Angular Patterns in the Ground State of a 2D Soft-Particle Cluster Model

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Abstract

Ordered cluster phases were detected but not fully understood in 2D arrays of soft interacting particles. In this thesis we attempt to analyse the orientational degrees of freedom of the clusters in terms of the small energy variations associated to different mutual angular orderings. We study a static model for a crystalline lattice of spontaneously clustering colloidal particles in the absence of a corrugation substrate. We execute a multipolar expansion for small cluster size of the interaction energy between clusters consisting of $n = 2$ and $3$ particles. This expansion highlights a dependence of the total energy on the appropriate multipolar terms compatible with the combined cluster and lattice symmetries.

Based on this multipolar expansion, we determine, through numerical minimization, the ground-state energies and configurations for the two cases. We show that for $n = 2$ the system exhibits a herringbone angular ordering, while for $n = 3$ rows of parallel clusters form.

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1 Introduction

Soft particles forming a crystalline cluster state are studied for their interest in the field of tribology, as examples of sliding objects with an internal structure. Previous work investigated a two-dimensional model of particles interacting with a soft potential energy, characterized by a cluster phase over a broad range of density and temperature \[1\]. In particular, in the \( T = 0 \) limit, ordered phases were detected, with non-trivial reciprocal angular orientations among neighbouring clusters. For increasing densities the following phases arose in the order: a single-particle phase, 2-particles clusters, 3-particles triangular clusters, 4-particles lozenge-shaped clusters and clusters composed of higher number of particles with more complex shapes. These phases were not investigated in detail, but different orderings were shown to involve relatively small energy differences.

The advantage of the pairwise interaction used in Ref. \[1\] is that particles can spontaneously form clusters under its effect, thus there is no necessity to add a corrugation potential to the system.

Colloidal-particle clusters interacting with periodic substrates were also studied for the variety of static and dynamical phases that assemblies of particles with orientational degrees of freedom can form \[2, 3\]. In these works \( N_c \) particles interact with each other with a Yukawa potential and are trapped in a triangular substrate whose number of minima is an integer divisor of \( N_c \). Clusters assume different forms and sizes depending on the driving force intensity and the substrate amplitude. 3-particles and 4-particles clusters, for example, are respectively triangles and squares whose size decreases for increasing amplitude. Clusters made of 5 or more particles can have a regular-polygon shape or, for lower amplitude, a shell ordering with one particle sitting at the centre of the substrate minimum surrounded by the others on higher-energy shells. Several orientational ordering are shown to arise due to quadrupolar or higher-order interactions between clusters, including a dimers herringbone state when the driving force is null and ferro-orientational and antiferro-orientational states. In these studies \[2, 3\] the clusters are ”extrinsic”, being the product of the external potential competing with the interparticle interactions, which tend to favour a uniform state.

In the present work we consider instead a model of interacting particles that form clusters spontaneously, even in the absence of an external corrugation potential. We study the statics of this model at \( T = 0 \), investigating the energy differences associated to the clusters orientational ordering to research the angular configuration which minimizes the total repulsive energy. To this aim, we execute a multipolar expansion of the cluster-cluster interaction energy for small clusters. The result is an effective Hamiltonian depending on the clusters orientation, from
Figure 1: The colloid-colloid pairwise interaction energy $\Phi_{cc}(r)$, Eq. (1).
Inset: detail of the flat region, $r \lesssim R_c$.

which we can understand what mutual orientations are favoured by the terms of different order in this expansion.

Obviously the largest-energy term in the expansion is the monopole-monopole, which is the energy we would have if all the particles were concentrated at the centre of the clusters. In order to minimize it, clusters will tend to stay as distant as possible from each other, so we can approximate their positions with the points of a triangular lattice. In our model the clusters have fixed centres, but are free to rotate around them, so each one has one rotational degree of freedom that influences the total energy.

We minimize the effective total energy obtained by this expansion by means of numerical techniques to find the actual ground state of the system.
2 The Model

As in Ref. [1], for naturally interacting soft colloids we consider the following pairwise interaction energy, displayed in Fig. 1:

\[
\Phi_{cc}(r) = \frac{A_0}{r^6} + \frac{B_0}{r^6}.
\] (1)

This potential energy is composed of two terms. The first one is a soft-core repulsive interaction and exhibits a low-distance flat behaviour for \( r \lesssim R_c \), where the two particles perceive a weak repulsive force. This term is responsible for clustering, since for large enough density it makes it energetically convenient for few colloids to gather together rather than forming a uniform triangular lattice. Cluster formation for particles interacting with a purely-repulsive potential bounded at \( r = 0 \) occurs, at high-enough density, when the Fourier transform of the potential has negative components [4, 5, 6]. A negative minimum in the Fourier transform causes instability in the uniform fluid phase at the corresponding wavenumber at low temperature or equivalently at high density, leading to multiple site occupation. The second term in Eq. (1) is a hard-core repulsion, which prevents particles from overlapping and thus clusters from collapsing to a single point, as they would do in the \( T \to 0 \) limit if only the \( A_0 \) term was present. Since we want this term to alter the soft-core interaction as little as possible we assume a small value \( B_0 = 5 \times 10^{-5} A_0 \).

For simplicity we model clusters as rigid \( n \)-particles structures, where particles are pointlike. In particular we focus on the cases \( n = 2 \) and \( n = 3 \), where particles sit respectively at the endpoints of a segment and at the vertices of an equilateral triangle. In both cases the typical reciprocal distance between colloids within a cluster is approximately \( wR_c = 0.3R_c \), corresponding to the distance where the repulsion \( \Phi_{cc}(r) \) exhibits an inflection point, thus the repulsive force has a minimum. In Ref. [1] it is shown that the optimal distance between clusters for a stable \( n \)-cluster phase is \( aR_c = 1.5R_c \). We adopt this significant value.

\( R_c \) represents the natural length unit of the system. \( E_0 = \frac{A_0}{R_c^6} \) is the energy unit. We also define the energy \( E_B = \frac{B_0}{R_c^6} = 5 \times 10^{-5} E_0 \), which will turn out to be a useful shorthand. To characterize clusters we define the dimensionless quantity \( \delta \), namely the distance of the colloids from their cluster’s centre of mass in units of \( R_c \). For \( n = 2 \), \( \delta = \frac{w}{2} = 0.15 \), for \( n = 3 \), \( \delta = \frac{w}{\sqrt{3}} \simeq 0.17321 \); either way, \( \delta \ll a \). In terms of the small dimensionless parameter \( \delta \) the problem is reduced to calculating the potential energy between small particles distributions around some centres which are distant from each other. To do this we first expand the interaction between each pair of colloids belonging to two different clusters.
in Taylor series in $\delta$, i.e. for small distance from the respective cluster centre. When then we sum over all possible pairs we obtain a multipolar expansion of the cluster-cluster potential energy.

3 Small-Cluster Expansion

With reference to Fig. 2 we label with $i$ the colloids of the right cluster and with $j$ those of the left cluster ($i, j = 1, \ldots, n$) and take the line joining the two centres e.g. as the $x$ axis. The interaction is a function of the positions $r_i$ and $r'_j$ of the colloids relative to the corresponding centre. These are vectors of fixed length $\delta R_c$ forming angles $\theta_i$ and $\varphi_j$ with the $x$ axis, as shown in Fig. 2. The potential energy contribution of pair $i,j$ is then:

$$
\Phi_{ij}(\delta, \theta_i, \varphi_j) = \frac{E_0}{\left[(a + \delta \cos \theta_i - \delta \cos \varphi_j)^2 + (\delta \sin \theta_i - \delta \sin \varphi_j)^2\right]^3 + 1} + \frac{E_B}{\left[(a + \delta \cos \theta_i - \delta \cos \varphi_j)^2 + (\delta \sin \theta_i - \delta \sin \varphi_j)^2\right]^3}. \tag{2}
$$

It is convenient to introduce

$$
s = (a + \delta \cos \theta_i - \delta \cos \varphi_j)^2 + (\delta \sin \theta_i - \delta \sin \varphi_j)^2, \tag{3}
$$
the squared distance between the colloids in $R_c^2$ units. In terms of $s$:

$$
\Phi_{ij}(\delta, \theta_i, \varphi_j) = \Phi(\sqrt{s}R_c) = \Phi(s) = \frac{E_0}{s^3 + 1} + \frac{E_B}{s^3}.
$$

(4)

To proceed we expand the composite function $\Phi(s(\delta))$ to a sufficiently high order in $\delta$. This Taylor expansion involves derivatives evaluated at $\delta = 0$. For example, the first derivative has the form $\frac{d\Phi}{d\delta} \frac{ds}{d\delta}$. For the calculation of the second derivative we must derive both factors, taking into account that the first one is still a composite function. The derivatives of $s(\delta)$ are evaluated at $\delta = 0$, while the derivatives of $\Phi(s)$ are evaluated at $s = s(\delta = 0) = a^2$. In order to simplify the calculation, notice that $s(\delta)$ is a quadratic function of $\delta$. As a result,

$$
\frac{ds}{d\delta} (\delta = 0) = 2a (\cos \theta_i - \cos \varphi_j)
$$

$$
\frac{d^2s}{d\delta^2} (\delta = 0) = 4 \left( 1 - \cos \theta_i \cos \varphi_j - \sin \theta_i \sin \varphi_j \right),
$$

(5)

and all higher-order derivatives of $s(\delta)$ vanish.

