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On the selective formation of cubic tetrastack crystals from tetravalent patchy particles

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ABSTRACT
Achieving the formation of target open crystalline lattices from colloidal particles is of paramount importance for their potential application in photonics. Examples of such desired structures are the diamond, tetrastack, and pyrochlore lattices. Here, we demonstrate that the self-assembly of tetravalent patchy particles results in the selective formation of cubic tetrastack crystals, both in the bulk and in the systems subjected to external fields exerted by the solid substrate. It is demonstrated that the presence of an external field allows for the formation of well-defined single crystals with a low density of defects. Moreover, depending on the strength of the applied external field, the mechanism of epitaxial growth changes. For weakly attractive external fields, the crystallization occurs in a similar manner as in the bulk, since the fluid does not wet the substrate. Nonetheless, the formed crystal is considerably better ordered than the crystals formed in bulk, since the surface induces the ordering in the first layer. On the other hand, it is demonstrated that the formation of well-ordered cubic tetrastack crystals is considerably enhanced by the increase in external field strength, and the formation of the thick crystalline film occurs via a series of layering transitions.

I. INTRODUCTION
It is well known that the self-assembly of colloidal particles is primarily governed by their shape and surface properties. Isotropic spherical colloids usually crystallize into simple face-centered cubic (fcc) and hexagonal close-packed (hcp) crystals, depending on the system properties and thermodynamic conditions. This behavior results from the similarity of such colloids to hard-sphere systems. Since spherical isotropic particles form only a very limited number of ordered structures, much of the recent interest focuses on anisotropic colloidal particles, which can be used as building blocks for new functional materials. The particles characterized by different shapes can now be obtained using many methods and are known to assemble into a variety of complex structures. However, there is a class of spherical colloidal particles with anisotropic interactions, which comprises the so-called patchy colloids, with chemically and/or physically modified surfaces. Already, the simplest patchy particles with only one attractive patch, known as Janus particles, exhibit surface chemical anisotropy, which can be tuned by the appropriate functionalization. Both the size and the chemical nature of attractive patches, influence the self-assembly of Janus particles and lead to the formation of various ordered structures in two- and three-dimensional systems. In the region of low and moderate densities, the formation of micelles, vesicles, and worm-like clusters has been observed. It has also been shown that Janus particles form crystals of different structures and densities.

The situation becomes more complex when the number of attractive patches increases. For example, the dissipative particle dynamics simulation of quasi two-dimensional triblock nanoparticles with two attractive patches located at the poles of each particle has shown the formation of two different ordered structures of different densities. In the ordered phase of lower density, the particles are arranged on the Kagomé lattice, while the high density phase shows close-packed hexagonal ordering. In three-dimensional...
systems, the number of possible ordered structures formed by tri- block particles is larger and also depends on the size of attractive patches. The size and shape of attractive patches determine the valence and, hence, the structure of crystal lattices. A particularly interesting class of ordered structures that can be obtained via the self-assembly of patchy colloids are the open lattice photonic bandgap crystals. Such materials may find numerous applications in the devices that allow them to control the propagation of light. Among the most promising are the crystals of diamond, tetrahedrally bound, and pyrochlore structures. The basic problem with such open crystals is that their synthesis is often hampered by low free energy differences between different polymorphic forms. The open structures resulting from the self-assembly of patchy particles are stabilized by larger rotational and vibrational entropy than in close-packed crystals. The synthesis of three-dimensional colloidal crystals with open lattices is considerably hampered since it usually leads to large numbers of stacking faults and grain boundaries. A possible way to force the formation of colloidal crystals with a desired lattice structure and possibly low defect density is through the use of external fields or templates. Trau et al. developed an electrohydrodynamic method enabling the assembly of multilayer colloidal crystals on electrode surfaces. Another possibility is the use of patterned substrates as templates for the assembly of three-dimensional colloidal crystals. The main advantage of epitaxial assembly is the formation of well-ordered crystals with very low defect densities. The problem with such approaches is, however, the necessity of using templates strictly commensurate with the assumed structure of colloidal crystals. Such methods have been primarily used to obtain open lattice colloidal crystals by the sedimentation of binary mixtures of colloidal particles characterized by different sizes and the subsequent removal of one of the components. It has recently been shown by our group that the presence of a uniform external field, exerted by the solid substrate, allows for the formation of a cubic diamond in systems of tetrahedral patchy particles. A key element of the successful growth of cubic diamond crystals is the structure of the first adsorbed layer, which is commensurate with the [110] face of the cubic diamond. It has also been demonstrated that the subsequent removal of the external field does not affect the generated structure, paving the way for further post-synthetic treatments.

