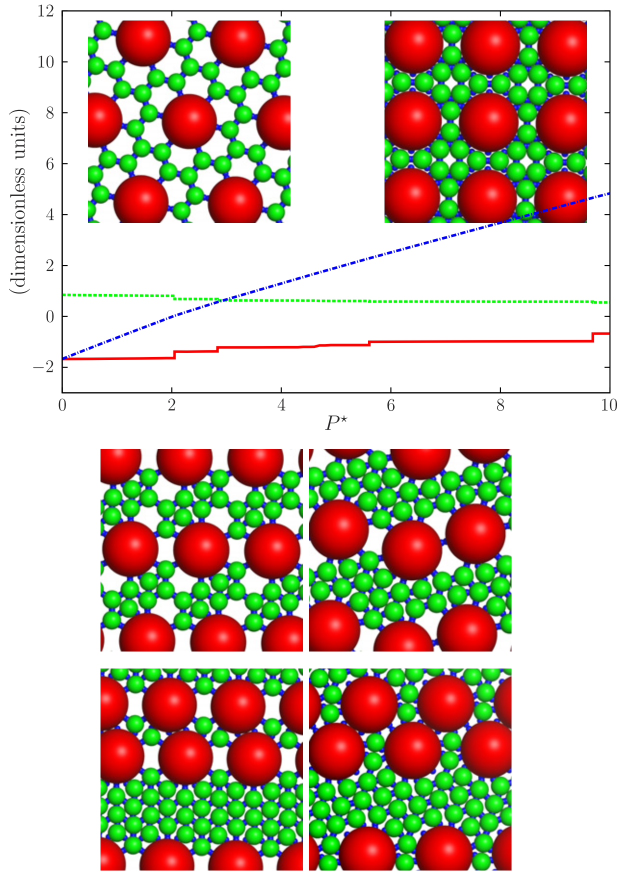

Figure 4. Top: Gibbs free energy, lattice sum and area of the energetically most favourable structures formed by the snub hexagonal system in the centre representation, as functions of the pressure. Insets: low pressure configuration (snub hexagonal tiling, left) and high pressure configuration (right). Bottom: intermediate pressure configurations, with increasing pressure from left to right and from top to bottom. The line styles are as in figure 2.

behaviour corresponds to a phase separation scenario (which our optimization algorithm could only detect in the limit of infinitely large unit cells). For the snub square system we observe exactly the same phase behaviour, since its unit cell in the centre representation consists of particle types and ratios identical to those of the elongated triangular one (cf table 2). Finally, particles designed for the trihexagonal tiling rather arrange at very low pressure values in a rectangular sublattice, formed by the larger particles, while the smaller particles (which are, by a factor of 3, smaller than the former ones) arrange in lanes of dimers between the larger particles. Increasing the pressure leads—via a double-lane structure—to the high pressure arrangement, which is now characterized by single lanes.

In an effort to realize the snub hexagonal lattice we require one large and eight small particles per unit cell, with a size disparity characterized by a factor of 3. The desired target structure is indeed stable for pressure values up to $P^\star \simeq 2.0$. Then, upon increasing the pressure, lane structures emerge with increasing complexity (cf figure 4). Finally, the large particles form a highly compact square lattice, hosting the eight small particles in the interstitial

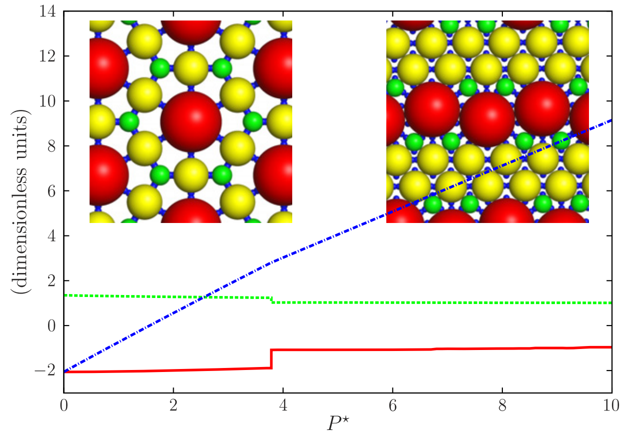

Figure 5. Gibbs free energy, lattice sum and area of the energetically most favourable structures formed by the rhombitrihexagonal system in the centre representation, as functions of pressure. Insets: low pressure configuration (rhombitrihexagonal tiling, left) and high pressure configuration (lane configuration, right). The line styles are as in figure 2.

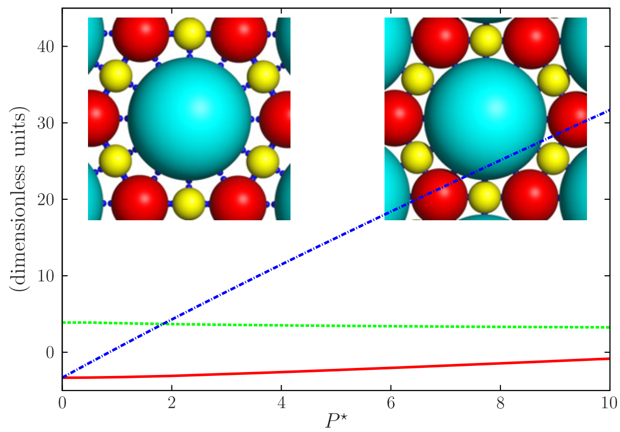

Figure 6. Gibbs free energy, lattice sum and area of the energetically most favourable structures formed by the truncated trihexagonal system in the centre representation, as functions of pressure. Insets: low pressure configuration (truncated trihexagonal tiling, left) and high pressure configuration (same configuration, with bond lengths optimized for close packing, right). The line styles are as in figure 2.