Technically, to obtain the expansion for both the soft-core and the hard-core term in the potential energy it is sufficient to expand the function $f_{ij}^{E,p}(\delta) = \frac{E}{s^3(\delta)+p}$ treating $\tilde{E}$ and $p$ as parameters and then substituting them with $E_0$, 1 and $E_B$, 0 respectively. The result of the Taylor expansion for the pairwise colloid interaction up to sixth order is the following:

$$
\Phi_{ij}(\delta, \theta_i, \varphi_j) = c_0 + c_1 \delta^1 \left( \cos \theta_i - \cos \varphi_j \right)
$$

$$
+ c_{2,1} \delta^2 \left( \cos \theta_i - \cos \varphi_j \right)^2
$$

$$
+ c_{2,2} \delta^2 \left( 1 - \cos \theta_i \cos \varphi_j - \sin \theta_i \sin \varphi_j \right)
$$

$$
+ c_{3,1} \delta^3 \left( \cos \theta_i - \cos \varphi_j \right)^3
$$

$$
+ c_{3,2} \delta^3 \left( \cos \theta_i - \cos \varphi_j \right) \left( 1 - \cos \theta_i \cos \varphi_j - \sin \theta_i \sin \varphi_j \right)
$$

$$
+ c_{4,1} \delta^4 \left( \cos \theta_i - \cos \varphi_j \right)^4
$$

$$
+ c_{4,2} \delta^4 \left( \cos \theta_i - \cos \varphi_j \right)^2 \left( 1 - \cos \theta_i \cos \varphi_j - \sin \theta_i \sin \varphi_j \right)
$$

$$
+ c_{4,3} \delta^4 \left( 1 - \cos \theta_i \cos \varphi_j - \sin \theta_i \sin \varphi_j \right)^2
$$

$$
+ c_{5,1} \delta^5 \left( \cos \theta_i - \cos \varphi_j \right)^5
$$

$$
+ c_{5,2} \delta^5 \left( \cos \theta_i - \cos \varphi_j \right) \left( 1 - \cos \theta_i \cos \varphi_j - \sin \theta_i \sin \varphi_j \right)
$$

$$
+ c_{5,3} \delta^5 \left( \cos \theta_i - \cos \varphi_j \right) \left( 1 - \cos \theta_i \cos \varphi_j - \sin \theta_i \sin \varphi_j \right)^2
$$

$$
+ c_{6,1} \delta^6 \left( \cos \theta_i - \cos \varphi_j \right)^6
$$

$$
+ c_{6,2} \delta^6 \left( \cos \theta_i - \cos \varphi_j \right)^4 \left( 1 - \cos \theta_i \cos \varphi_j - \sin \theta_i \sin \varphi_j \right)
$$

$$
+ c_{6,3} \delta^6 \left( \cos \theta_i - \cos \varphi_j \right)^2 \left( 1 - \cos \theta_i \cos \varphi_j - \sin \theta_i \sin \varphi_j \right)^2
$$

$$
+ c_{6,4} \delta^6 \left( 1 - \cos \theta_i \cos \varphi_j - \sin \theta_i \sin \varphi_j \right)^3 + O(\delta^7).
$$

(6)
Here $c_h = c_h(a)$ are coefficients depending on the distance $aR_c$ between the two centres of mass and containing suitable combinations of energy derivatives evaluated at $\delta = 0$. Their expressions are reported in Table 1. The table also reports their values for $a = 1.5$ and the adopted hard-core parameter $E_B = 5 \times 10^{-5} E_0$.

The power $k$ of $\delta^k$ is the order of the corresponding term in the expansion, contributing to the $2^k$-pole. This means that the constant $\delta^0$ term gives the monopolar interaction (all the mass condensed at the centre), the one proportional to $\delta^1$ provides the dipolar interaction, those proportional to $\delta^2$ the quadrupolar terms, and so on.

We will use the expansion of Eq. (6) as the building block to construct the effective potential energy between clusters, which is obtained by summing over $i$ and $j = 1, ..., n$. Expansion (6) and the derived summations are approximate when the series is truncated to a finite order. We will later discuss the precision of this approximation.

For both $n$ values illustrated above the particles are positioned at equidistant points along a circumference, so their angular orientations are

$$\theta_i = \theta + \frac{2\pi}{n} i,$$
$$\varphi_j = \varphi + \frac{2\pi}{n} j,$$  

in terms of $\theta$ and $\varphi$ indicating the angular positions of an arbitrarily chosen particle (the cluster is invariant for rotations by integer multiples of $\frac{2\pi}{n}$) in each cluster. With these definitions we write the effective cluster-cluster interaction energy as

$$\Phi_{\text{eff}}(\delta, \theta, \varphi) = n \sum_{i=1}^{n} \sum_{j=1}^{n} \Phi_{ij}(\delta, \theta_i, \varphi_j).$$

When computing this double summation, a number of noteworthy simplifications occur. The following identities can be easily demonstrated for any integer $n$:

$$\sum_{i=1}^{n} \cos \theta_i = 0,$$  
$$\sum_{i=1}^{n} \sin \theta_i = 0.$$  

The sum in Eq. (9) appears in the $\delta^1$ term of Eq. (6), which therefore vanishes when summing. This reflects the obvious fact that these clusters have null dipolar moment in the expansion. Using Eq. (9) we can show that the term following the
Table 1: Energy coefficients $c_h = c_h(a)$ arising in the potential expansion \( \text{Eq. (6)} \), and their numerical values obtained for $a = 1.5$ and $E_B = 5 \times 10^{-5} E_0$.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Expression</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_0$</td>
<td>$E_0 \frac{1}{a^{3+1}} + E_B \frac{1}{a^7}$</td>
<td>0.0807157E0</td>
</tr>
<tr>
<td>$c_1$</td>
<td>$-6 \left[ E_0 \frac{a^2}{(a^6+1)^2} + E_B \frac{1}{a^7} \right] $</td>
<td>$-0.29678833E0$</td>
</tr>
<tr>
<td>$c_{2,1}$</td>
<td>$12 \left[ E_0 a^4 \frac{2a^6-1}{(a^6+1)^2} + 2E_B \frac{1}{a^7} \right] $</td>
<td>0.69563060E0</td>
</tr>
<tr>
<td>$c_{2,2}$</td>
<td>$-6 \left[ E_0 \frac{a^2}{(a^6+1)^2} + E_B \frac{1}{a^7} \right] $</td>
<td>$-0.19785888E0$</td>
</tr>
<tr>
<td>$c_{3,1}$</td>
<td>$-8 \left[ E_0 a^3 \frac{10a^{12} - 16a^6 + 1}{(a^6+1)^2} + 10E_B \frac{1}{a^7} \right] $</td>
<td>$-1.27871416E0$</td>
</tr>
<tr>
<td>$c_{3,2}$</td>
<td>$24 \left[ E_0 a^4 \frac{2a^6-1}{(a^6+1)^2} + 2E_B \frac{1}{a^7} \right] $</td>
<td>0.92750746E0</td>
</tr>
<tr>
<td>$c_{4,1}$</td>
<td>$48 \left[ E_0 a^8 \frac{5a^{12} - 17a^6 + 5}{(a^6+1)^2} + 5E_B \frac{1}{a^7} \right] $</td>
<td>2.03414534E0</td>
</tr>
<tr>
<td>$c_{4,2}$</td>
<td>$-24 \left[ E_0 a^2 \frac{10a^{12} - 16a^6 + 1}{(a^6+1)^2} + 10E_B \frac{1}{a^7} \right] $</td>
<td>$-2.55742832E0$</td>
</tr>
<tr>
<td>$c_{4,3}$</td>
<td>$12 \left[ E_0 a^2 \frac{2a^6-1}{(a^6+1)^2} + 2E_B \frac{1}{a^7} \right] $</td>
<td>0.30916915E0</td>
</tr>
<tr>
<td>$c_{5,1}$</td>
<td>$-96 \left[ E_0 a^7 \frac{7a^{18} - 42a^{12} + 30a^6 - 2}{(a^6+1)^2} + 7E_B \frac{1}{a^7} \right] $</td>
<td>$-2.37350206E0$</td>
</tr>
<tr>
<td>$c_{5,2}$</td>
<td>$192 \left[ E_0 a^2 \frac{7a^{12} - 17a^6 + 5}{(a^6+1)^2} + 7E_B \frac{1}{a^7} \right] $</td>
<td>5.16849863E0</td>
</tr>
<tr>
<td>$c_{5,3}$</td>
<td>$-24 \left[ E_0 a^2 \frac{10a^{12} - 16a^6 + 1}{(a^6+1)^2} + 10E_B \frac{1}{a^7} \right] $</td>
<td>$-1.70495221E0$</td>
</tr>
<tr>
<td>$c_{6,1}$</td>
<td>$64 \left[ E_0 a^{6} \frac{2a^{24} - 26a^{18} + 357a^{12} - 77a^6 + 1}{(a^6+1)^2} + 28E_B \frac{1}{a^7} \right] $</td>
<td>2.01150473E0</td>
</tr>
<tr>
<td>$c_{6,2}$</td>
<td>$-480 \left[ E_0 a^{6} \frac{7a^{18} - 42a^{12} + 30a^6 - 2}{(a^6+1)^2} + 7E_B \frac{1}{a^7} \right] $</td>
<td>$-7.91167352E0$</td>
</tr>
<tr>
<td>$c_{6,3}$</td>
<td>$288 \left[ E_0 a^{6} \frac{5a^{12} - 17a^6 + 5}{(a^6+1)^2} + 5E_B \frac{1}{a^7} \right] $</td>
<td>5.16849863E0</td>
</tr>
<tr>
<td>$c_{6,4}$</td>
<td>$-8 \left[ E_0 a^{6} \frac{10a^{12} - 16a^6 + 1}{(a^6+1)^2} + 10E_B \frac{1}{a^7} \right] $</td>
<td>$-0.37887827E0$</td>
</tr>
</tbody>
</table>
coefficient $c_{3,2}$ vanishes too when summing over $i$ and $j$, because it only contains terms proportional to either $\sum_{i=1}^{n} \cos \theta_i$ or $\sum_{j=1}^{n} \cos \varphi_j$:

$$\sum_{i=1}^{n} \sum_{j=1}^{n} (\cos \theta_i - \cos \varphi_j) (1 - \cos \theta_i \cos \varphi_j - \sin \theta_i \sin \varphi_j) =$$

$$\sum_{i=1}^{n} \sum_{j=1}^{n} (\cos \theta_i - \cos \varphi_j) - \sum_{i=1}^{n} \cos^2 \theta_i \sum_{j=1}^{n} \cos \varphi_j + \sum_{i=1}^{n} \cos \theta_i \sum_{j=1}^{n} \cos^2 \varphi_j$$

$$- \frac{1}{2} \sum_{i=1}^{n} \sin (2\theta_i) \sum_{j=1}^{n} \sin \varphi_j + \frac{1}{2} \sum_{i=1}^{n} \sin \theta_i \sum_{j=1}^{n} \sin (2\varphi_j) = 0. \quad (11)$$

For the same reason the term following the coefficient $c_{2,2}$ gives:

$$\sum_{i=1}^{n} \sum_{j=1}^{n} (1 - \cos \theta_i \cos \varphi_j - \sin \theta_i \sin \varphi_j) = n^2. \quad (12)$$

Applying Eq. (9) one can also easily see that the angle-dependent factor of the first non-constant term in the cluster-cluster interaction energy is

$$\sum_{i=1}^{n} \sum_{j=1}^{n} (\cos \theta_i - \cos \varphi_j)^2 = n \left( \sum_{i=1}^{n} \cos^2 \theta_i + \sum_{j=1}^{n} \cos^2 \varphi_j \right). \quad (13)$$

Consequently, the application of Eqs. (9) and (10) significantly simplifies the calculation of the sums in Eq. (8) to:

$$\Phi_{eff}(\theta, \varphi) = n^2 c_0 + nc_{2,1}\delta^2 \left( \sum_{i=1}^{n} \cos^2 \theta_i + \sum_{j=1}^{n} \cos^2 \varphi_j \right) + n^2 c_{2,2}\delta^2$$

$$+ \sum_{i=1}^{n} \sum_{j=1}^{n} \left[ c_{3,1}\delta^3 (\cos \theta_i - \cos \varphi_j)^3 + c_{4,1}\delta^4 (\cos \theta_i - \cos \varphi_j)^4 \right. \right.$$

$$+ c_{4,2}\delta^4 (\cos \theta_i - \cos \varphi_j)^2 (1 - \cos \theta_i \cos \varphi_j - \sin \theta_i \sin \varphi_j)$$

$$+ c_{4,3}\delta^4 (1 - \cos \theta_i \cos \varphi_j - \sin \theta_i \sin \varphi_j)^2$$

$$+ c_{5,1}\delta^5 (\cos \theta_i - \cos \varphi_j)^5$$

$$+ c_{5,2}\delta^5 (\cos \theta_i - \cos \varphi_j)^3 (1 - \cos \theta_i \cos \varphi_j - \sin \theta_i \sin \varphi_j)$$

$$+ c_{5,3}\delta^5 (\cos \theta_i - \cos \varphi_j) (1 - \cos \theta_i \cos \varphi_j - \sin \theta_i \sin \varphi_j)^2$$

$$+ c_{6,1}\delta^6 (\cos \theta_i - \cos \varphi_j)^6$$

$$+ c_{6,2}\delta^6 (\cos \theta_i - \cos \varphi_j)^4 (1 - \cos \theta_i \cos \varphi_j - \sin \theta_i \sin \varphi_j)$$

$$+ c_{6,3}\delta^6 (\cos \theta_i - \cos \varphi_j)^2 (1 - \cos \theta_i \cos \varphi_j - \sin \theta_i \sin \varphi_j)^2$$

$$+ c_{6,4}\delta^6 (1 - \cos \theta_i \cos \varphi_j - \sin \theta_i \sin \varphi_j)^3 + O(\delta^7) \right] . \quad (14)$$

We can obtain further simplifications for the two cluster shapes corresponding to $n = 2$ and $n = 3$. We now consider them separately and highlight which terms of Eq. (8) affect significantly the cluster mutual orientation.
\[ \varphi = \pi/2 \quad a = 1.5 \quad \theta = \pi/2 \]

(a)

\[ \varphi = \pi/3 \quad a = 1.5 \quad \theta = 0 \]

(b)

Figure 3: The optimal reciprocal orientation of two dimers (a) and two trimers (b) with fixed centres. Distances are in units of \(R_c\).

3.1 Dimers

Dimers consist of two colloids having opposite angular orientations. The following relation holds:

\[ \sum_{i=1}^{2} \cos^{l_1} \theta_i \sin^{l_2} \theta_i = 0, \]

(15)

where \(l_1\) and \(l_2\) are nonnegative integers such that \(l_1 + l_2\) is odd. As a consequence, sums over \(i\) and \(j\) of all odd-order terms in Eq. (14) vanish.

We also observe that

\[ \sum_{i=1}^{2} \cos^2 \theta_i = 2 \cos^2 \theta \]

(16)

\[ \sum_{i=1}^{2} \sin^2 \theta_i = 2 \sin^2 \theta \]

(17)

\[ \sum_{i=1}^{2} \cos^4 \theta_i = 2 \cos^4 \theta \]

(18)

\[ \sum_{i=1}^{2} \sin (2 \theta_i) = 2 \sin (2 \theta) \]

(19)

Using Eq. (16), the \(\delta^2\) term of Eq. (14) can be written as

\[ 4c_{2,1} \delta^2 (\cos^2 \theta + \cos^2 \varphi) \]

(20)
since two angles that differ by $\pi$ have opposite cosines. This is the dominant angle-dependent term in the effective interaction energy, because it is the leading non-zero term. The two cosines in Eq. (20) affect independently the orientation of the two dimers. As $c_{2,1}$ is positive, their sum is zero when both $\theta$ and $\varphi$ measure $\frac{\pi}{2} + n\pi$, for other angles it is positive. This means that if we consider only two dimers with fixed centres, the most energetically convenient arrangement for them is to stay perpendicular to the line joining the centres, as shown in Fig. 3a. This is the effect of the leading quadrupole moment, neglecting higher-order interactions, which are smaller. At this leading order the potential-energy terms are of quadrupole-monopole type, and thus depend on the orientation of each single cluster independently. All other second-order dipole-dipole coupling terms, proportional to the product $\cos \theta_i \cos \varphi_j$, vanish once we sum on $i$ and $j$, as discussed above.