In this paper, we use molecular dynamics simulations to investigate the formation of open lattice colloidal crystals by the adsorption of patchy particles on a structureless attractive substrate. The only role of the substrate is to provide an external field leading to the adsorption of particles, but the emerging structure of adsorbed films is entirely determined by the assumed structure of patchy particles and the inter-particle interactions governing their self-assembly. It is well known that the interaction between colloidal particles is rather short-range, but the external fields that determine the formation of ordered structures are usually of a longer range. In particular, it is gravity that leads to self-assembly resulting from the sedimentation of colloidal particles immersed in suspensions.

In this work, it is shown that the self-assembly of tetravalent model patchy particles leads to the selective formation of cubic tetra stack (CT) structures in the bulk as well as in the external field. However, the formation of well-ordered crystals in the bulk is hampered by the presence of numerous defects and grain boundaries between nucleating crystals. On the other hand, when the "disordered fluid" of patchy particles is placed in contact with the solid substrate, it forms quite well-ordered crystals via a sequence of layering transitions that occur upon a decrease in temperature.

II. METHODS

A. Patchy particle model

The patchy particle model used in our simulations is identical to that used in our previous papers, with the only difference being the patch’s arrangement. Each particle is comprised of a spherical unit of a diameter $\sigma_p$ on which surface four patches are displaced, each of a diameter $\sigma_a$ that are embedded to a certain extent. The latter can be manipulated by the parameter $I$. A schematic representation of model parameters is shown in Fig. 1. The active sites are arranged on a square on the surface, intersecting the central plane of the sphere. All the entities in the patchy particles interacted via truncated and shifted Lennard-Jones (12,6) potential. $\sigma_p = \sigma_a$ and $\epsilon_{pp} = \epsilon$ were defined to be units of length and energy, respectively. In the current case, we have chosen the set of parameters to be equal: $\sigma_a = 0.2\sigma$, $\sigma_p = 1.0\sigma$, and $I = 0.45\sigma$. Parameter $I = 0.45\sigma$ ensures that every active site can form three bonds, resulting in 12 neighbors in total.

The association energy was fixed to $\epsilon_{aa} = 5.0\epsilon$ whereas $\epsilon_{pp} = \epsilon_{pp} = 1.0\epsilon$. The range of the interactions was set to $r_{cut,aa} = 2.0\sigma_{cut}$, and the remaining were $r_{cut,ij} = 1.0\sigma_{cut}$ with $(ij = pp, ap)$. Choosing this set of parameters ensures that the only attraction in the system is due to the association energy, while the remaining interactions are soft-repulsive.

To maintain the rigidity and geometry of patchy particles, we used harmonic spring potentials for bonds and bond angles. The corresponding constants were equal to $k_b = 1000\epsilon/\sigma^2$ and $k_\theta = 1000\epsilon/\text{rad}^2$ for bonds and bond angles, respectively, ensuring negligible fluctuations.

To study the surface-directed self-assembly of patchy particles, we introduced the structureless external wall modeled by the Lennard-Jones ($9,3$) potential, defined as follows:

$$U^{ext}(z) = \epsilon_{uc} \left[ \frac{2}{15} \left( \frac{\sigma}{z} \right)^{9} - \left( \frac{\sigma}{z} \right)^{3} \right]$$

if $z \leq 5\sigma$. (1)

where $\epsilon_{uc}$ indicates the depth of the potential well for interactions.

The potential acted solely on the core of the patchy particle, which should result in the introduction of isotropy in how the patchy particles will be arranged with respect to the wall. The following

![FIG. 1. Schematic representation of a model of patchy particles and its parameters. The central spherical core and active sites are shown by purple and white spheres, respectively. The green square depicts the planar surface formed by the centers of active sites. The scale is not preserved for better clarity of the sketch.](https://example.com/figure1.png)
results will be described in terms of the change in the ratio $\xi$ of attraction strengths, defined as $\xi = \varepsilon_{\text{wc}}/\varepsilon_{\text{nat}}$.

Table I gives a full overview of the system parameters.

### B. 3D order parameter

To detect the formed three-dimensional tetrastack crystalline network, we employed a routine based on the calculation of the Steinhardt order parameter\(^3\) given by

$$q_l = \sqrt{\frac{4\pi}{2l+1} \sum_{m=-l}^{l} |q_{lm}|^2},$$

with

$$q_{lm} = \frac{1}{N_b(i)} \sum_{j \in N_b(i)} Y_{lm}(\theta_{ij},\phi_{ij}),$$

where $Y_{lm}$ are spherical harmonics. For a given sphere $i$, we choose a set of its nearest neighbors, $N_b(i)$. We define that any two spherical particles are connected by a bond if they are neighbors, that is, if $j \in N_b(i)$. Each vector $\mathbf{n}_j$ is characterized by its angles in spherical coordinates $\theta_{ij}$ and $\phi_{ij}$ on the unit sphere, evaluated between the bond and an arbitrary but fixed reference frame. The set of all bond vectors is called the bond network.

