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Structure and cohesive energy of dipolar helices

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This paper deals with the investigation of cohesive energy in dipolar helices made up of hard spheres. Such tubular helical structures are ubiquitous objects in biological systems. We observe a complex dependence of cohesive energy on surface packing fraction and dipole moment distribution. As far as single helices are concerned, the lowest cohesive energy is achieved at the highest surface packing fraction. Besides, a striking non-monotonic behavior is reported for the cohesive energy as a function of the surface packing fraction. For multiple helices, we discover a new phase, exhibiting markedly higher cohesive energy. This phase is referred to as ZZ tube consisting of stacked crown rings (reminiscent of a pile of zig-zag rings), resulting in a local triangular arrangement with densely packed filaments parallel to the tube axis.

1 Introduction

Particles with permanent dipole moments, such as magnetic particles, are well known for their outstanding self-assembly properties.^{1–3} In biology, tubular and helical structures are relevant self-assembled objects, for instance, found in bacterial flagella⁴ and microtubules.^{5,6} Other instances of such tubular/helical structures can be found in various materials with specific building units that can be: carbon atoms,⁷ coiled carbon nanotubes,⁸ DNA,⁹ nanoparticles,¹⁰ or amphiphilic molecules.^{11–13} Self organization of cubic magnetic nanoparticles¹⁴ and asymmetric colloidal magnetic dumbbells¹⁵ into helical architectures were recently reported without the need for pre-existing templates.

On a more theoretical side, hard spherical particles confined in narrow cylinders spontaneously assemble into helical structures^{16,17} and this is also seen experimentally.¹⁸ Hard-spheres with permanent moment can be employed as a paradigm for more complex helical molecular superstructures, ¹⁹ or microtubules.^{20,21} The pioneering theoretical work of Jacobs and Bean²² and later that of de Gennes and Pincus²³ shed some light on the microstructure of selfassembled unconstrained (spherical) dipoles. More recently, the paper²⁴ advocated the ground states of self-assembled magnetic structures. The authors proved that for a sufficiently high number of particles the ground state is obtained via ring stacking into tubes.²⁴ On the other hand, Vella et al.²⁵ showed an illustrative example in which a macroscopic straight portion of the chain spontaneously wraps itself building a tube. At larger scales, the Janus chain model was able to reproduce well the formation of superstructures and double helical conformations

of amphiphilic molecules.^{26,27} The competition between toroidal and rod-like conformations, as possible ground states for DNA condensation, was studied using a polymer chain model function of stiffness and short range interactions.^{28,29} Also the recently introduced polymorphic dynamics model^{30,31} was able to reproduce the behavior of the microtubule lattice based on a rough understanding of underlying atomic level processes. The general scientific problem of understanding the processes by which building blocks (dipoles) self-assemble and obtain their functionality is highly challenging.^{32–36}

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The goal of this paper is to address the intimate link between microstructure and cohesive energy. Tubular helical structures can be obtained either (i) through ring stacking or (ii) by rolling one or multiple helices on a confining cylindrical surface (Section 2). The dipolar interaction model is introduced and a link between the dipole distribution and the microstructure is established in Section 3. In Section 4, starting from the most simple case corresponding to a single helix, we discuss the relationship between the surface packing and the resulting macroscopic properties such as the cohesive energy or overall polarization. Then, the more complex situation of multiple helices with densely packed constitutive particles is addressed. There, the degree of alignment (especially in the ground state) between the dipole moment orientation and the helix axis is analyzed.

2 Geometry of helices

2.1 Geometry of the single helix

In the framework of this paper, helices are composed of hard spherical particles and confined to a cylinder's surface, *i.e.*, the helices are created by rolling threads on the cylindrical surface of radius R_{cyl} . Geometrical parameters that define a single helix are: the azimuthal angular shift Γ between the centers of two

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Fig. 1 Illustration of a single helix with the relevant geometrical parameters $(R, \Gamma, \Delta z)$ labelled. The bold line connecting spherical particle centers represents the backbone of the helix. In the upper part of the figure, the azimuthal dipole moment orientation α is defined in a local coordinate system with its origin corresponding to the particle center. The z'-axis is parallel to the cylinder axis.

successive particles and the radius of the helix $R = R_{cyl} + d/2$, where *d* stands for the hard sphere diameter, see Fig. 1. The radius *R* represents physically the distance of the closest approach between the cylinder axis and the center of the spherical particle.