Using Eqs. (15) and (16)-(19), we can simplify the general expansion for the effective cluster-cluster interaction Eq. (14) to

$$\Phi_{dd}(\delta, \theta, \varphi) = 4 \left[ c_{2,1} \delta^2 (\cos^2 \theta + \cos^2 \varphi) 
+ (6c_{4,1} + 2c_{4,2} + c_{4,3}) \delta^4 \cos^2 \theta \cos^2 \varphi 
+ c_{4,3} \delta^4 \sin^2 \theta \sin^2 \varphi 
+ \frac{1}{2} (c_{4,2} + c_{4,3}) \delta^4 \sin(2\theta) \sin(2\varphi) 
+ c_{4,1} \delta^4 (\cos^4 \theta + \cos^4 \varphi) + c_{4,2} \delta^4 (\cos^2 \theta + \cos^2 \varphi) 
+ (6c_{6,2} + 4c_{6,3} + 3c_{6,4}) \delta^6 \cos^2 \theta \cos^2 \varphi 
+ 3c_{6,4} \delta^6 \sin^2 \theta \sin^2 \varphi 
+ \frac{1}{2} (2c_{6,3} + 3c_{6,4}) \delta^6 \sin(2\theta) \sin(2\varphi) 
+ (15c_{6,1} + 4c_{6,2} + c_{6,3}) \delta^6 (\cos^4 \theta \cos^2 \varphi + \cos^2 \theta \cos^4 \varphi) 
+ 2 (2c_{6,2} + c_{6,3}) \delta^6 (\cos^3 \theta \sin \theta \cos \varphi \sin \varphi + \cos \theta \sin \theta \cos^3 \varphi \sin \varphi) 
+ c_{6,1} \delta^6 (\cos^6 \theta + \cos^6 \varphi) + c_{6,2} \delta^6 (\cos^4 \theta + \cos^4 \varphi) 
+ c_{6,3} \delta^6 (\cos^2 \theta + \cos^2 \varphi + \cos^2 \theta \sin^2 \varphi + \sin^2 \theta \cos^2 \varphi \sin^2 \varphi) \right] + E_{dd}^{\text{ave}} + O(\delta^7), \tag{21}$$

for the case of two dimers. Here

$$E_{dd}^{\text{ave}} = 4 \left( c_0 + c_{2,2} \delta^2 + c_{4,3} \delta^4 + c_{6,4} \delta^6 \right) \tag{22}$$

collects the angle-independent terms, which are irrelevant for the clusters’ rotational dynamics.

Further simplifications occur when we put several dimers in a periodic crystal. This can be modelled e.g. with a supercell to which suitable periodic boundary conditions are applied. We consider a triangular lattice crystal and use a
Figure 4: Scheme of a $6 \times 6$ dimers cell, with the lattice generators, $a_1$ and $a_2$, and clusters' nearest neighbours. A symbolic notation with exponents labelling a cluster's nns is used (see page 14).

parallelogram-shaped supercell. The sides of the supercell are the vectors $N_1 a_1$ and $N_2 a_2$, $a_1$ and $a_2$ being the triangular lattice primitive vectors: $a_1 = a R_c \left( \frac{1}{2} \right)$, $a_2 = a R_c \left( \frac{1}{\sqrt{3}} \right)$. The supercell contains therefore $N = N_1 \cdot N_2$ clusters, numbered as in Fig. 4, where we show a cell with $N_1 = N_2 = 6$. Periodic boundary conditions allow us to simulate an infinitely wide plan. The supercell is reproduced through discrete translations of $m_1 N_1 a_1 + m_2 N_2 a_2$, where $m_1$ and $m_2$ are any integers, in order to cover the whole plan.

In our model the cluster centres are fixed at the lattice sites. Therefore, each cluster has one degree of freedom, namely its angular orientation, which affects the potential energy of the supercell. A crucial approximation that we make is to consider only the interactions with the six nearest neighbours (which we will shorten to "nns"), since the intensity decreases very rapidly with the distance ($\frac{1}{r^6}$). This is equivalent to setting a cutoff radius for the colloid-colloid interaction at $\frac{1}{R_c} \approx 2$.

We have previously seen that the energy contributions which determines
the orientation of a dimer when it sits close to another is proportional to $\cos^2 \theta$. However, once the dimer is surrounded by several others located at the sites of a triangular lattice we have to sum the contributions of the interaction energy with all of them. Let us consider one dimer and label with $\eta$ ($\eta = 0, ..., 5$) its nns. We introduce

$$ \theta^n = \theta - \frac{\pi}{3} \eta, \quad (23) $$

namely the orientation angles of the cluster relative to the individual bonds to its nns, as a function of $\theta$, the angle formed with the $x$ axis, assumed to be one of the primitive directions of the hexagonal lattice. This definition is necessary since, we recall, angles in all previous expansions including Eq. (21) are relative to the bond direction. Observing that

$$ \sum_{\eta=0}^{5} \cos^2 \theta^n = 3, \quad (24) $$

we conclude that the sum over nns of the quadrupolar term of Eq. (20) does not depend on the dimer’s orientation in the hexagonal lattice, but it only adds a contribution to $E_{d-tot}^{ave}$. At the quadrupolar order the dimers’ orientation does not influence the total energy, hence we need to consider higher-order terms, namely the hexadecapole, as we have already shown that the third-order octupole terms vanish. At order $\delta^4$ we finally find some non-null coupling terms, which affect the mutual cluster orientations in the lattice.

The total energy of the supercell is the sum of Eq. (21) on all the possible pairs of nn clusters. Instead of summing on all nns of each cluster and then dividing the result by two, in order not to consider each “bond” twice, we can pretend that each cluster interacts only with three nns, drawn in Fig. 4. Here cluster number 8 interacts with numbers 9, 14 and 13 and its other three bonds are accounted for when considering the interactions originated from clusters 7, 2 and 3. We label the three nns of cluster number $\sigma$ with $\sigma^n$, $\eta = 0, 1, 2$. For a generic cluster at the middle of the supercell, $\sigma^0 = \sigma + 1$, $\sigma^1 = \sigma + N_1$ and $\sigma^2 = \sigma + N_1 - 1$. These simple rules do not hold when $\sigma$ is at the boundary of the supercell, because in this case one has to take into account the boundary conditions: the cell adjoins other identical cells, thus the cluster interacts with one at the opposite border. For example, in Fig. 4 the nns of cluster 6 are clusters 1, 12, 11. Having named $\theta_\sigma$, $\sigma = 1, ..., N$, the absolute angle of the $\sigma$-th cluster
measured from the fixed x axis, the supercell energy $E_{d}^{\text{tot}}$ is calculated as follows:

$$E_{d}^{\text{tot}}(\theta_1, \ldots, \theta_N) = \sum_{\sigma=1}^{N} \sum_{\eta=0}^{2} \Phi_{\sigma\eta}(\theta_{\sigma}^\eta, \theta_{\sigma}^\eta) =$$

$$\sum_{\sigma=1}^{N} \sum_{\eta=0}^{2} 4 \left[ (6c_{4,1} + 2c_{4,2} + c_{4,3}) \delta^4 \cos^2 \theta_{\sigma}^\eta \cos^2 \theta_{\sigma}^\eta 
+ c_{4,3} \delta^4 \sin^2 \theta_{\sigma}^\eta \sin^2 \theta_{\sigma}^\eta 
+ \frac{1}{2} (c_{4,2} + c_{4,3}) \delta^4 \sin (2\theta_{\sigma}^\eta) \sin (2\theta_{\sigma}^\eta) 
+ (6c_{6,2} + 4c_{6,3} + 3c_{6,4}) \delta^6 \cos^2 \theta_{\sigma}^\eta \cos^2 \theta_{\sigma}^\eta 
+ 3c_{6,4} \delta^6 \sin^2 \theta_{\sigma}^\eta \sin^2 \theta_{\sigma}^\eta 
+ \frac{1}{2} (2c_{6,3} + 3c_{6,4}) \delta^6 \sin (2\theta_{\sigma}^\eta) \sin (2\theta_{\sigma}^\eta) 
+ (15c_{6,1} + 4c_{6,2} + c_{6,3}) \delta^6 
(\cos^4 \theta_{\sigma}^\eta \cos^2 \theta_{\sigma}^\eta + \cos^2 \theta_{\sigma}^\eta \cos^4 \theta_{\sigma}^\eta) 
+ 2 (2c_{6,2} + c_{6,3}) \delta^6 
(\cos^3 \theta_{\sigma}^\eta \sin \theta_{\sigma}^\eta \cos \theta_{\sigma}^\eta, \sin \theta_{\sigma}^\eta \sin \theta_{\sigma}^\eta \sin \theta_{\sigma}^\eta \sin \theta_{\sigma}^\eta) 
+ c_{6,3} \delta^6 (\cos^2 \theta_{\sigma}^\eta \sin^2 \theta_{\sigma}^\eta \sin^2 \theta_{\sigma}^\eta \sin^2 \theta_{\sigma}^\eta + \sin^2 \theta_{\sigma}^\eta \cos^2 \theta_{\sigma}^\eta \sin^2 \theta_{\sigma}^\eta \sin^2 \theta_{\sigma}^\eta) \right]$$