The ideal tetrastack network is comprised of alternating hexagonal and Kagomé layers. In the crystal lattice, we identify two types of local environments where every particle has either 10 or 12 near-neighbors (NN). We found that the sets of $q_4$ and $q_6$ are the best for discrimination. For an ideal lattice with $NN = 12$, Steinhardt parameters are equal to $q_4 = 0.206$ and $q_6 = 0.558$, and we allow for the 10% error due to the fluctuations present in the simulations. On the other hand, for $NN = 10$, the Steinhardt order parameter gives a few different values that are close to one another in the range of $0.25 < q_4 < 0.325$ and $0.55 < q_6 < 0.61$. Based on the above-mentioned values, molecules with exactly 10 or 12 neighbors were included in crystalline environments or labeled as liquid-like if any of these conditions were not fulfilled.

### C. 2D order parameter

To identify two-dimensional ordering, including discrimination between the hexagonal and Kagomé structures that form alternating layers in three-dimensional tetrastack crystalline networks, we employed a parameter that has been proposed quite recently by Eslami et al.\(^3,4\) It is defined as follows:

$$\lambda_1(i) = \frac{1}{N_b(i)} \sum_{j \in N_b(i)} \left[ \sum_{m=-4}^{4} \hat{q}_{lm}^* q_{lm}^* - \frac{1}{4} \sum_{m=-4}^{4} \sum_{n=+4}^{-4} \hat{q}_{ln}^* q_{ln}^* \right],$$

and

$$\lambda_2(i) = \frac{1}{N_b(i)} \sum_{j \in N_b(i)} \left[ \sum_{m=-4}^{4} \hat{q}_{lm}^* q_{lm}^* - \frac{1}{4} \sum_{m=-4}^{4} \sum_{n=+4}^{-4} \hat{q}_{ln}^* q_{ln}^* \right],$$

where

$$\hat{q}_{lm} = \frac{q_{lm}(i)}{\left( \sum_{n=-l}^{l} |q_{ln}(i)|^2 \right)^{1/2}}.$$

The hexagonal and Kagomé networks are identified in the order parameter space ($\lambda_1, \lambda_2$) with the values of (0,0,0.8) and (0.65,0.7), respectively. These values correspond to the perfect lattices, and we allowed for 10% uncertainty during the discrimination procedure to take into account fluctuations present in the simulations.

### D. 2D orientational profile

To get further insight into the tetrastack crystal structure, we examined how the patchy particles are arranged in the layers with respect to the surface. To do that, we calculate the cross product between the vectors pointing from the center of the patchy particle to the centers of the two neighboring active sites. This results in a new vector $\mathbf{u}_i$ that is perpendicular to the plane formed by these two vectors [green square in Fig. 1(a)]. Next, for each of the particles, we calculate the dot product between the plane and the reference z-axis (wall-direction), $\hat{e}_z$. The results are presented in the form of the distribution function of the angles and the particle’s z-coordinate $h(z, \alpha)$, where $\alpha = \text{arccos}(\mathbf{u}_i \cdot \hat{e}_z)$. Using this definition of $\alpha$, the plane containing patches is parallel to the substrate surface when $\alpha = 0^\circ$.

### E. Simulation details

Molecular dynamics simulations were launched using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) simulation package\(^5\). Trajectories were evolved using the velocity Verlet algorithm, with a timestep of $\tau = 0.001$. The temperature was controlled using the Nosé–Hoover chains thermostat\(^6\) with a damping factor $\tau_{\text{Neff}} = 10\tau$ and a number of chains equal to 3. The systems comprised 8100 or 16 129 patchy particles, respectively. In the slab geometry used here, the periodic boundary conditions were applied in the x- and y-directions, while the z-direction was bound by the
Lennard-Jones (9,3) potential and the reflecting wall at the bottom and top sides, respectively. Additional simulations were carried out for the simulation boxes with the distance between the walls \( (L_z) \) equal to \( L_z = 25\sigma, L_z = 60\sigma, \) and \( L_z = 80\sigma, \) and with the numbers of particles equal to 13456, 24336, and 32761, respectively. The bulk system was composed of 3375 patchy particles at distinct densities ranging from \( \rho = 0.6 \) to \( \rho = 1.3. \) The motivation for performing simulations in the canonical ensemble \( \text{NVT} \) rather than in other ensembles is as follows. We wanted to examine the behavior of patchy particles when the system has a constant density. This, of course, does not necessarily correspond to the coexistence points in all cases; nonetheless, it allows one to assess the stability of the formed ordered phases under such off-coexistence conditions, which are also of experimental interest. Each of the systems was gradually cooled down from disordered states, starting at temperatures \( T \) that varied depending on the system’s density \( \rho \) and surface potential \( \xi, \) with an increment in temperature equal to \( \Delta T = 0.01. \) Once the Steinhardt order parameter indicated the nucleation event, the increment was changed to \( \Delta T = 0.005. \) Simulations were launched for \( 2 \times 10^8 - 1 \times 10^9 \) simulation steps at every thermodynamic state for the equilibration period. Further production runs were launched for at least \( 10^7 \) timesteps. In order to ensure the results do not change from one replica to another, we performed three independent simulation runs for all the cases studied.