The Cartesian coordinates of particle *i* in a single helix are calculated as: $x_i = R\cos(i\Gamma)$, $y_i = R\sin(i\Gamma)$, and $z_i = i\Delta z$, where $i \in Z$ and assuming that one particle is at (x,y,z) = (R,0,0). The distance between the centers of each two successive particles along the helix axis is labelled Δz , see Fig. 1. When constructing a helix, its radius *R* and the azimuthal angular distance Γ have to be chosen in a way that ensures non-overlapping of hard spheres. The non-overlapping constraint is expressed for any two particles *i*, *j* as

 $|\dot{r}_{ii}| \geq d$. Since the helix thread is connected everywhere, any two successive particles are touching. We can obtain Δz as a function of other two variables: $\Delta z = \sqrt{d^2 + 2(\cos \Gamma - 1)R^2}$. Thereby, variables Δz , R and Γ are not independent. Clearly, with decreasing Δz (*i.e.*, increasing Γ) helices become more compact. Because of the connectivity, every particle in a helix has at least two neighbors, *i.e.*, the coordination number, n_c , is always greater or equal than two $(n_c \ge 2)$. The highest packing density of the particles for the prescribed confinement radius R will be achieved when the successive helix turns touch. In this situation of touching turns, the coordination number n_c can be either four or six. Therefore, in general, $n_c \in \{2, 4, 6\}$, where the case $n_c = 2$ corresponds to non-touching turns. Based on the coordination number n_c , we can classify helices as follows (see Fig. 2a–c). Examples of helices with two neighbors $n_c = 2$ and four neighbors $n_c = 4$ at a prescribed cylindrical confinement, *e.g.*, R/d = 1.78, are sketched in Fig. 2a and b, respectively. For a number of well-defined radii, as discussed later in this paper, densely packed helices with six neighbors $(n_c = 6)$ can be formed, see Fig. 2c. In the following sections, we will also investigate stacked rings forming the so-called tubes, also depicted in Fig. 2d-f.

2.2 Order parameters for single helices

The surface packing fraction, $\eta = S/S_{\text{avail}}$, is defined as the ratio of the area $S = \pi d^2/4$ covered by one particle and the area available for one particle S_{avail} , in an unrolled configuration.

Following the definition of the surface packing density we obtain:†

$$\eta = \frac{d^2}{8\Delta z R}.$$
 (1)

For comparison we are also going to derive the packing fraction for the tubes:‡

• The surface packing fraction of AA tubes is given by $\eta_{AA} = N_{\text{ring}}d/8R_{AA}$ for an AA tube with N_{ring} particles per ring and the confinement radius $R_{AA}/d = 1/[2\sin(\pi/N_{\text{ring}})]$, see Fig. 2d for a microstructure with $R_{AA}/d = 1.93$.



Fig. 2 Illustration of different classes of helices, based on the coordination number $n_c = 2$, 4, and 6. (a) Helix with *non-touching* turns ($n_c = 2$). (b) Helix with touching turns ($n_c = 4$). (c) Densely packed helix ($n_c = 6$). The other panels illustrate the so-called (d) AA, (e) AB, and (f) ZZ tubes. The tubes can be created by strict axial stacking of unit rings. For AA and AB tubes unit rings are flat, whereas, for ZZ tubes the unit ring has a crown shape (reminiscent of the pile of 'zig-zag' rings). The radii of AA and AB tubes are the same R/d = 1.93.

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• Similarly, for AB tubes, the packing fraction is $\eta_{AB} = N_{ring}d^2/8R_{AB}\Delta z_{AB}$, with $R_{AB} = R_{AA}$. Here, the elevation Δz_{AB} between two consecutive rings is:

$$\Delta z_{\rm AB} = (d/2)\sqrt{2 + 2\cos(\pi/N) - \cos^2(\pi/N)}.$$
 (2)

• For ZZ tubes, the packing fraction is $\eta_{ZZ} = N_{\text{ring}} d/8R_{ZZ}$, with the confinement radius $R_{ZZ}/d = \sqrt{3}/[4\sin(\pi/N_{\text{ring}})]$.

To further characterize the helical microstructures, we introduce an additional geometrical order parameter ξ which is valid for $n_c = 4$ and 6. This order parameter connects an individual reference particle 0 located at \vec{r}_0 in the helix with its two neighbors: its immediate successive particle 1 in the turn $(\vec{r}_{01} = \vec{r}_1 - \vec{r}_0)$ and a neighboring particle 2 from the next turn $(\vec{r}_{02} = \vec{r}_2 - \vec{r}_0)$, see Fig. 3(a).

The angular coordination order parameter is conveniently defined as:

$$\xi = 2 \frac{|\vec{r}_{01} \cdot \vec{r}_{02}|}{d^2}.$$
 (3)

In the two limiting cases, the angular coordination order parameter has values: $\xi_{\min} = 0$, for a locally square lattice on a cylinder (*e.g.*, AA tubes, check Fig. 2d) and $\xi_{\max} = 1$, for a locally triangular lattice (*e.g.* AB tubes, check Fig. 2e). In all other cases, the value of the angular coordination order parameter ξ is between those two extreme values, *i.e.*, $0 < \xi < 1$.