$$+ \frac{3}{4} c_{6,1} \delta^6 \sum_{\sigma=1}^{N} \cos (6\theta_{\sigma}) + E_{d-\text{tot}}^{\text{ave}} + O(\delta^7) , \quad (25)$$

where

$$E_{d-\text{tot}}^{\text{ave}} = N \left[ 12c_0 + 12 (c_{2,1} + c_{2,2}) \delta^2 + (9c_{4,1} + 12c_{4,2} + 12c_{4,3}) \delta^4 
+ \left( \frac{15}{2} c_{6,1} + 9c_{6,2} + 12c_{6,3} + 12c_{6,4} \right) \delta^6 \right] . \quad (26)$$

In Eq. (25) the subscript on angles indicates which cluster we are considering, while the superscript $\eta$, $\eta = 0, 1, 2$, indicates which bond the angle is measured from, according to Eq. (23). To obtain Eq. (25) we have used

$$\sum_{\eta=0}^{2} \cos^2 \theta_{\sigma}^\eta = \frac{3}{2} \quad (27)$$

$$\sum_{\eta=0}^{2} \cos^4 \theta_{\sigma}^\eta = \frac{9}{8} \quad (28)$$

$$\sum_{\eta=0}^{2} \cos^6 \theta_{\sigma}^\eta = \frac{3}{32} \left[ \cos (6\theta) + 10 \right] . \quad (29)$$

These identities allow us to make a few simplifications, considering that each cluster is the origin of three bonds and is involved in other three bonds originated
from other clusters. Its angle is measured relatively to a direction increasing by \(\frac{\pi}{3}\) each time, so Eqs. (27), (28) and (29) can be applied to each three bonds. As a result,

\[
\sum_{s=1}^{N} \sum_{\eta=0}^{2} \left( \cos^{2} \theta_{s}^{\eta} + \cos^{2} \theta_{s}^{\eta} \right) = 3N
\]

\[
\sum_{s=1}^{N} \sum_{\eta=0}^{2} \left( \cos^{4} \theta_{s}^{\eta} + \cos^{4} \theta_{s}^{\eta} \right) = \frac{9}{4}N
\]

\[
\sum_{s=1}^{N} \sum_{\eta=0}^{2} \left( \cos^{6} \theta_{s}^{\eta} + \cos^{6} \theta_{s}^{\eta} \right) = \sum_{s=1}^{N} \frac{3}{16} \left[ \cos (6\theta_{s}) + 10 \right]. \tag{30}
\]

In order to remove the angles superscript \(\eta\) at least from the leading fourth-order terms of Eq. (25) and from certain \(\delta^{6}\) terms (to have angles measured from the \(x\) axis), we introduce the following symbols, where it is understood that the first, second and third entry of each set in the right-hand side refers to \(\eta = 0, 1, 2\) respectively:

\[
\chi_{11\eta} = \left( 0, \frac{3}{4}, \frac{3}{4} \right) \quad \chi_{12\eta} = \left( 0, -\frac{\sqrt{3}}{4}, \frac{\sqrt{3}}{4} \right)
\]

\[
\chi_{21\eta} = \left( 0, -\frac{\sqrt{3}}{4}, \frac{\sqrt{3}}{4} \right) \quad \chi_{22\eta} = \left( 1, \frac{1}{4}, \frac{1}{4} \right)
\]

\[
\chi'_{11\eta} = \left( 1, \frac{1}{4}, \frac{1}{4} \right) \quad \chi'_{12\eta} = \left( 0, \frac{\sqrt{3}}{4}, -\frac{\sqrt{3}}{4} \right)
\]

\[
\chi'_{21\eta} = \left( 0, \frac{\sqrt{3}}{4}, -\frac{\sqrt{3}}{4} \right) \quad \chi'_{22\eta} = \left( 0, \frac{3}{4}, \frac{3}{4} \right). \tag{31}
\]

We also define the functions:

\[
f^{1}(x) = \sin (2x)
\]

\[
f^{2}(x) = \cos (2x). \tag{33}
\]

Using these and recalling the trigonometric identities \(\cos^{2} \theta = \frac{1}{2} [1 + \cos (2\theta)]\),
\[
\sin^2 \theta = \frac{1}{2} [1 - \cos (2\theta)],
\]
we can express the total energy as:

\[
E_{\text{d}}^{\text{tot}} (\theta_1, \ldots, \theta_N) = \sum_{\sigma=1}^{N} \left\{ \sum_{\alpha=1}^{2} \sum_{\beta=1}^{2} \sum_{\eta=0}^{2} \left[ \frac{1}{4} \left\{ (6c_{4,1} + 2c_{4,2} + 2c_{4,3}) \delta^4 \chi_{\alpha\beta\eta} f^{\alpha} (\theta_\sigma) f^{\beta} (\theta_{\sigma\eta}) + 2 (c_{4,2} + c_{4,3}) \delta^4 \chi_{\alpha'\beta\eta}' f^{\alpha} (\theta_\sigma) f^{\beta} (\theta_{\sigma\eta}) + (30c_{6,1} + 14c_{6,2} + 10c_{6,3} + 2c_{6,4}) \delta^6 \chi_{\alpha\beta\eta} f^{\alpha} (\theta_\sigma) f^{\beta} (\theta_{\sigma\eta}) + (4c_{6,2} + 5c_{6,3} + 6c_{6,4}) \delta^6 \chi_{\alpha\beta\eta} f^{\alpha} (\theta_\sigma) f^{\beta} (\theta_{\sigma\eta}) \right] \right. \\
\left. + \sum_{\eta=0}^{2} \delta^6 \left( \frac{105}{4} c_{6,1} + 7c_{6,2} + \frac{3}{2} c_{6,3} \right) \cos (2\theta_{\sigma}) + \cos (2\theta_{\sigma\eta}) \right) \right. \\
+ \left. \left( \frac{15}{4} c_{6,1} + c_{6,2} \right) \cos (4\theta_{\sigma}) + \cos (4\theta_{\sigma\eta}) \right) \\
+ \left. \left( \frac{15}{4} c_{6,1} + c_{6,2} + \frac{1}{2} c_{6,3} \right) \cos (4\theta_{\sigma}) \cos (2\theta_{\sigma\eta}) + \cos (2\theta_{\sigma}) \cos (4\theta_{\sigma\eta}) \right) \\
+ \left. \left( c_{6,2} + \frac{1}{2} c_{6,3} \right) \sin (4\theta_{\sigma}) \sin (2\theta_{\sigma\eta}) + \sin (2\theta_{\sigma}) \sin (4\theta_{\sigma\eta}) \right) \right\} + \sum_{\sigma=1}^{N} \cos (6\theta_{\sigma}) + E_{\text{d-tot}}^{\text{ave}} + O(\delta^7),
\]

where \(E_{\text{d-tot}}^{\text{ave}}\) absorbs a few more constant terms:

\[
E_{\text{d-tot}}^{\text{ave}} = N \left[ 12c_0 + 12 (c_{2,1} + c_{2,2}) \delta^2 + (27c_{4,1} + 18c_{4,2} + 18c_{4,3}) \delta^4 \right.
\]
\[
+ (30c_{6,1} + 33c_{6,2} + 26c_{6,3} + 30c_{6,4}) \delta^6 \right].
\]