### III. RESULTS AND DISCUSSION

#### A. Phase behavior of the bulk system

Before we turn to the main subject of the study, i.e., the assembly of model patchy particles subjected to the external field, it seems reasonable to begin with the discussion of bulk behavior. To this end, we have performed extensive simulations over a wide range of temperatures and at different densities. It should be emphasized that we have not attempted to evaluate the entire phase diagram but rather to demonstrate its topology and determine the structure of different ordered phases. In particular, we have confined the calculations to densities up to \( \rho = 1.30. \) At still higher densities, the simulations turned out to be very slowly converging, and the time needed to reach equilibrium states appeared prohibitively long.

Figure 2(a) shows the snapshot, being a representative example of configurations emerging from the simulations at low temperatures, below \( T = 0.92, \) and at densities between \( \rho = 1.0 \) and 1.2. This
A detailed analysis of the CT phase has allowed us to construct its unit cell. The upper left panel of Fig. 3(a) presents the lattice of the fcc structure with high symmetry space group F4\(\overline{3}m\), seen from the [111] direction. The three-fold inversion axis can be directly noticed. Adding the Kagomé layers between the fcc layers [see the lower left panel of Fig. 3(a)] lowers the system’s symmetry [see the right panels of Fig. 3(a)]. One should note the periodic shifts in particle’s positions in the subsequent layers of the fcc and Kagomé lattices. The new symmetry of the resulting CT structure is rhombohedral R\(\overline{3}m\). In this case, the three-fold inversion axis remains unchanged. Figure 3(b) presents the unit cell projection with atoms’ positions and their heights (colored numbers), together with the symmetry elements related to this symmetry group. The black numbers are the height of the symmetry elements (inversion centers). The red hexagon in Fig. 3(b) represents the equivalent cell used to describe a rhombohedral system.

We have generated a perfect CT phase and found that the lattice unit cell, containing 21 particles, is characterized by the lattice vectors \(\mathbf{a} = (2, 0, 0)\), \(\mathbf{b} = (0, 2, 0)\), and \(\mathbf{c} = (0, 0, 4.8)\). The fractional positions of all atoms in the unit cell are summarized in Table II.

In order to determine the changes in the ordering of the bulk with temperature and density, we have considered the behavior of the Steinhardt order parameters \(q_4\) and \(q_6\). For the ideal CT structure, these order parameters allow us to discriminate between particles with 10 and 12 nearest neighbors, as discussed in Sec. II B.

The calculations of temperature change for \(q_4\) and \(q_6\) allowed us to estimate the contributions of particles belonging to the ordered phases, measured by the ratio of particles classified as belonging to the crystalline phase to the total number of particles, \(x_{cr} = N_{cr}/N_{total}\).

The results are given in Fig. 4(a) and show that an increase in temperature leads to a gradual decrease of \(x_{cr}\), up to the temperature, \(T_{tr}(\rho)\), at which \(x_{cr}\) drops to zero. This sudden disordering suggests the presence of a first-order transition. Figure 4(a) also shows

![Graph](image-url)
that the transition temperature increases with \( \rho \). Besides, from the calculated order parameters, we have found that for \( \rho \leq 1.0 \), the disordering transition occurs between the CT ordered phase and the fluid, while at a density equal to 1.20, the CT phase is stable only at temperatures up to about 0.92. At higher temperatures, a vast majority of particles involved in the crystalline phase have been found to have 12 nearest neighbors and form the fcc crystal. The example of the configuration recorded for \( \rho = 1.20 \) and at \( T = 1.05 \) has already been shown in Fig. 2(b).

The results have allowed us to conclude that the bulk phase diagram looks like that shown in Fig. 4(b), and its topology is qualitatively similar to that found by Romano et al.\(^\text{25}\) for tetrahedral patchy particles. Therefore, the system does not exhibit the gas–liquid transition but only the transition between the fluid and solid phases. Notice, however, that such an evaluated phase diagram is only schematic, as we were mainly interested in the approximate estimation of its topology and the coexistence regions. Moreover, we cannot completely exclude the possibility of the existence of a metastable liquid phase. To unequivocally establish its presence would require rather tedious calculations and was beyond the scope of this article. At temperatures up to about 0.92, the fluid coexists with the CT ordered phase. It should be noted, however, that the solid is not a perfectly ordered CT crystal but contains a small fraction (between 10% and 15%) of the fcc structure. At temperatures above 0.92, the solid phase exhibits the fcc structure. It should be emphasized that at densities equal to 1.20 and 1.30 and at temperatures below 0.92, we have observed the presence of coexisting CT and fcc structures. Therefore, it can be anticipated that at sufficiently high densities, the solid phase should be a pure fcc crystal. This expectation is supported by the high temperature behavior, which demonstrates that only the fcc structure coexists with the disordered liquid. Therefore, one expects that upon cooling the system at a sufficiently high density, it will form a pure fcc crystal. It has to be emphasized, however, that the location of the line delimiting the region of densities over which the CT and fcc structures coexist, from the high density region in which only the fcc structure occurs, has not been estimated. Nonetheless, it is bound to appear at a density higher than 1.3.