regions. In the construction of the rhombitrihexagonal lattice, three particle species are involved, the size disparity between the largest and the smallest species being characterized by a factor of 3. Indeed, the desired target structure remains stable over a relatively large pressure range, i.e., up to $P^\star \simeq 3.8$, then transforming into a complex lane structure (cf figure 5). Particles designed for the truncated square tiling arrange in the desired target structure, two superposed square lattices decorated with the two particle species. This tiling is the only one that these particles form: as the pressure is increased, the system is homogeneously compressed until a close-packed configuration is reached, maintaining the desired lattice structure. In order to build up the truncated hexagonal tiling, two particle species with a size disparity factor of 6.46 are required. Particles arrange in the desired target structure, which is compressed for higher pressure values. Finally, we require three particle species to realize the truncated trihexagonal tiling; the largest and the smallest of these particles differ in their size by a factor of 3.732. Like for the truncated square lattice, particles arrange for all pressure values investigated in one single structure, which represents the desired particle arrangement (cf figure 6). An increase in pressure only reduces the lattice constants.

4. Conclusions

In this contribution we have addressed the question of whether—via a bottom-up strategy—patchy particles can be designed in such a way as to self-assemble in well-defined two-dimensional target structures. For these particle arrangements we have chosen the Platonic and the Archimedean tilings, which are characterized by an edge-to-edge tiling of the plane with polygons such that all their vertices are of the same type. Due to these characteristic features, which are of particular use in practical tiling problems, these tilings have been studied ever since antiquity. For the particular purpose of this contribution these ordered structures are ideally suited, since for a particular tiling all vertices are identical and all distances between two vertices are the same. In an effort to realize these tilings via suitably decorated patchy particles, two obvious alternatives are possible: either to place the particles on the vertices or in the centres of the regular polygonal building units of the tiling.

In order to parametrize the interactions between the patchy particles we have used a model that is meanwhile well established in literature [11, 12]. The ordered equilibrium structures have been identified with an optimization technique based on ideas of genetic algorithms. Working for convenience in the *NPT* ensemble and at zero temperature, the particle arrangements have been determined by minimizing the Gibbs free energy, which reduces at $T = 0$ to a sum over the lattice sum and a volume term. The competition between these two terms finally decides the resulting equilibrium structure.

We anticipate that the rather trivial Platonic tilings can be realized via both the vertex and the centre representation: the rather compact square tiling is able to survive up to intermediate pressure values, while the rather open hexagonal tiling is stable only at relatively low pressure values. Both then transform into the stable triangular high pressure arrangement.

In the vertex representation one requires—with one exception—only one particle species. We find that only two tilings are stable at intermediate or even elevated pressure values, namely the elongated triangular and the snub square tilings; both are characterized by rather compact structures, involving only triangles and squares as building polygonal units. This fact provides an explanation of why these two tilings are stable in the vertex representation: while at low pressure full bond saturation is guaranteed by definition, these two tilings are characterized by a rather small area compared to the other, more open tilings. Furthermore we have found that both tilings emerge as intermediate structures of other particle arrangements formed by differently decorated particles; this provides an indication of the central role of the elongated triangular and the snub square tilings in the vertex representation. Obviously, these ordered structures represent an excellent compromise between the two competing factors that determine the equilibrium configuration, namely patch saturation and area minimization. The fact that the elongated triangular tiling is 'relatively close' to a quasicrystalline particle arrangement [9] might be an indication that such systems could form (meta)stable quasicrystalline structures. However, a definite answer can only be given by investigations carried out at finite temperatures.

With all these conclusions in mind it is obvious that the rather open tilings (involving hexagons, octagons and dodecagons as building polygonal units) can be stabilized via the centre representation. Indeed, the elongated triangular and the snub square tilings are now unstable even at vanishingly low pressure values, while the snub hexagonal, the rhombitrihexagonal, the truncated square, the truncated hexagonal and the truncated trihexagonal tilings can be stabilized at least at low, sometimes even at intermediate, pressure values by patchy particles suitably designed in our bottom-up strategy. The reasons for this stability are again obvious: the large areas required by the hexagons, octagons and dodecagons that could not be stabilized in the vertex representation are now stabilized by the particles which are located in the centres of the building units.

Only the trihexagonal tiling could not—despite considerable effort—be realized, either using the vertex or the centre representation.

We have thus given evidence that it is possible to decorate patchy particles in a bottom-up strategy in a suitable way such that they self-assemble even in complex particle arrangements, represented by Archimedean tilings. These findings provide hope that patchy particles represent a suitable building unit for self-assembly processes of even larger units, including—possibly—three-dimensional structures.

Finally, we point out that all calculations presented in this contribution have been carried out at vanishing temperature. The question of which of these identified, ordered equilibrium structures will survive at finite temperatures can only be answered either via suitable theoretical concepts that can be used to evaluate the entropic contribution to the thermodynamic potential in a reliable and efficient way or via thermodynamic integration, based on suitably adapted computer simulations [23].

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