Executing sums over \(\alpha\), \(\beta\) and \(\eta\) and rearranging the terms leads to the expression:

\[
E_{\text{d}}^{\text{tot}} (\theta_1, \ldots, \theta_N) = \sum_{\sigma=1}^{N} \sum_{\eta=0}^{2} \left\{ \delta^4 \left[ D_1 \cos (2\theta_\sigma - 2\theta_{\sigma\eta}) + D_2 \cos (2\theta_\sigma + 2\theta_{\sigma\eta} + \frac{2\pi}{3} \eta) \right] \\
+ \delta^6 \left[ D_3 \cos (2\theta_\sigma - 2\theta_{\sigma\eta}) + D_4 \cos (2\theta_\sigma + 2\theta_{\sigma\eta} + \frac{2\pi}{3} \eta) \right] \\
+ D_5 (\cos (2\theta_{\sigma}) + \cos (2\theta_{\sigma\eta})) + D_6 (\cos (4\theta_{\sigma}) + \cos (4\theta_{\sigma\eta})) \\
+ D_7 (\cos (4\theta_{\sigma} - 2\theta_{\sigma\eta}) + \cos (2\theta_{\sigma} - 4\theta_{\sigma\eta})) \\
+ D_8 (\cos (4\theta_{\sigma} + 2\theta_{\sigma\eta}) + \cos (2\theta_{\sigma} + 4\theta_{\sigma\eta})) \right\} \right\} + \sum_{\sigma=1}^{N} \cos (6\theta_{\sigma}) + E_{\text{d-tot}}^{\text{ave}} + O(\delta^7).
\]
Where we have defined the coefficients:

\[ D_1 = 3c_{4,1} + 2c_{4,2} + 2c_{4,3} = 1.60591768E_0 \]
\[ D_2 = 3c_{4,1} = 6.10243602E_0 \]
\[ D_3 = 15c_{6,1} + 9c_{6,2} + \frac{15}{2}c_{6,3} + 4c_{6,4} = 3.78426408E_0 \]
\[ D_4 = 15c_{6,1} + 5c_{6,2} + \frac{5}{2}c_{6,3} - 2c_{6,4} = 4.29320647E_0 \]
\[ D_5 = \frac{105}{4}c_{6,1} + 7c_{6,2} + \frac{3}{2}c_{6,3} = 5.17303247E_0 \]
\[ D_6 = \frac{15}{4}c_{6,1} + c_{6,2} = -0.36853078E_0 \]
\[ D_7 = \frac{15}{8}c_{6,1} + c_{6,2} + \frac{1}{2}c_{6,3} = -1.55585284E_0 \]
\[ D_8 = \frac{15}{8}c_{6,1} = 3.77157137E_0 \]
\[ D_9 = \frac{3}{4}c_{6,1} = 1.508628549E_0 , \quad (37) \]

whose numerical values are obtained from Table [1].

We now focus on the leading \( \delta^4 \) terms. The \( D_2 \) term in Eq. (36), which has the largest coefficient, is minimum for \( \theta_\sigma + \theta_{\sigma'} = \frac{\pi}{2} - \frac{\pi}{3} \eta + l\pi \). The \( D_1 \) term is minimum for \( \theta_\sigma - \theta_{\sigma'} = \frac{\pi}{2} + l\pi \). One simple configuration, for three clusters, which satisfies

\[
\begin{align*}
\cos (2\theta_\sigma + 2\theta_{\sigma'}) &= -1 \\
\cos (2\theta_\sigma - 2\theta_{\sigma'}) &= -1 \\
\cos (2\theta_\sigma - 2\theta_{\sigma'}) &= -1 
\end{align*}
\]

and can be replicated for the whole lattice is: \( \theta_\sigma = \frac{\pi}{4} \), \( \theta_{\sigma'} = \frac{\pi}{4} \), \( \theta_{\sigma'} = -\frac{\pi}{4} \), \( \theta_{\sigma} = -\frac{\pi}{4} \). Other equivalent configurations are obtained by rotating the three superscripts in Eq. (38) and adding to \( 2\theta_\sigma + 2\theta_{\sigma'} \) the corresponding angular increment \( +\frac{2\pi}{3} \eta \).
3.2 Trimers

The calculation gives even more simplifications for clusters of three colloids located at the vertices of an equilateral triangle. Relevant relations include:

\[
\begin{align*}
\sum_{i=1}^{3} \cos^{2} \theta_i &= \frac{3}{2} \\
\sum_{i=1}^{3} \sin^{2} \theta_i &= \frac{3}{2} \\
\sum_{i=1}^{3} \cos^{4} \theta_i &= \frac{9}{8} \\
\frac{1}{2} \sum_{i=1}^{3} \sin (2\theta_i) &= 0,
\end{align*}
\]

where \( \theta_i \) is given in Eq. (7). Using Eq. (9) and (39), we immediately notice that the sums of all terms up to fourth order in the potential energy Eq. (14) are constant apart from the one proportional to \((\cos \theta_i - \cos \varphi_j)^3\). When we study this term, though, we find a similar result as we had with \((\cos \theta_i - \cos \varphi_j)^2\) for dimers. Indeed, using Eq. (9) and the definition Eq. (23):

\[
\begin{align*}
\sum_{i=1}^{3} \sum_{j=1}^{3} (\cos \theta_i - \cos \varphi_j)^3 &= \sum_{i=1}^{3} \cos^{3} \theta_i - \sum_{j=1}^{3} \cos^{3} \varphi_j \\
&= \frac{3}{4} \cos (3\theta) - \frac{3}{4} \cos (3\varphi).
\end{align*}
\]

This expression is still uncoupled and has a maximum (thus the energy term has a minimum because its coefficient \(c_{3,1}\) is negative as we see in Table 1) for \( \theta = \frac{2\pi}{3} l, \varphi = \frac{\pi}{3} + \frac{2\pi}{3} l \), which means that for two trimers close to each other, this octupole-monopole interaction favours the orientation shown in Fig. 3b.

Using the identities:

\[
\begin{align*}
\sum_{i=1}^{3} \cos \theta_i \sin \theta_i &= 0 \\
\sum_{i=1}^{3} \sin^{3} \theta_i &= -\frac{3}{4} \sin (3\theta) \\
\sum_{i=1}^{3} \cos^{2} \theta_i \sin \theta_i &= \frac{3}{4} \sin (3\theta) \\
\sum_{i=1}^{3} \cos^{5} \theta_i &= \frac{15}{16} \cos (3\theta) \\
\sum_{i=1}^{3} \cos \theta_i \sin^{2} \theta_i &= -\frac{3}{4} \cos (3\theta) \\
\sum_{i=1}^{3} \cos^{6} \theta_i &= \frac{3}{32} \left[ \cos (6\theta) + 10 \right],
\end{align*}
\]

and recalling Eq. (39) and (40), we find that the trimer-trimer interaction energy
\[ \Phi_{tt}(\delta, \theta, \varphi) = \frac{3}{4} c_{3,1} \delta^3 [\cos (3\theta) - \cos (3\varphi)] \\
+ \left( \frac{225}{16} c_{5,1} + \frac{45}{8} c_{5,2} \right) \delta^5 [\cos (3\theta) - \cos (3\varphi)] \\
- \frac{9}{4} \left( 5 c_{6,1} + \frac{3}{2} c_{6,2} + c_{6,3} + c_{6,4} \right) \delta^6 \cos (3\theta) \cos (3\varphi) \\
- \frac{9}{4} \left( \frac{3}{2} c_{6,2} + c_{6,3} + c_{6,4} \right) \delta^6 \sin (3\theta) \sin (3\varphi) \\
+ \frac{9}{32} c_{6,1} \delta^6 [\cos (6\theta) + \cos (6\varphi)] \\
+E_{tt}^{ave} + O(\delta^7). \]  

Where

\[ E_{tt}^{ave} = 9c_0 + 9 (c_{2,1} + c_{2,2}) \delta^2 + \frac{27}{2} \left( \frac{3}{2} c_{4,1} + c_{4,2} + c_{4,3} \right) \delta^4 \\
+ \frac{45}{2} \left( \frac{5}{2} c_{6,1} + \frac{3}{2} c_{6,2} + c_{6,3} + c_{6,4} \right) \delta^6 \]  

again contains the constant terms.

We now consider only the first term in the right member of Eq. (40), but the consideration that follows is valid for the second one as well. A cluster in a triangular lattice is surrounded by six nns in pairs with opposite directions. If we consider its interactions with two opposite nns, as in Fig. 5, the line joining the centres is the same but with opposite orientation. \( \cos (3\theta) \) is an odd function under the shift \( \theta \mapsto \theta + \pi \), thus the energy terms proportional to \( \cos (3\theta) \) are opposite for these two bonds. For any bond between nn clusters we find another bond which brings an opposite energy contribution to \( E^{tot} \).