**B. Ordering in the external field**

It is well known that the formation of adsorbed films is primarily determined by the relative strengths of the particle–particle (\( \epsilon_{\text{pa}} \)) and particle–wall (\( \epsilon_{\text{pw}} \)) interactions.\(^\text{25}\) Here, we have studied the self-assembly of patchy particles subjected to an external field of varying strength, measured by the parameter \( \xi \) (cf. Sec. II A). We have considered four different values of \( \xi = 0.4, 0.8, 1.2, \) and 1.6 and performed simulations at different temperatures for two different values of the total density equal to \( \rho = 0.173 \) and 0.352.

In order to study the development of adsorbed films, the density profiles, \( \rho(z) \), have been recorded and used to calculate the surface excess densities, \( \Gamma \),

\[
\Gamma = \frac{1}{S} \int_0^{L_{z,\text{max}}-L_{z,\text{min}}} [\rho(z) - \rho_b] dz.
\]

In the above equation, \( S = L_x L_y \) is the surface area, \( L_{z,\text{max}} = 35 \), and \( \rho_b \) is the bulk density. The bulk density has been calculated as

\[
\rho_b = \frac{1}{S(L_{z,\text{max}} - L_{z,\text{min}})} \int_{L_{z,\text{min}}}^{L_{z,\text{max}}} \rho(z) dz,
\]

with \( L_{z,\text{min}} = 25 \). The selected value of \( L_{z,\text{max}} \) is beyond the range of \( z \), over which the density profiles have shown the peaks associated with the formation of adsorbed layers. At the same time, \( L_{z,\text{max}} = 35 \) ensures that any undesired effects stemming from the presence of the reflecting wall are avoided.

The central results of our calculations are given in Fig. 5, which presents the changes in the surface excess density with temperature for different values of \( \xi \) (cf. Sec. II A) and for \( \rho = 0.352 \) [part (a) of Fig. 5] and 0.173 [part (b) of Fig. 5]. In all cases, the surface excess density exhibits a series of jumps, which indicate the formation of a gradually increasing number of adsorbed layers in the film when the temperature drops. The sequence of these layering transitions changes when the strength of the surface potential increases and also depends on the total density.

In the case of the weakest surface potential, with \( \xi = 0.4 \), we have performed the simulation for the bulk density \( \rho = 0.352 \) and...
found only one transition leading to the formation of a very thick film. Figure 6(a) shows the density profiles recorded at the temperatures below \(T = 0.65\) and above \(T = 0.66\) during the transition leading to the condensation of particles and the formation of the thick film. It is evident that at \(T = 0.66\), only a fraction of the first layer is covered, while a vast majority of particles remain in the uniform bulk phase. On the other hand, at \(T = 0.65\), the film consists of 18 layers, while the bulk density is very low. Therefore, the transition may be treated as bulk condensation, and such behavior is characteristic of systems that do not exhibit wetting. It should be noted that the heights of subsequent peaks corresponding to odd layers, 1, 3, ..., are considerably higher than those corresponding to even layers, 2, 4, ..., and that the heights of all maxima gradually decrease with \(z\). Nonetheless, the integration of density profiles has shown that the ratio of densities in neighboring odd and even layers is equal to \(1.34 \pm 0.03\) across the entire film. This suggests that the film was ordered into the CT structure, in which the ratio of densities of the fcc and Kagomé layers is equal to \(4/3 \approx 1.33\). A gradual decay of subsequent maxima at the density profile demonstrates that the interface between the ordered film and the bulk dilute (gas) phase is rough since the filling of higher layers is only partial [see the snapshot given in part (b) of Fig. 6].

In the case of the stronger surface potential, with \(\xi = 0.8\) and \(\rho = 0.352\), the first transition, at \(T \approx 0.73\), leads to the formation of ten filled layers [see the density profile given in Fig. 6(c)], and is followed by the transition, at \(T = 0.72\), leading to the mutual condensation of the next two layers. A further lowering of temperature, down to \(T = 0.68\), causes a gradual increase in the film thickness, but the interface between the film and the bulk is not as rough as in the case of \(\xi = 0.4\). This is illustrated by the snapshot given in Fig. 6(d) and recorded for the system with \(\xi = 0.8\) and at \(T = 0.68\). The results given in Fig. 5(a) clearly demonstrate that the mode of film development is strongly affected by the strength of the surface potential. For the still stronger surface fields, with \(\xi = 1.2\) and 1.6, the first layering transition involves a mutual condensation of only four layers on top of an already existing monolayer film.