2.3 Multiple helices at high surface packing fraction

The densely packed helices ($n_c = 6$) can be created, in analogy with carbon nanotubes, by rolling a ribbon of a triangular lattice on a cylinder surface.³⁷ We deal with cylindrical geometry, infinite in one direction. We can generate these helical structures by periodical reproduction of a curved patch (unit cell) along the helical line with spanning vectors (\vec{a}_1 , \vec{a}_2). This curved unit cell has n_1 particles along the \vec{a}_1 direction and n_2 particles in the \vec{a}_2 direction.§

Since we deal with hard spheres and we aim to build very dense structures, the parameter space $(R,\Delta z,n_1,n_2)$ is significantly restricted. We are going to find out that only two of these parameters are independent. There exists a relationship linking the elevation angle $\Theta = \arcsin(\Delta z/d)$ and the confinement radius R, see ref. 37. Bearing in mind that for any pair (n_1,n_2) or equivalently (n_2,n_1) , we have a unique corresponding structure



Fig. 3 (a) Illustration of a helix made of hard spheres, helix backbone (solid line), and the vectors connecting a reference particle 0 located at (x,y,z) = (R,0,0) with its neighbors: an immediate successive particle 1 in the turn located at (\vec{r}_{01}) and a neighboring particle 2 from the next thread turn at (\vec{r}_{02}) . (b) An overview of the principal geometrical parameters of $n_c = 4$ and 6 helices: elevation angle Θ and azimuthal angular shifts Γ_1 and Γ_2 (see eqn (7)). In our notation, densely packed directions along the helical superstructure are called threads. The corresponding elevation distances of successive particles along helix axes $\Delta z_{1,2}$ (see eqn (9)) are also given for two possibilities for the rolling of the same helix configuration.

with $n_c = 6$, one arrives at the following two independent equations:

$$\Theta(n_1, n_2) = \arctan\left(\frac{\sqrt{3}n_2}{2n_1 + n_2}\right) \tag{4}$$

and

$$180^{\circ} = n_1 \arcsin\left[\left(\frac{d}{4R}\right) \frac{2n_1 + n_2}{\sqrt{n_1^2 + n_2^2 + n_1 n_2}}\right] + n_2 \arcsin\left[\left(\frac{d}{4R}\right) \frac{2n_2 + n_1}{\sqrt{n_1^2 + n_2^2 + n_1 n_2}}\right].$$
(5)

We have solved those two equations and obtained the sets $(\Theta, R/d)$ shown in Fig. 4. For each value of *R* there are two different values of Θ , symmetric around $\Theta = 30^{\circ}$, which correspond to lattice constant pairs (n_1, n_2) and (n_2, n_1) , respectively. The (n_1, n_2) pairs are actually identical structures with opposite chirality.³⁸ The sixfold rotational symmetry of the lattice restricts $\Theta \in [0^{\circ}, 60^{\circ}]$.

We now look into properties of (n_1,n_2) pairs in order to characterize the multi-thread structure of six neighbor helices $(n_c = 6)$. First, we identify the link between $n_c = 6$ -tubes and the

[†] The available area per particle is $S_{avail} = 2\pi R \Delta z$, where the distance between successive particles along the tube axis is Δz . We take for the surface covered by particle $S = \pi d^2/4$, *i.e.*, neglecting curvature. This results in a small overestimation of the packing fraction (less then 2% for large curvatures, *e.g.*, $R/d = \sqrt{3/2}$).

[‡] The tubes are obtained *via* ring stacking. It is convenient to calculate the surface packing fraction as the ratio of the area covered by the particles in a unit ring and the available area per ring. The surface covered is $S = N_{\text{ring}}\pi d^2/4$. The available area per ring is $S_{\text{avail}} = 2\pi R\Delta z$, where Δz is the distance between successive rings. The distance between successive rings is $\Delta z = d$ for AA and ZZ tubes.

[§] The values n_1 and n_2 can be seen as the two possible widths of the ribbon generating the same helical structure.



Fig. 4 Phase diagram in the $(\Theta, R/d)$ -plane showing possible unit cells characterized by (n_1, n_2) pairs. Solid lines represent unit cells with n_2 fixed, and the dashed ones represent unit cells with n_1 fixed. The three horizontal lines (dot-dashed) correspond to tubes.

 (n_1,n_2) pair values. The pairs $(0,n_2)$ and $(n_1,0)$ leading to $\Theta = 60^{\circ}$ and 0° , respectively, represent AB tubes, *cf.* Fig. 4. The pairs with $n_1 = n_2$ corresponding to $\Theta = 30^{\circ}$ lead to ZZ tubes that are characterized by constitutive straight filaments parallel to the ZZ tube axis, see Fig. 2f. The curve with $n_1 = 1$ (with $n_2 \ge 3$) corresponds to a single helix, $n_1 = 2$ (with $n_2 \ge 3$) to a double helix, $n_1 = 3$ (for any $n_2 \ge 4$) to a triple helix, and more generally an n_1 -helical structure is obtained when $n_2 \ge n_1 + 1.\P$

We employ Cartesian coordinates to express positions of particles in an *n*-helix similarly to the single helix case, using two indices, $i \in Z$ and $j = \{1, n\}$:

$$x_{i+jn} = R \sin(i\Gamma_1 + j\Gamma_2)$$

$$y_{i+jn} = R \cos(i\Gamma_1 + j\Gamma_2)$$

$$z_{i+jn} = i\Delta z_1 + j\Delta z_2.$$
(6)