As a result, the overall contribution of these octupole-monopole terms to the total energy of the cell vanishes. The same sign change affects every combination \( \left( \sum_{i=1}^{3} \cos^{l_1} \theta_i \right) \left( \sum_{i=1}^{3} \sin^{l_2} \theta_i \right) \) with odd \( l_1 + l_2 \). For this reason all multipolar terms up to \( \delta^5 \) vanish in the lattice. Indeed, also fifth-order coupling terms can be shown to lead to vanishing sums and the uncoupled ones appear with opposite sign for \( \theta \) and \( \varphi \). Using this fact, we can sum on all pairs of nns to calculate the
Figure 5: The angles of orientation of a cluster with respect to two opposite nearest neighbours, which make term in Eq. (40) bring null contribution to the supercell energy.

Energy $E_{t\text{-tot}}$ of the supercell:

$$E_{t\text{-tot}}(\theta_1, \ldots, \theta_N) = \sum_{\sigma=1}^{N} \sum_{\eta=0}^{2} \Phi_{\sigma\eta}(\theta_{\sigma}^{\eta}, \theta_{\eta}^{\sigma}) =$$

$$\sum_{\sigma=1}^{N} \sum_{\eta=0}^{2} \delta^6 \left\{ F_1 \cos (3\theta_{\sigma} - 3\theta_{\sigma\eta}) ight. + F_2 \cos (3\theta_{\sigma} + 3\theta_{\sigma\eta}) \\ + F_3 \left[ \cos (6\theta_{\sigma}) + \cos (6\theta_{\sigma\eta}) \right] \} + E_{t\text{-ave}} + O(\delta^7), \quad (44)$$

where

$$E_{t\text{-ave}} = N \left[ 27c_0 + 27(c_{2,1} + c_{2,2}) \delta^2 + \frac{81}{2} \left( \frac{3}{2} c_{4,1} + c_{4,2} + c_{4,3} \right) \delta^4 \right. + \frac{135}{2} \left( \frac{5}{2} c_{6,1} + \frac{3}{2} c_{6,2} + c_{6,3} + c_{6,4} \right) \delta^6 \right]. \quad (45)$$
In Eq. (44) we have removed the superscript η from angles, because it only adds multiples of 2\(\pi\) to the argument of cosines. This means that angles are now measured relatively to the \(x\) axis. From Table 1 we obtain the numerical values for the coefficients:

\[
F_1 = -\frac{9}{4} \left( \frac{5}{2} c_{6,1} + \frac{3}{2} c_{6,2} + c_{6,3} + c_{6,4} \right) = 4.61053821 E_0 \tag{46}
\]

\[
F_2 = -\frac{45}{8} c_{6,1} = -11.31471412 E_0 \tag{47}
\]

\[
F_3 = \frac{9}{32} c_{6,1} = 0.56573571 E_0. \tag{48}
\]

Eq. (44) is the function we need to minimize in order to find the static ground-state configuration.

If we analyse the \(\delta^6\) terms in Eq. (44) we notice that \(\cos (3\theta_\sigma - 3\theta_{\sigma'})\), whose coefficient, Eq. (46), is positive, favours a relative orientation: \(\theta_\sigma - \theta_{\sigma'} = \frac{\pi}{3} + \frac{2\pi}{3} l\). \(\cos (3\theta_\sigma + 3\theta_{\sigma'})\) is preceded by a larger negative coefficient \(F_2\), Eq. (47), so it favours \(\theta_\sigma + \theta_{\sigma'} = \frac{2\pi}{3} l\), which corresponds to an opposite-angle mutual orientation. In fact, this antiferro-orientational tendency is frustrated by the tripartite lattice structure. Indeed, a triangular lattice cannot support a global configuration with antiparallel spins. The last term, whose coefficient, Eq. (48), is small and positive, tends to orient each cluster to \(\theta_\sigma = \frac{\pi}{6} + \frac{\pi}{3} l\). These competing interactions of the same \(\delta^6\) order lead therefore to non-trivial ground states.

4 Numerical Analysis

To minimize the total supercell potential energy for dimers, Eq. (34), and trimers, Eq. (44) as a function of all angles \(\theta_1, ..., \theta_N\), we use the downhill simplex method in multidimensions described in Ref. [7]. The advantage of this algorithm is that it does not require evaluations of the gradient of the function, thus we do not need to calculate the partial derivatives of \(E_{\text{tot}}\) with respect to the clusters angles. It is also self-contained and can be implemented in relatively few lines of code. On the downside, it converges slowly, requiring a rather high number of function evaluations. It is though quickly ready and useful to solve problems of relatively small dimensions. Hence the necessity to limit the dimensions of the supercell to \(8 \times 8\) or smaller, in order to have the algorithm working in a reasonable time and give reliable results. We ran tests with different cell sizes and analysed the variation of the minimum energy per particle when increasing the size up to \(8 \times 8\). Based on these results we also discuss what to expect from larger cells.

It is clear that fixing the supercell shape constrains the periodicity of the patterns that can form and can determine further limitations to the angular pat-
tern, which has non-trivial effects if the dimensions of the cell do not match those of the optimal patterns that would arise in the limit of an infinite-size supercell. By comparing the minimum energies for different cells we try to recognise which patterns are favoured and hopefully identify a possible best primitive cell.

An issue to deal with is that the simplex minimization does not ensure us to find a global minimum, but it can easily remain trapped in a local one. We get around this problem by running several tests with different randomly generated starting configurations, since the algorithm requires a set of \( N + 1 \) starting points in the \( N \)-dimensions space, the vertices of the geometrical simplex. If all these minimizations lead to the same minimum energy value, we take it as the ground-state energy, otherwise we take the lowest value from a wide enough set of minimizations.

4.1 Minimization

We have realised a c++ program that, given \( n = 2 \) or 3 and the values of \( N_1 \) and \( N_2 \), creates a starting simplex, consisting of \( N + 1 \) randomly chosen points in the space of \((\theta_1, \ldots, \theta_N)\) vectors. The simplex algorithm then minimizes the function \( E_{\text{tot}}(\theta_1, \ldots, \theta_N) \), evaluated for \( a = 1.5 \), returning the minimum energy and the angular configuration for which it is realised. The total energy is calculated according to Eq. (34) or (44), taking the periodic boundary conditions. \( E_{\text{tot}}(\theta_1, \ldots, \theta_N) \) only includes the potential energy between nn clusters, excluding the trivial (large but constant) energy

\[
E_{\text{cluster}} = \frac{1}{2}n(n-1)N \left( \frac{E_0}{w^6 + 1} + \frac{E_B}{w^6} \right),
\]

(49)
giving the colloid-colloid repulsion within clusters. This clusters formation energy (equal to 0.53392931834 \( n(n-1)NE_0 \) for the standard values \( w = 0.3, E_B = 5 \times 10^{-5}E_0 \)) can be added later, as it does not need to be minimized.

4.1.1 Dimers

For a \( 2 \times 2 \) supercell of dimers, several minimizations with different randomly generated starting configurations always return a ground-state energy per particle \( E = 1.08494289507E_0 \) and six equivalent angular configurations, shown in Fig. 6.

We notice that these configurations all display a herringbone ordering and differ from each other only for a \( \frac{\pi}{3} \) or \( \frac{2\pi}{3} \) rotation of the whole system around a lattice site and a reflection. In particular, in Fig. 6a, 6c and 6e we can identify rows of parallel dimers oriented along the three different directions of translational symmetry of the lattice, while Fig. 6a, 6d and 6f are obtained from
Figure 6: The six symmetry-equivalent ground-state configurations for a $2 \times 2$ dimers cell, corresponding to a ground-state energy per particle $E = 1.08494289507E_0$. 
them respectively through a reflection relative to the direction perpendicular to these rows. This sixfold degeneration in the ground state is due to the symmetry of the triangular lattice under rotations of $\frac{\pi}{3}l$, where $l = 0, 1, 2$ rather than $l = 0, ..., 5$ because a rotation by $\pi$ transforms the pattern back into itself, and under reflections with respect to the $y$ axis. Rows consist of dimers with two different orientations, nearly perpendicular to each other. Dimers in contiguous rows form angles of $\pm \bar{\theta}$, $\bar{\theta} = 44.4870^\circ$, with their row direction.

For a $3 \times 3$ cell the lowest energy per particle is $E = 1.08610917754E_0$, larger than for the $2 \times 2$ cell. This energy occurs for several symmetry-equivalent angular configurations, two of which are reported in Fig. 7.

$4 \times 4$, $6 \times 6$ and $8 \times 8$ cells in the ground state consist in repetitions of a $2 \times 2$ cell and their energy per particle is again $E = 1.08494289507E_0$.

Starting from $5 \times 5$ several minimizations made with the same parameters

Table 2: Minimum energies for cell size from $2 \times 2$ to $8 \times 8$ for dimers.

<table>
<thead>
<tr>
<th>Cell size</th>
<th>Minimum energy per particle</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2 \times 2$</td>
<td>$1.08494289507E_0$</td>
</tr>
<tr>
<td>$3 \times 3$</td>
<td>$1.08610917754E_0$</td>
</tr>
<tr>
<td>$4 \times 4$</td>
<td>$1.08494289507E_0$</td>
</tr>
<tr>
<td>$5 \times 5$</td>
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<td>$6 \times 6$</td>
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</tr>
<tr>
<td>$7 \times 7$</td>
<td>$1.08537385590E_0$</td>
</tr>
<tr>
<td>$8 \times 8$</td>
<td>$1.08494289507E_0$</td>
</tr>
</tbody>
</table>
Minimum energy per particle ($E_0$)

$N_1 = N_2$

Figure 8: The minimum energies for cell size from $2 \times 2$ to $8 \times 8$ for dimers.

give slightly different energy results. For this reason we have run 500 minimizations and reported in Table 2 the one resulting in the lowest energy as the best configuration for the system subjected to this constraint.

The minimum energies for the cells we have considered, which all have $N_1 = N_2$, are reported in Table 2 and plotted in Fig. 8. This figure highlights that the lowest energy per particle occurs for even $N_1 = N_2$, while for odd $N_1 = N_2$ the energy decreases for increasing size. This result suggests that the patterns of Fig. 6 are the optimal patterns that would arise even in an infinitely large crystal.

We had already supposed that the dominant $\delta^4$ terms in Eq. (36) favoured a $\pi/4$, $-\pi/4$ orientation of the dimers. This is confirmed by minimizations executed with even-side cells but dropping $\delta^6$ terms in Eq. (34), which return configurations similar to Fig. 6, where though dimers in contiguous rows are perfectly perpendicular. Therefore, these sixth-order terms are responsible for the slight deviation from the $\pi/4$, $-\pi/4$ configuration. As a further confirmation, we made a few minimizations with different $\delta$, from plausible values near 0.15 to the unphysical (because of the high energy cost to form clusters) limit $\delta \to 0$, and obtained the angle $\overline{\theta} = \overline{\theta}(\delta)$ formed by the dimers of one row with the row direction. For the other row the angle is $-\overline{\theta}$. E.g., for $\delta = 0.16$ instead of 0.15, the $\delta^6$ terms
Figure 9: The deviation $45^\circ - \bar{\theta}(\delta)$. It shows the $\bar{\theta} \to 45^\circ$ tendency for $\delta \to 0$.

have a higher relative importance and $\bar{\theta}$ assumes the lower value $\bar{\theta} = 44.4085$. Fig. 9 highlights that the difference $45^\circ - \bar{\theta}(\delta)$ decreases to 0 as $\delta \to 0$, where the relative importance of the sixth-order terms decreases.

4.1.2 Trimmers

For a $2 \times 2$ supercell of trimers the minimum energy configuration consists of alternated rows of clusters with orientations $\frac{\pi}{2}$ and $-\frac{\pi}{2}$, as shown in Fig. 10. Its energy per particle is $E = 1.89459203264E_0$.

The ground-state energy in a $3 \times 3$ cell is lower, namely $E = 1.89457993734E_0$. The corresponding configuration exhibits an alternation of two rows of trimers forming an angle of $-14.9537^\circ$ with the $x$ axis and one forming an angle of $23.4759^\circ$, or other equivalent patterns, drawn in Fig. 11

$4 \times 4$ and $6 \times 6$ cells consist of four replica of $2 \times 2$ and $3 \times 3$ respectively and therefore exhibit the same energy per particle.

Comparing the energies of different size cells, reported in Table 3, we find that the lowest energy occurs for $N_1 = N_2 = 3l$ and is realised for a cell made of $l^2$ repetitions of the $3 \times 3$ cell, similarly to the dimers behaviour for even-side cells. This result suggests that the $3 \times 3$ is large enough to hold the ground-state angular pattern.
Figure 10: Two equivalent lowest-energy configurations for a $2 \times 2$ trimers cell, corresponding to an energy per particle $E = 1.89459203264 E_0$.

Figure 11: A few symmetry-related ground-state configurations for a $3 \times 3$ trimers cell, corresponding to the same energy per particle $E = 1.89457993734 E_0$. The sloped lines highlight rows of parallel trimers.
Table 3: Minimum energies for cell size from $2 \times 2$ to $7 \times 7$ for trimers.

<table>
<thead>
<tr>
<th>Cell size</th>
<th>Minimum energy per particle</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2 \times 2$</td>
<td>$1.89459203264 E_0$</td>
</tr>
<tr>
<td>$3 \times 3$</td>
<td>$1.89457993734 E_0$</td>
</tr>
<tr>
<td>$4 \times 4$</td>
<td>$1.89459203264 E_0$</td>
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</tr>
<tr>
<td>$6 \times 6$</td>
<td>$1.89457993734 E_0$</td>
</tr>
<tr>
<td>$7 \times 7$</td>
<td>$1.89458780421 E_0$</td>
</tr>
</tbody>
</table>

4.1.3 The optimal patterns

For the two detected optimal patterns we can identify the primitive cells shown in Fig. 12. For dimers, the cell contains two clusters, while for trimers it contains three clusters. Either way, these primitive cells contain more than one lattice site, as sites differ by the cluster orientations, indicating that no ferro-orientational order is favoured in these systems.

4.2 Comparison with the exact $E^{tot}$

We have also executed a few tests to compare the expansion for the supercell energy with the same quantity obtained with the exact code used in Ref. [1]. We have calculated the energy of a $6 \times 6$ supercell containing dimers placed in the same configuration, and compared the resulting total potential energy for decreasing $\delta$ from 0.15 to 0.01. Eq. (34), truncated to sixth order, should deviate from the exact $E^{tot}$ at order $\delta^8$, because $\delta^7$ terms vanish when summing on particles.
within dimers, exactly as lower odd-order terms, see Eq. (15). Therefore, we expect the difference between the exact and the approximate energy to decrease to 0 proportionally to $\delta^8$.

For this comparison we only consider the soft-core part of the potential energy ($B_0 = 0$), since the hard-core part diverges to infinite for small $\delta$, thus making differences difficult to evaluate numerically.

Fig. 13 reports the deviation $(E_{\text{tot,approx}} - E_{\text{tot,exact}})^{\frac{1}{8}}$ for different $\delta$ and highlights the expected linear behaviour. The error we are committing when truncating the potential energy expansion is less than $5 \times 10^{-5} E_0$ per particle for the adopted value $\delta = \frac{w}{2} = 0.15$.

5 Conclusions

Systems of interacting soft colloids can display crystalline cluster phases, where the orientational degrees of freedom of the clusters form patterns minimizing the total energy. We have studied, in a model with clusters located at fixed positions, the ground-state angular configurations for $n = 2$ and 3. From the multipolar expansion of the cluster-cluster interaction energy we understand that, for a pair of dimers, the leading term responsible for their reciprocal orientation is
the quadrupole-monopole, which though has an angle-independent contribution to the total energy in a triangular lattice of clusters. One has to consider the quadrupole-quadrupole fourth-order terms to have a non-trivial angle dependence of the total energy. Numerical analysis shows that the optimal configuration is realized by a herringbone ordering, where angles are slightly tilted relative to the \(\frac{\pi}{4}\) and \(-\frac{\pi}{4}\) directions because of the sixth-order terms. This ordering is similar to the one detected in a different model for colloids interacting with a Yukawa potential and trapped in a periodical substrate whose minima are half the number of particles [2]. We can identify a primitive cell containing two perpendicular dimers.

Similarly, for trimers, the lowest-order non constant terms in the interaction energy between two clusters are of order 3, but again they only provide a constant energy contribution in the lattice. The sixth-order terms are thus responsible for the ordering of the ground state, which displays rows of parallel clusters. In this case, the primitive cell contains three clusters.

Comparison with numerical simulations of the full model (for the dimers case) shows that in the delicate balance between competing interactions the translational degrees of freedom of the clusters do play a role of essentially equal importance to the multipolar interactions analysed in this thesis, resulting in complicated long-periodicity phases where clusters move slightly away from the lattice sites.
References