In the system with the lower total density, equal to \(\rho = 0.173\) and \(\xi = 0.8\), there is only one transition, which leads to the formation of six filled layers [see part (b) of Fig. 5]. The film thickness is lower than in the case of \(\rho = 0.352\) since the number of particles in the system allows for the formation of only six layers. However, the density profile recorded for the system with \(\rho = 0.173\) at \(T = 0.65\) demonstrates quite similar behavior to that found for thick films in the system with \(\rho = 0.352\). In particular, the ratio of densities in the odd and even layers is practically the same as in the system with \(\rho = 0.352\), which implies that the film structure is also the same.

It should be noted that in all systems with \(\xi \geq 0.8\) that are quite dense and disordered, monolayer films are formed at temperatures above the first layering transition. However, the first layering transition induces ordering in the entire film, and, again, the odd layers assume the structure corresponding to the [111] face of fcc crystal, while the even layers are ordered into the Kagomé lattice. A gradual decrease in temperature leads to a series of layering transitions involving the mutual condensation of an even number of layers. This behavior can be attributed to the growth of the CT phase, which retains the highest stability when the number of layers with
hexagonal and Kagomé orderings is the same. We recall that the first layer exhibits hexagonal ordering; hence, the top layer is bound to order into the Kagomé lattice.

In order to confirm that thick films are ordered into the CT phase, we have calculated the two-dimensional order parameters \( \lambda_i(z) \) and \( \lambda_j(z) \) for subsequent layers, \( i \), of thick films (cf. Sec. II C). The regions of \( z \) corresponding to each layer have been estimated from the density profiles, and these order parameters allowed us to estimate the contributions of particles involved in the Kagomé and hexagonal lattices. A representative example of the results is given in Table III, which demonstrates that odd layers are well-ordered into the hexagonal lattice, while even layers are ordered into the Kagomé lattice.

Our model assumes that all four attractive patches are arranged in a plane. The calculations of two-dimensional orientation profiles (cf. Sec. II D) have revealed that in even layers, i.e., those forming the Kagomé lattice, the planes containing the patches are predominantly oriented perpendicular to the substrate surface, while in the case of hexagonally ordered odd layers, those planes are tilted with respect to the surface by the angle \( \alpha = 35^\circ \pm 1^\circ \). This is quite well illustrated by the behavior of the distribution function \( h(z, \alpha) \), recorded for the system with \( p = 0.352 \) and \( \xi = 1.6 \), at \( T = 0.68 \), and shown in Fig. 7.

Although we have not attempted to calculate the distribution function \( h(z, \alpha) \) in bulk, nevertheless, it is very likely that it behaves in the same way. It should be remembered that the evaluation of \( h(z, \alpha) \) is performed with respect to the plane, dependent on the orientation of the crystal. In the bulk phase, the orientation of the crystal evolves during the run; hence, the calculation of the distribution function \( h(z, \alpha) \) would require a continuous adjustment of the crystal orientation relative to the chosen reference plane. Such calculations are possible, of course, but would require very time consuming calculations.

In order to study the stability of the developed films ordered into the CT phase, we have performed simulations by gradually increasing the temperature and using the configurations corresponding to the films of different thicknesses. In Fig. 8(a), we present the results for the systems with \( \xi = 0.4 \) and 1.6, and the bulk density equal to \( p = 0.352 \). In the case of \( \xi = 0.4 \), the only possible starting point is the film with the surface excess density equal to \( \Gamma = 13 \), appearing at \( T = 0.685 \) [see the inset to Fig. 8(a)], while in the system with \( \xi = 1.6 \), we have used configurations with different numbers of occupied layers [see the main part of Fig. 8(a)].

The results given in Fig. 8(a) demonstrate that in both cases of \( \xi = 0.4 \) and 1.6, the runs starting at high surface excess densities lead to a smooth decay \( \Gamma \) when the temperature increases and result in wide hysteresis loops. However, the mechanism of the film disordering depends on the strength of the external field. In the case of weak fields, with \( \xi = 0.4 \), the density profiles, shown in the left-hand panel of Fig. 8(b), demonstrate that upon the increase in temperature, the densities of all layers gradually decrease, but even at the temperature of 0.77, there are 16 partially occupied layers. Only when the temperature becomes closer to the total disordering of the film, which occurs at \( T \approx 0.8 \), does the film thickness start to decay.