In eqn (6), Γ_1 represents the azimuthal angular shift between each two consecutive particles along a given thread and Γ_2 is the angular shift between threads, *i.e.*, densely packed directions in a superstructure, see Fig. 3(b). The azimuthal angle Γ_1 is merely provided by:

$$\Gamma_1 = \arccos\left[1 - \left(\frac{d}{\sqrt{2R}}\cos\Theta\right)^2\right].$$
 (7)

The angular shift Γ_2 between threads is more delicate to derive. Knowing that starting from the reference particle it is possible to reach the same particle position following two paths along threads (in \vec{a}_1 or \vec{a}_2 -direction), one can arrive at a relation linking Γ_1 and Γ_2 : $360^\circ = (n_1 + n_2)\Gamma_1 - n_2\Gamma_2$.

The dependence of angular parameters Γ_1 and Γ_2 on the reduced helix radius *R*/*d* is displayed in Fig. 5, for $\Theta < 30$ in the



Fig. 5 Dependence of azimuthal angular shift parameters Γ_1 and Γ_2 stemming from the corresponding spanning vectors \vec{a}_1 , \vec{a}_2 , respectively, on a reduced helix radius R/d, for single ($n_2 = 1$), double ($n_2 = 2$), and quadruple ($n_2 = 4$) helices.

single helix $(n_2 = 1, n_1 \ge 4)$, the double helix $(n_2 = 2, n_1 \ge n_2)$ and the quadruple helix $(n_2 = 4, n_1 \ge n_2)$.

As the helix radius R/d increases, the value of Γ_1 monotonically decreases, since additional particles are added to a turn. The angular parameter Γ_2 monotonically decreases only for $n_2 = 1$. The scenario becomes qualitatively different at $n_2 \ge 2$ where non-monotonic behavior is found, see Fig. 5. This feature can be rationalized as follows. The smallest compatible radii R with $n_2 \ge 2$ and $\Theta < 30^\circ$ are obtained when $n_1 = n_2$ (cf. Fig. 4) corresponding to Z tubes where $\Gamma_2 = 0$. Besides that, Γ_2 tends to zero for the vanishing cylinder curvature ($R/d \rightarrow \infty$). These are the reasons why the profile of $\Gamma_2(R/d)$ is non-monotonic when $n_2 \ge 2$.

The surface packing fraction of densely packed multiple helices is simply obtained by multiplying the surface packing fraction of a single helix with the number of threads n_2 ($\eta_{\text{multi}} = n_2 \eta$, see eqn (1)):

$$\eta_{\text{multi}} = n_2 \frac{d^2}{8\Delta z_1 R},\tag{8}$$

where the elevation distance Δz_1 (shown in Fig. 3b) is given by:

$$\Delta z_1 = \sqrt{d^2 - 4R^2 \sin^2\left(\frac{\Gamma_1}{2}\right)}.$$
(9)

The calculated surface packing fraction of single $(n_2 = 1)$, double $(n_2 = 2)$, and quadruple $(n_2 = 4)$ helices is shown in Fig. 6. At a given confinement curvature (fixed R/d), adding threads results in higher surface packing fraction, see Fig. 6.

3 Dipole moments

3.1 Dipolar interaction model

We now want to address the situation where the constitutive particles are dipolar. Each particle carries an identical dipole moment in magnitude, $m = |\vec{m}_i|$, where $\vec{m}_i = (m_i^x, m_i^y, m_i^z)$ defines

[¶] In our notation, multiple helices are named after the smallest unit patch dimension, *i.e.*, the smallest number of generating threads.



Fig. 6 Surface packing fraction η , see eqn (8) as a function of reduced helix radius R/d for single ($n_2 = 1$), double ($n_2 = 2$), and quadruple ($n_2 = 4$) helices.

the dipole moment of particle *i*, see also Fig. 1. The potential energy of interaction $U(\vec{r}_{ij})$ between two point-like dipoles whose centers are located at \vec{r}_i and \vec{r}_j can be written as:

$$U(\vec{r}_{ij}) = C \frac{1}{r_{ij}^3} \left[\vec{m}_i \cdot \vec{m}_j - 3 \frac{\left(\vec{m}_i \cdot \vec{r}_{ij} \right) \left(\vec{m}_j \cdot \vec{r}_{ij} \right)}{r_{ij}^2} \right]$$
(10)

for $r_{ij} \ge d$ or ∞ otherwise, where *C* represents a constant that depends on the intervening medium, and $r_{ij} = |\vec{r}_{ij}| = |\vec{r}_j - \vec{r}_i|$. It is convenient to introduce the energy scale defined by $U_{\uparrow\uparrow} \equiv Cm^2/d^3$ that physically represents the repulsive potential value for two parallel dipoles in contact standing side by side as clearly suggested by the notation. Therefore, the total potential energy of interaction in a given structure U_{tot} is given by

$$U_{\text{tot}} = \sum_{\substack{i,j\\i>i}} U(\vec{r}_{ij}).$$
(11)

One can then define the reduced potential energy of interaction u (per particle) of N magnetic spheres. It reads $u = U_{tot}/(U_{\uparrow\uparrow}N)$, which will be referred to as the cohesive energy.

Since we are dealing with infinitely long structures (in one direction), we shall consider only periodic structures in that direction that greatly facilitate the calculation of the cohesive energy. The method of choice is provided by the Lekner sum for systems with periodicity in one direction.³⁹ The central feature in the Lekner method is the choice of the periodic cell. For $n_c = 2$, 4, we can always find helical parameters with a finite number of particles in the unit cell. The periodicity is achieved by imposing a condition on the angular shift parameter Γ that a helix has to make an integer number of turns within the unit cell.

3.2 Dipole moment orientation prescribed by helix threads

Because of the symmetry it is intuitive to envision dipole moments following helix threads. In order to have dipole moments tangential to the helical backbone, we introduce two components of dipole moments. The parallel component with respect to the helix axis is given by $m^z = m\Delta z/d$ and the orthogonal one is given by $|\vec{m}^{xy}| = m\sqrt{1 - (\Delta z/d)^2}$. Hence, the dipole moment of particle *i*



Fig. 7 The representative structures including dipole moment distributions are displayed. For AB tubes with patch parameters $(n_1,n_2) = (8,0)$ dipole distributions which correspond to spanning unit cell vectors (a) $\vec{a_1}$ (oblique to cylinder's axis), (b) $\vec{a_2}$ (closer to cylinder's axes), and (c) ground state dipole distribution. For a single helix $(n_1,n_2) = (9,1)$ dipole distributions which correspond to (d) $\vec{a_1}$ and (e) $\vec{a_2}$ (closer to helix axes) spanning vectors, and(f) ground state dipole distribution. For a double helix $(n_1,n_2) = (8,2)$ dipole distributions which correspond to (g) $\vec{a_1}$, (h) $\vec{a_2}$ (closer to helix axes) spanning vectors, and (i) the ground state dipole distribution. In the case of ZZ tubes (j) $\vec{a_1}$ and (k) $\vec{a_2}$ dipole distributions are shown. The ground state of ZZ tubes follows $\vec{a_2}$ dipole distribution (parallel to cylinder's axis).

in the single thread helix reads: $m_i^x = -m^{xy} \sin(i\Gamma)$, $m_i^y = m^{xy} \cos(i\Gamma)$, and $m_i^z = m_z$.

In the multi-thread case, the Cartesian dipole moment components are given by:

$$m_{i,j}^{x} = -m^{xy} \sin(i\Gamma_{1} + j\Gamma_{2})$$

$$m_{i,j}^{y} = m^{xy} \cos(i\Gamma_{1} + j\Gamma_{2})$$

$$m_{i,j}^{z} = m\Delta z/d,$$
(12)

where $i \in Z$ is the internal particle label within a thread and $j = \{1, n_2\}$ stands for the thread's label. In dense helices $(n_c = 4, 6)$ dipole moments can follow two directions \vec{a}_1 and \vec{a}_2 . In Fig. 7, representative dipole moment distributions are shown.

3.3 Energy minimization

In general, the dipole moments do not have to follow thread structure. To find the dipole moment distribution that yields minimal energy, we first perform minimization of the cohesive energy using a constrained minimization algorithm.^{24,40} A randomly oriented dipole moment is assigned to every particle of the helical structure in the following way: dipole moment is defined in the spherical coordinate system. Two important features stemming from these energy minimization calculations are:

(i) Dipole moments are tangential to the cylinder's surface.

(ii) The component of dipole moment in the *z*-axis direction m_z for a given structure is identical for all particles.

Therefore we need just one angular parameter to characterize the dipole moment orientation. We choose the dipole moment angular parameter, $\alpha \in [-180^{\circ}, 180^{\circ}]$, relative to the *z*-axis, see Fig. 1. Doing so we arrive at:

$$m_{i,j}^{x} = -m \sin(\alpha) \sin(i\Gamma_{1} + j\Gamma_{2})$$
$$m_{i,j}^{y} = m \sin(\alpha) \cos(i\Gamma_{1} + j\Gamma_{2})$$
$$m_{i,j}^{z} = m \cos(\alpha), \qquad (13)$$

where the indices *i* and *j* have the same meaning as in eqn (12). Consequently, the angular parameter α is most of the time a unique variable, at prescribed helical structures, entering into the energy minimization routine.

4 Cohesion energy and microstructure

4.1 Compression of a single helix

A simple way to deform a helix is to compress (or extend) it along its axis, *i.e.*, the *z*-direction, while ensuring the dipole moments follow the thread (for details of implementation, see Section 3.2). Compression of a helix results in a continuous increase of its surface packing fraction η . Fig. 8 shows the evolution of cohesive energy u_R with the surface packing fraction η for a single helix with reduced radius ($R/d \simeq 1.7$, chosen in the vicinity of $n_c = 6$ point). Recalling geometrical considerations in Section 2.1 the increase of the azimuthal angular shift Γ at prescribed curvature results in a continuous decrease of Δz and compression of the helix. The compression process begins with



Fig. 8 Compression of a single helix on a cylindrical confinement with a fixed radius ($R/d \simeq 1.7$). Dependence of cohesive energy (upper left panel) and the overall polarization order parameter, *i.e.*, the axial component of the dipole moment (in lower left panel), on the packing fraction is shown for two characteristic dipole moment orientations: one that follows the helix, *i.e.*, the spanning vector $\vec{a_1}$ and the ground state dipole moment orientation obtained by energy minimization. Comparative microstructures at different η values (A–F) are depicted on the right panel. Configurations (A, B, C and E) correspond to a dipole moment distribution following the helix whereas configurations D and F correspond to ground state distributions.

a fully extended helix (*i.e.*, $\eta \rightarrow d/8R \approx 0.073$) where the chain stands up with $\Delta z/d = 1$, and the cohesive energy of infinite chain $u \simeq -2.404$.²⁴ The compression ends when two successive turns of the helix touch, *i.e.*, the coordination number of particles in the helix changes from $n_c = 2$ to $n_c = 4$.

We also address the minimal energy of the helix with respect to the dipole moment distribution (*i.e.*, not necessarily prescribed by tangentially following the helix). From Fig. 8, we observe that $u_R = u_R(\eta)$ is non-monotonic. We can identify two regimes:

• At small packing fractions up to $\eta \leq 0.4$ (with no touching turns), the compression of the helix requires energy input and therefore cohesive energy increases. The reason for this is that two distant consecutive turns of the helix experience weaker attraction upon increasing η .

• In the regime of high $\eta \gtrsim 0.4$ where successive turns are allowed to be close or even touching, the cohesive energy starts to decrease as η increases, *i.e.*, the helix would compress on its own without input of energy. This is a consequence of enhanced attraction caused by the discreteness of the constitutive dipolar beads, see ref. 41.

The overall polarization order parameter $\langle m_z \rangle$ is also analysed in Fig. 8. During most of the course of the helix compression, see Fig. 8, a dipole moment orientation following the helix corresponds to the ground state structure up to $\eta \approx 0.8$, *cf.* points C and D in Fig. 8 (for details of ground state calculations, see Section 3.3). Only for very high packing fractions, *i.e.*, $\eta > 0.8$, the ground state dipole orientation starts to rapidly deviate from the helix direction accompanied by a significant reduction in cohesive energy (see points E and F in Fig. 8). The highest difference in $\langle m_z \rangle$ occurs for $\eta \approx 0.887$, where $n_c = 4$ helix with touching turns is formed, and the energy difference $u_R^E - u_R^F \simeq 0.06$.

4.2 From the square to triangular arrangement for a single helix

Having successfully parameterized helices and introduced dipole moments, it is natural to ask how cohesive energy depends on structural changes and especially on curvature. With increasing curvature the structure will change from the triangular to square arrangement and *vice versa* through a continuous series of rhombic configurations. We first study in detail systems with dipole moments following the spanning vector that are most oblique to helix axes, see Fig. 7d. For the sake of comparison with tubes (AA/AB tubes), we also chose dipole moments that are building vortices along the rings for them, *cf.* Fig. 7a. Motivation for that choice stems from a previous study,²⁴ where we have shown that finite AB tubular systems are energetically favorable, see Fig. 7a (dipole moment orientation is perpendicular to the tube's axis).

The surface packing fraction η (eqn (1)), the angular coordination order parameter ξ (see eqn (3)), and the cohesive energy per particle u_R (eqn (11)) are plotted *versus* the reduced helix radius R/d in Fig. 9.

 $[\]parallel$ We have found that under some circumstances the dipole moment orientations alternate, *i.e.*, antiferromagnetic-like coupling between the neighboring threads. This actually occurs with any AA tube. Similar behavior is reported for some moderately dense $n_{\rm c}$ = 4-helical structures.



Fig. 9 Dependence of (a) the angular coordination order parameter ξ , (b) the packing density η and (c) the cohesive energy u_R on the helix radius R/d, for $\vec{a_1}$ dipole orientation. AA and AB tube points are clearly indicated, they bracket the parameter values of helices, like a kind of envelope (solid and dashed lines connecting the tube points are power law fits).

Actually, the energy and structural properties change in an oscillatory quasi-periodic manner and they are enveloped from both sides with the properties of AA and AB tubes, see Fig. 9. In Fig. 10 behavior of these observables is depicted within one period $(R/d \in [2.09, 2.26])$, arbitrary chosen). In one period, the number of particles (n) in a constitutive ring of (AA/AB) tubes is increased for one, *i.e.*, from *n*-ring to n + 1-ring. Within this period, the order parameter changes from $\xi = 0$, *i.e.*, square arrangement, to $\xi = 1$, *i.e.*, triangular arrangement, *via* a continuous rhombic transformation, see Fig. 10a. The radii of densely packed helices are roughly in the middle between two corresponding (AB/AA) tube radii, see Fig. 10a. This is a result of the radial constraint and the excluded volume. Though in a single thread helical structure we cannot close rings in the plane perpendicular to the cylinder axis, one can nevertheless realize a full 360° helix turn with roughly n + 1/2 particles. We observe discontinuity and strong asymmetry of the angular coordination order parameter ξ at the mid-period ($R_{(13,1)}/d \approx 2.17$), see Fig. 10a. This is due to a change in the number of lateral threads n_2 , see Fig. 7e for illustration, at the mid period going from $n_2 = 9$ to $n_2 = 10$, see Fig. 10a.



Fig. 10 Dependence of (a) the angular coordination order parameter ξ , (b) the packing density η and (c) the cohesive energy u_R on the helix radius R/d, for a segment in the vicinity of $R_{(13,1)}/d = 2.17$ of Fig. 9. Tubes AA and AB are represented by discrete points since they can be formed only with a fixed number of particles in a ring, the fitted (power law) curves serve only as a guide to the eye. The point which represents the dense helix with $(n_1,n_2) = (13,1)$ and $R_{(13,1)}/d = 2.17$ is marked with a rectangle.

With decreasing curvature, the surface packing fraction increases globally, see Fig. 9b. We observe oscillatory behavior as the system continuously evolves from the square to triangular arrangement and *vice versa*. The AA and AB tubes still roughly bound have the values taken by the surface packing fraction. At the helix radius R/d > 3.4, see Fig. 9b, we are already within 3% of the asymptotic expected values in the planar case. In contrast to the angular coordination parameter ξ , the surface packing density η is continuous everywhere, compare Fig. 10a and b. Moreover, at mid-period the η value is slightly (and systematically, see Fig. 9b) above the interpolated stemming from AB tubes (see Fig. 10b). In Fig. 9b and c, it can be clearly seen that the profiles of energy oscillations u_R and the surface packing fraction η are anti-correlated. The mid-period values u_R coincide with interpolated stemming from AB tube radii (confirmed by Fig. 9c and 10c).

4.3 Looking for the ground state

At this point, we would like to discuss mechanisms which govern the minimal energy dipole moment orientation near the midperiod transition point (more details about implementation are provided in Section 3.3). There are three privileged directions in

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a helix: two which follow helix spanning vectors (determined by \vec{a}_1, \vec{a}_2) and the third one which is the direction of the helix axis. These privileged directions come into play in two competing mechanisms:

• The first mechanism is typically dictated by first neighbor interactions which favor dipole moments following the thread directions.

• The distant–neighbor interactions favor the distribution of dipole moments parallel to the helix axis.

We can justify these two mechanisms as follows. It is well known for a small finite system that rings are formed with dipole moments building vortices, *cf.* ref. 24. When a helix turn is projected along the *z*-axis, the resulting figure is highly reminiscent of the vortex discussed above. The head to tail configuration is favored at long distances, explaining the second advocated mechanism.

The abrupt change in polarization (or magnetization) in the direction of the axis $\langle m_z \rangle$, seen in Fig. 11b, is correlated with the discontinuous change in the angular coordination order parameter ξ in the vicinity of transition, see Fig. 10a. At the mid-period point $R_{(13,1)}/d = 2.17$ magnetization in the direction of the axis $\langle m_z \rangle$ is close to one, but not exactly one, see Fig. 11.

For the sake of comparison with tubes (AA/AB tubes), we choose dipole moments that are parallel with the helix axis, see Fig. 7c. The fact that the system is able to relax its dipole moment orientation to the ground state results in more dependence of energy on confinement curvature around the mid-point. The degree of asymmetry of u_R is stronger around the transition point, see Fig. 11b, than in the excited state in Fig. 10c. The ground state calculations confirm the high stability of AB tubes (see Fig. 10c).

4.4 Cohesion energy for multiple helices at high surface packing fraction

In this part, we consider the high surface packing fraction regime with $n_c = 6$. Some representative structures including dipole moment streamlines are displayed in Fig. 7. The streamlines following spanning unit cell vectors \vec{a}_1 (oblique to the helix axis) and \vec{a}_2 (more aligned to the helix axis) are also shown.** Dipole moment distributions in the ground states are also indicated for comparison in Fig. 7. In analogy with the study of a single helix case (see Section 4.2), we start analysis with a dipole moment distribution prescribed by tangentiality with the thread backbone. In Fig. 12, cohesive energy for the \vec{a}_1 -generated dipole moment distribution is shown for different helical structures.

The cohesive energy in a planar triangular lattice, $u_{\infty} \simeq -2.759$, represents the energy value which will be reached asymptotically $(R/d \rightarrow \infty)$ for all considered structures. As already found for AB tubes in ref. 24, cohesive energy exhibits the scaling law of the form $u_R - u_{\infty} \sim R^{-2}$, see Fig. 12. The cohesive energies of all three helices and AB tubes are weakly dependent on the number of threads for \vec{a}_1 -generated dipole moment distribution.



Fig. 11 Dependence of (a) cohesive energy u_R and (b) the overall polarization order parameter $\langle m_z \rangle$ on the helix radius R/d (in the ground state), for a chosen segment of Fig. 9. Tubes AA and AB are represented by discrete points since they can be formed only with a fixed number of particles in a ring, the fitted (power law) curves serve only as a guide to the eye. The point which represents the dense helix with $(n_1, n_2) = (13, 1)$ and $R_{(13, 1)}/d = 2.17$, is marked with a rectangle.



Fig. 12 Dependence of cohesive energy u_R on the helix radius R/d, for single, double, and quadruple helices at high surface packing fraction, and AB tubes, with $\vec{a_1}$ dipole orientation.

^{**} It is possible to polarize the helix by a homogeneous external field parallel to its axis. For symmetry reasons, a reversal of the magnetic field should result in the reversal of the dipole orientation. In the case of magnetic dipoles, it should also be possible to polarize the system to follow $\vec{a_1}$ and $\vec{a_2}$ spanning vectors by combination of a curling magnetic field of electric current flowing through the confining cylinder and the homogeneous external magnetic field parallel to its axis.



Fig. 13 Dependence of cohesive energy u_R on the helix radius R/d, for families of single, double, and quadruple helices at a high surface packing fraction, *i.e.*, $n_2 = \{1, 2, 4\}$, respectively, and AB tubes, with \vec{a}_2 and optimized dipole moment orientation.

This is in accordance with surface packing fraction behavior reported in Fig. 6. A comparison with the azimuthal angular shift parameter Γ_1 , see Fig. 5, and the corresponding cohesive energy (for \vec{a}_1 -generated dipole moment distribution) clearly reveals a correlation between these two quantities.

In Fig. 13, cohesive energy for \vec{a}_2 -generated dipole moment distribution is compared with ground state energy for a different number of threads. There exists an analogous correlation (as discussed for \vec{a}_2 -dipole distribution) between the azimuthal shift Γ_2 and the resulting cohesive energy, compare Fig. 5 and 13.

The smallest compatible radius *R* for multi thread helices $(n_2 = 2, 4)$ is obtained for ZZ tubes $(n_1 = n_2)$. In Fig. 13, the corresponding radii read $R_{(2,2)}/d = 0.61$ and $R_{(4,4)}/d = 1.13$. In this case the \vec{a}_2 and ground state dipole moment orientations are the same, see Fig. 7k. Strikingly, ZZ tube ground states converge very fast to the expected planar value u_{∞} at the smallest accessible radii, *i.e.*, the largest curvature, within less than 1% of the planar case, see Fig. 13 for $R_{(2,2)}/d = 0.61$. A structural similarity of ZZ tubes, with typical experimental images of microtubules is striking, see Fig. 7k. Structurally, ZZ tubes can be created by closing the rectangular strip on a cylinder and decomposition into chains which are analogous to biological filaments which the microtubules are made of.

5 Conclusions

We have presented a study about cohesive energy of helical structures composed of hard spheres with permanent dipole moments. Helices were created by replication of a particle or patch (of particles) on a confining cylindrical surface. Even for the most simple situation, namely the single thread helix, a non-trivial behavior is found when monitoring the cohesive energy as a function of surface packing (*i.e.*, axial compression). In particular, we observe a non-monotonic dependence of the

cohesive energy on the packing fraction (or equivalently the amount of compression) as a result of a delicate interplay of dipole–dipole interactions and excluded volume effects. The lowest cohesive energy is achieved at the highest packing fraction with touching turns. In parallel, the magnetization (or polarization) order parameter, *i.e.*, the mean dipole moment per particle in $\langle m_z \rangle$, also exhibits a striking non-monotonic behavior as a function of the extent of compression. In the regime of very high surface packing fraction with local triangular arrangement compatible with certain cylinder radius (*R*) *vs.* particle diameter (*d*) ratio (*R*/*d*), a pronounced cohesive energy is found. Concomitantly, the magnetization order parameter indicates a sharp change in the dipole moment orientation, which tends to be parallel to the helix axis.

Finally, we compare cohesive energies of dense multiple (*i.e.*, double or quadruple) helices, as well as, AB and ZZ-tubes made up of stacking rings that can also be seen as special multiple helices. A remarkable finding is the enhanced cohesive energy for the ZZ-tube structure. The latter already emerges at strong substrate curvature with cohesive energies very close to that obtained at vanishing curvatures. In these ZZ-tube structures, an alignment of the helix threads with its axis is a microstructural signature for this low cohesive energy. As a final note, we would like to emphasize that our model mimics nicely the geometry and microstructure of microtubules. It could also provide a possible clue about the self-assembly mechanisms and cohesion within microtubular structures.

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