On the other hand, the density profiles obtained for the system with \( \xi = 1.6 \) given in the right-hand panel of Fig. 8(b), indicate that the densities of the layers close to the surface are only slightly affected by the increase in temperatures, and the disordering

<table>
<thead>
<tr>
<th>Layer ((i))</th>
<th>(z_{\text{min}}(i))</th>
<th>(z_{\text{max}}(i))</th>
<th>% Kagomé</th>
<th>% Hexagonal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.6</td>
<td>1.2</td>
<td>0.0</td>
<td>93.58</td>
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<td>2</td>
<td>1.3</td>
<td>1.7</td>
<td>75.19</td>
<td>0.0</td>
</tr>
<tr>
<td>3</td>
<td>2.2</td>
<td>2.7</td>
<td>0.0</td>
<td>82.86</td>
</tr>
<tr>
<td>4</td>
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<td>3.4</td>
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**FIG. 7.** Two-dimensional orientational profile, \( h(z, \alpha) \), recorded for the system’s density \( p = 0.352 \) at \( T = 0.68 \) and \( \xi = 1.6 \). Part (b): Fragments of fcc (odd layers) and CT (even layers) formed by patchy particles. The cores of patches and active sites are colored in purple and white, respectively.
FIG. 8. Part (a): Changes of the surface excess density $\Gamma$ with temperature for systems with the total density $\rho = 0.352$, $\xi = 1.6$, and $\xi = 0.4$ (inset to this figure). Filled and open symbols correspond to the condensation and evaporation simulations, respectively. In the main part of panel (a), the starting temperatures for evaporation simulations were $T = 0.67$ (orange curve), $T = 0.7$ (green curve), and $T = 0.785$. Part (b): Density profiles along the evaporation curves at different temperatures for the systems with $\xi = 0.4$ (left-hand side panel) and $\xi = 1.6$ (right-hand side panel).

Involves the top layers mostly and leads to a gradual decrease in the film thickness. At the temperature of $T = 0.75$, the film still consists of 14 layers, while at $T = 0.79$, it has only six layers. A further increase in temperature to 0.8 leads to the disordering of two top layers, and the four-layer film remains stable up to a temperature of about 0.82.

Figure 9 shows the examples of snapshots recorded at gradually increasing temperatures for the systems with $\xi = 0.4$ [parts (a)–(c)] and $\xi = 1.6$ [parts (d)–(f)], starting from $T = 0.65$ and $T = 0.66$, respectively. In both systems, the disordering spreads at the interface of the crystal and fluid, but in different ways. In the case of a weak surface field, the roughness of that interface causes the region of disordering to be primarily determined by the roughness of the crystal surface and may go down to the substrate surface, while the partially filled and ordered layers retain high thickness. This causes a gradual decrease in all peaks of density profiles when temperature increases. On the other hand, a strong surface field pins the film to the substrate and causes the first six layers to be completely filled, even at quite high temperatures. Therefore, the disordering of the upper part of the film occurs in the same way as in the case of a weak surface field, and only the layers adjacent to the substrate surface exhibit higher stability.

Wide hysteresis loops between the runs corresponding to the decreasing and increasing temperatures suggest that the once-formed multilayer ordered structure remains stable at quite high temperatures. Does it represent truly stable states, or is it just a manifestation of metastability? A possible way to clarify this question would be to calculate the free energy changes along the paths of decreasing and increasing temperature using the method of thermodynamic integration. Such calculations are feasible but would require knowledge about the free energies at certain "reference" points and much computational effort.

C. Removal of the external field potential

A rather convincing evidence of the intrinsic high stability of CT crystal is provided by the results obtained when the external field was switched-off. We have used the configuration obtained for the system with $\xi = 1.6$ at $T = 0.67$, with the surface excess density $\Gamma \approx 13$, and calculated the changes in the fraction of particles involved in the ordered CT phase when the temperature increases. The results are given in Fig. 10 and demonstrate that the system undergoes a gradual disordering when the temperature increases up to $T \approx 0.78$. It has to be emphasized that in the initial state, taken from simulations in the presence of an external field, the system is not in bulk solid–vapor coexistence. Therefore, partial melting of the solid is bound to occur until the coexistence pressure of a vapor
FIG. 10. Temperature changes of the ratio of crystalline particles to the total number of molecules $x_c$ when the external field is turned off. The starting point was $T = 0.67$ and $\xi = 1.6$ at the systems’ density $\rho = 0.352$.

phase is reached. The same scenario will emerge with the increase in temperature until the entire crystal eventually melts at $T \approx 0.78$. Figure 11 presents the snapshots recorded at gradually increasing temperatures.

This finding provides rather strong evidence that the ordered CT phase retains stability at a wide range of temperatures and vanishes only when the temperature approaches about 0.78. Recall that the bulk system of the density $\rho \approx 0.352$ is disordered at considerably lower temperatures, below $T \approx 0.7$ [cf. Fig. 4(b)]. However, as already stated, in order to unambiguously determine the stability of the CT phase, rigorous free energy calculations are required. Nevertheless, even if it were not thermodynamically stable, the appearance of such a crystal could be observed in both simulations and experiments.

FIG. 11. The examples of snapshots at different temperatures for the systems with the external field turned off. The starting point was $T = 0.67$ and $\xi = 1.6$ at the systems’ density $\rho = 0.352$. Green and red sticks correspond to the particles with 10 and 12 nearest neighbors, respectively.

FIG. 12. The comparison of density profiles evaluated at $T = 0.78$ (a), $T = 0.74$ (b), and $T = 0.69$ (c) for the separation distance between the walls $L_z = 25\sigma$, 40\sigma, 60\sigma$ and $L_z = 80\sigma$ for a system with $\xi = 1.6$. The legend also displays values of the bulk density $\rho_b$. Part (d): The relation of bulk density $\rho_b$ with the separation distance $L_z$. 
D. The effects due to the simulation box size in the z-direction

Since we have performed the simulations in the NVT ensemble, it is reasonable to verify the importance of the plausible effects stemming from the insufficiently large system size in the z-direction. A comparison of the results obtained for the system with a total density equal to \( \rho = 0.352 \) and different \( L_z \) is shown in Fig. 12. As the separation distance between the walls increases, the developing crystalline layer can become thicker. This effect becomes more pronounced when the temperature drops [cf. Fig. 12(c)]. Nevertheless, it is evident that the growth of the crystalline network still occurs in a layer-by-layer fashion. The number of growing layers is always even, which is consistent with the proposed mechanism of the crystallization of the cubic tetrastack phase.

One should also notice a slight increase in the bulk density, \( \rho_z \), when \( L_z \) becomes larger, and it occurs at all temperatures considered, as shown in Fig. 12(d). However, the differences in \( \rho_z \) gradually decrease as the size of the simulation box becomes larger and are expected to vanish for sufficiently large \( L_z \). In fact, the results at \( T = 0.69 \) and 0.74 demonstrate that for \( L_z = 60 \) and 80, the bulk density is the same, within statistical error limits. We conjecture that the changes in \( \rho_z \), with \( L_z \) can be attributed to the finite size of the system and the finite length of simulations in the NVT ensemble. Together with the increase in \( L_z \), the number of particles in the system of the same total density is also larger, resulting in the necessity of sampling a much larger phase space in order to obtain reliable results, and so the simulation time becomes prohibitively long.

The above-described behavior is an artifact of simulations in the NVT ensemble. With the total number of molecules fixed, we have a limited reservoir of particles able to adsorb on the surface. Upon the increase of \( L_z \), while keeping the same total density, the number of molecules increases, which allows for the formation of a higher film, as shown in Fig. 12. This could be potentially alleviated by performing the simulations in the grand canonical ensemble \( \mu \) \( \rho \). However, we have already explained the motivation for choosing the canonical ensemble in Sec. II E.

IV. FINAL REMARKS

In the present work, we have shown that tetravalent particles with patches located at the corners of a square belonging to the plane passing through the particle center assembled into the cubic tetrastack crystals both in the bulk and in the presence of the external field. However, the external field is crucial, as it facilitates the formation of well-defined clusters with significantly fewer defects compared to the bulk phase. As the strength of the external field increases, the epitaxial growth mechanism changes from a thin–thick film to a series of layering transitions as the adhesion increases, which also has an impact on whether the crystal will exhibit a rough or smooth interface with the coexisting fluid.

The selective formation of an open lattice such as cubic tetrastack is of paramount importance as this polymorph exhibits a complete photonic band gap, making it potentially useful in terms of photonic crystal applications. Additionally, the crystalline structures remain stable when the external field is turned off and even upon heating, allowing one to test them for their photonic applications and also make specific post-synthetic adjustments.

Although a selective formation of cubic tetrastack crystals has been reported for several systems involving star polymers\(^{35}\) or triblock particles with triangular patches,\(^ {26}\) the use of tetravalent particles with circular patches is arguably more feasible in terms of experimental realization. In particular, the latter is supported by a recent study, where the formation of a tetrastack lattice has been predicted to be formed by a four-component mixture of icosahedral and octahedral patchy particles.\(^ {39}\) The authors confirmed its emergence using patchy DNA origami and were able to perform the first-ever experimental formation of such an open lattice. Moreover, another experimental study demonstrated that random aggregates have been observed during the self-assembly of particles with triangular patches. The main difficulty with directing the formation of well-ordered structures is connected with the lack of appropriate methods to obtain particles with triangular patch sizes.

Therefore, we believe that another approach, using a different geometry of patchy particles and, most importantly, a one-component system, can be used in the near future for the experimental preparation of tetrastack crystals.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Łukasz Baran: Funding acquisition (lead); Investigation (equal); Methodology (equal); Supervision (lead); Writing – original draft (equal). Dariusz Tarasewicz: Investigation (supporting); Methodology (supporting). Daniel M. Kamiński: Investigation (supporting); Methodology (supporting). Andrzej Patrykiewicz: Investigation (equal); Writing – original draft (equal). Wojciech Rżysko: Investigation (equal); Methodology (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES


