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ABSTRACT

The emergence of helicity from the densest possible packings of equal-sized hard spheres in narrow cylindrical confinement can be understood in terms of a density maximization of repeating microconfigurations. At any cylinder-to-sphere diameter ratio \( D \in (1 + \sqrt{3}/2, 2) \), a sphere can only be in contact with its nearest and second nearest neighbors along the vertical \( z \)-axis, and the densest possible helical structures are results of a minimized vertical separation between the first sphere and the third sphere for every consecutive triplet of spheres. By considering a density maximization of all microscopic triplets of mutually touching spheres, we show, by both analytical and numerical means, that the single helix at \( D \in (1 + \sqrt{3}/2, 1 + 4\sqrt{3}/7) \) corresponds to a repetition of the same triplet configuration and that the double helix at \( D \in (1 + 4\sqrt{3}/7, 2) \) corresponds to an alternation between two triplet configurations. The resulting analytic expressions for the positions of spheres in these helical structures could serve as a theoretical basis for developing novel chiral materials.

I. INTRODUCTION

Helical structures emerge in many different areas of science, from condensed matter physics all the way to structural biology. A fundamental understanding of the nature and origin of helical structures would help advance the development of new molecules or materials, where notable examples reported in recent years include chiral photonic crystals, supramolecular helical systems, and chiral nematic liquid crystals. An ideal platform for a comprehensive study of helicity is a model system of equal-sized hard spheres in cylindrical confinement, where many of the densest possible structures discovered from computer simulations are helical (Fig. 1). Of great experimental relevance to such a model system, helical structures have been observed for a variety of systems in cylindrical confinement, where notable examples include nanotube-confined fullerenes, nanochannel-confined copolymers, colloidal crystal wires, glass-confined thermoresponsive microspheres, capillary-tube-confined microbubbles, fluid-driven assembly of polymeric beads, and packings of fruits inside a cylinder (Fig. 2). Although these systems exhibit interactions of different types and scales, in many cases their densest possible structures resemble those of the above-mentioned model system of equal-sized hard spheres. This suggests that geometric confinement could be an important contribution to the helicity of a physical system, even at the molecular level, and that we could achieve and manipulate such helicity through confinement if we master the geometric interplay between the confining space and the confined entities. For such confined systems, the densest possible structures, which depend solely on the ratio \( D \equiv \text{cylinder diameter/sphere diameter} \) (i.e., cylinder diameter expressed in units of the sphere diameter), were, in most cases, discovered computationally, without any rigorous proof that they are indeed the densest possible ones. Therefore, a long-standing goal has been to derive those densest possible structures analytically and to understand why they change from one to another at specific diameter ratios. Some of the previous theoretical attempts and their corresponding limitations are described as follows:

An analytic theory that maps the problem to a two-dimensional scenario of disk packing has been worked out to explain...
FIG. 1. Densest possible structures at various regimes of $1 \leq D \leq 2$. These include three achiral structures (a), (b), and (e), and two chiral structures (c) and (d).

FIG. 2. Helical packings of oranges, apples, and lemons in cylindrical confinement.

the emergence of many of those helical structures. In this theory, each helical structure is thought of as a line slip of macroscopic regions of close-packed disks, as a result of the periodicity imposed by the cylindrical confinement. The theory works for a particular range of narrow confinement at $2 \leq D \leq 1 + 1/\sin(\pi/5)$, where all spheres of any densest possible packing are in contact with the cylindrical boundary. Yet, it cannot be used to explain the emergence of the single- and double-helix structures at $D < 2$, where no two spheres can be placed at the same vertical $z$-position in cylindrical polar coordinates, nor does it apply generally to cases of wider cylindrical space at $D > 1 + 1/\sin(\pi/5)$, where some spheres of densest possible packings are located away from the boundary.

On the other hand, it has been shown numerically that the densest possible structures at $1 \leq D < 1 + 1/\sin(\pi/5)$ can all be constructed microscopically through a method of sequential deposition. In this microscopic approach, spheres are dropped one by one onto their lowest possible positions to guarantee a local maximization of the packing fraction, and each columnar structure is optimized to be the densest possible through a fine-tuning of its underlying template. While this method shows great promise from a practical point of view, the original papers do not provide physical insights into the microscopic mechanism behind the successful construction of those densest possible structures.

The aim of this work is to examine, from a novel microscopic perspective, how the densest possible single- and double-helix structures at $D < 2$ emerge, where there has not been any comprehensive theory that explains the emergence of these two helical structures. By means of both numerical calculations and analytic derivations, we show that these structures are results of a density maximization of repeating local microconfigurations of spheres, thus giving rise to a global maximum of the packing fraction. Neighboring microconfigurations are coupled in a way that the same type of handedness (right or left) is propagated across the whole system, resulting in a uniform helicity across the columnar structure.

This paper is organized as follows. In Sec. II, we present a microscopic model of three mutually touching spheres and, also, the corresponding definitions of chirality for such systems. In Sec. III, we show, by both numerical and analytical means, that, at $D \in (1 + \sqrt{3}/2, 1 + 4\sqrt{3}/7)$, there exists a unique density-maximized...
configuration of the triplet of spheres and that the densest possible single-helix structure corresponds to a repetition of this optimal triplet configuration. In Sec. IV, we show, also both numerically and analytically, that at $D \in (1 + 4\sqrt{3}/2, 2)$, there exist two different density-maximized configurations of the triplet and that the densest possible double-helix structure corresponds to a repeated alternation between these two densest possible triplet configurations. For both densest possible helical structures, the exact positions of spheres, as well as the allowed ranges of $D$, are derived analytically from the corresponding optimal triplet configurations. Our results are summarized and discussed in Sec. V.

II. MODEL OF A TRIPLET OF MUTUALLY TOUCHING SPHERES

Microconfigurations of triplets of mutually touching spheres exist for the densest possible structures at $D \in (1 + \sqrt{3}/2, 2)$. We begin our discussion by defining, in cylindrical polar coordinates $(\rho, \phi, z)$, the chirality of such a microconfiguration as follows. At $D < 2$, there is enough space for any sphere to be placed in contact with its nearest and second nearest neighbors along the vertical $z$-direction of the cylindrical polar coordinates, but there is not enough space for any two spheres to be placed at the same vertical $z$-position. Any triplet of mutually touching spheres can then be indexed as $[1, 2, 3]$ in ascending order of their vertical $z$-positions, $z_1 < z_2 < z_3$. When viewed vertically from the top of the coordinate system (Fig. 3), any microconfiguration is described as right handed if the sequence $[1, 2, 3]$ follows a counterclockwise rotation, whereas it is described as left handed if the sequence of indices follows a clockwise rotation, with $\Delta \phi_0 \in (0, 2\pi)$ and $\Delta \phi_3 \in (-2\pi, 0)$ denoting, respectively, a counterclockwise and a clockwise angular displacement of magnitude $|\Delta \phi_0|$ from the center of sphere $i$ to the center of sphere $j$. With the signs of $\Delta \phi_0$ defined to be handedness-dependent, the magnitudes of $\Delta \phi_0$ must generally be allowed to exceed $\pi$ such that all possible arrangements of spheres could be considered. The corresponding angular displacements of the triplet of spheres are given by $\Delta \phi_{13} \equiv \Delta \phi_{12} + \Delta \phi_{23} \in (0, 2\pi)$ with $\Delta \phi_{12} \in (0, 2\pi)$ and $\Delta \phi_{23} \in (0, 2\pi)$ for any right-handed configuration, and $\Delta \phi_{13} \equiv \Delta \phi_{12} + \Delta \phi_{23} \in (-2\pi, 0)$ with $\Delta \phi_{12} \in (-2\pi, 0)$ and $\Delta \phi_{23} \in (-2\pi, 0)$ for any left-handed configuration.

Let $\Delta z_i \equiv z_j - z_i$ be the vertical displacement from the center of sphere $i$ to that of sphere $j$. For a triplet of mutually touching spheres at any given diameter ratio, our method is to work out the relation between $\Delta \phi_{13}$ and $\Delta \phi_{12}$ and then to find out the triplet configurations that correspond to a minimum possible value of $\Delta z_{13}$. The two densest possible helical structures considered in this study belong to a regime of $D$ where all spheres of any densest possible packing are in contact with the cylindrical boundary, i.e., all at a radial position of $\rho = (D - 1)/2$. This allows for a simpler mathematical procedure in our analysis, where the equation that describes two spheres $i$ and $j$ in mutual contact is simplified to

$$ (\Delta z_0)^2 = 1 - (D - 1)^2 \sin^2(\Delta \phi_0/2), $$

where all length quantities are expressed in units of the sphere diameter. The angular displacements among a triplet of mutually touching spheres are then interrelated as follows:

$$ \sqrt{1 - (D - 1)^2 \sin^2(\Delta \phi_{13}/2)} = \sqrt{1 - (D - 1)^2 \sin^2(\Delta \phi_{12}/2) + \sqrt{1 - (D - 1)^2 \sin^2(\Delta \phi_{23}/2)}}. $$

Since $\Delta \phi_{23} \equiv \Delta \phi_{13} - \Delta \phi_{12}$, Eq. (2) can be used to work out the dependence of $\Delta \phi_{13}$ on $\Delta \phi_{12}$ as well as the dependence of $\Delta z_{13}$ on $\Delta z_{12}$. Taking into account the extremum condition

$$ [\partial \Delta z_{13}/\partial \Delta \phi_{12}]_D = 0 $$

for a minimization of $\Delta z_{13}$, a differentiation of both sides of Eq. (2) with respect to $\Delta \phi_{12}$ leads to a "symmetric" relation between $\Delta \phi_{12}$ and $\Delta \phi_{23}$, $\Delta \phi_{13}$ and $\Delta \phi_{12}$,

$$ F(\Delta \phi_{12}) = F(\Delta \phi_{23}), $$

where

$$ F(x) \equiv [\sin(x/2) \cos(x/2)]/\sqrt{1 - (D - 1)^2 \sin^2(x/2)}. $$

Multiplying each side of Eq. (4) by itself and using the trigonometric identity $\cos^2(x/2) \equiv 1 - \sin^2(x/2)$, we obtain a quadratic relation between $\Delta \phi_{12}$ and $\Delta \phi_{23}$,

$$ C_1 \sin^2(\Delta \phi_{23}/2) + C_2 \sin^2(\Delta \phi_{23}/2) + C_3 = 0, $$

where

$C_1$, $C_2$, and $C_3$ depend on

Fig. 3. Schematic illustration of (a) a right-handed and a (b) left-handed configuration for a consecutive triplet of spheres $[1, 2, 3]$, where the spheres are indexed in ascending order of their vertical positions, i.e., $z_1 < z_2 < z_3$. 


where \( C_1 \equiv 1 - (D - 1)^2 \sin^2(\Delta \phi_{12}/2) \), \( C_2 \equiv -[1 - (D - 1)^2 \sin^2(\Delta \phi_{12}/2)] \), and \( C_3 \equiv \sin^2(\Delta \phi_{12}/2)[1 - \sin^2(\Delta \phi_{12}/2)] \). Equation (6) has a trivial solution of
\[
\sin^2(\Delta \phi_{23}/2) = \sin^2(\Delta \phi_{12}/2)
\]
(7)
as well as a nontrivial solution of
\[
\sin^2(\Delta \phi_{23}/2) = \frac{[1 - \sin^2(\Delta \phi_{12}/2)]}{[1 - (D - 1)^2 \sin^2(\Delta \phi_{12}/2)]}
\]
(8)
where these solutions correspond, respectively, to the densest possible single-helix and double-helix structures at \( D < 2 \).

### III. Densest Possible Single Helix at \( D \in (1 + \sqrt{3}/2, 1 + \sqrt{3}/7) \)

In this section, we show that the densest possible structure at \( D \in (1 + \sqrt{3}/2, 1 + \sqrt{3}/7) \) is a single helix with the same configuration for all consecutive triplets of spheres, i.e., \{1, 2, 3\}, \{2, 3, 4\}, \{3, 4, 5\}, ... Figure 4(a) shows a plot of \( \Delta z_{13} \) against \( \Delta z_{12} \) for an arbitrary triplet of mutually touching spheres, \{1, 2, 3\}, at various values of \( D \in (1 + \sqrt{3}/2, 1 + \sqrt{3}/7) \). For all those cases, it was numerically found that the minimum possible value of \( \Delta z_{13} \) satisfies the relation
\[
\Delta z_{13} = 2\Delta z_{12} = 2(\Delta z/\Delta N),
\]
(8)
where \((\Delta z/\Delta N)\) is the average vertical separation between adjacent spheres and its values are obtained from a conversion of existing packing-fraction data \(^{6,24}\) via the relation
\[
(\Delta z/\Delta N) = \frac{2}{(3D^2 V_F)}
\]
(9)
where \( V_F \) is the packing fraction. The results imply that the density of every consecutive triplet of spheres is maximized, with all vertical separations between adjacent spheres being the same \((\Delta z_{12} = \Delta z_{23} = \Delta z_{34} ...) \) as consistent with the definition of a single helix. Figure 4(b) shows a corresponding angular-displacement plot of \( |\Delta \phi_{13}| \) vs \( |\Delta \phi_{12}| \) for the same set of \( D \) values. According to Eq. (1), for each value of \( D \), the minimum possible value of \( \Delta z_{13} \) as shown in Fig. 4(a) corresponds to the minimum possible value of \( |\Delta \phi_{13}| \) as shown in Fig. 4(b), where the relation \( |\Delta \phi_{13}| = 2|\Delta \phi_{12}| \) holds for such a minimum. Note that the value of \( |\Delta \phi_{12}| \) corresponding to this minimum possible value of \( |\Delta \phi_{13}| \) exhibits a deviation from \( \pi \). This implies that, for the density of the triplet configuration to be maximized, sphere 2 has to be shifted away from its lowest possible position \( |\Delta \phi_{12}| = \pi \) with respect to sphere 1 such that there is space for sphere 3 to be placed at the above-mentioned optimal position (see Fig. 5).

It can be shown analytically, based on our consideration of microconfigurations, that this densest possible single-helix structure emerges only at \( D \in (1 + \sqrt{3}/2, 1 + \sqrt{3}/7) \), as consistent with
existing results\textsuperscript{15,20,28} The trivial solution given by Eq. (7) implies \( \Delta \phi_{12} = 2 \Delta \phi_{13} = 2 \Delta \phi_{23} \) and \( \Delta z_{12} = 2 \Delta z_{13} = 2 \Delta z_{23} \). Applying this result to all consecutive triplets of spheres, i.e., \( \Delta z_{12} = \Delta z_{23} = \Delta z_{34} = \Delta z_{45} = \cdots \), we conclude that any pair of consecutive spheres shares the same angular and vertical separations, as consistent with the definition of an infinitely long single-helix structure. From Eq. (1), we obtain the following expressions for the relative positions between any two consecutive spheres:

\[
\Delta \phi_{12} = \cos^{-1} \left[ 1 - \sqrt{3}/(D - 1) \right] \tag{11}
\]

and

\[
\Delta z_{12} = \left( \Delta z / \Delta N \right) = \sqrt{1 - \left[ \sqrt{3}(D - 1)/2 \right]^2}, \tag{12}
\]

where, as shown in Fig. 4(a), the numerical values computed from Eq. (12) are in agreement with values computed from existing volume-fraction data. According to Eq. (2), we have

\[
\sqrt{1 - (D - 1)^2} \sin^2 (\Delta \phi_{12}) = 2 \sqrt{1 - (D - 1)^2} \sin^2 (\Delta \phi_{12}/2). \tag{13}
\]

By differentiating Eq. (2) twice with respect to \( \Delta \phi_{12} \) and taking into account the extremum condition \( \left[ \partial \Delta \phi_{12} / \partial \Delta \phi_{12} \right]_{D} = 0 \) as well as Eqs. (11)–(13), we are able to express the second derivative \( \left[ \partial^2 \Delta \phi_{12} / \partial \Delta \phi_{12}^2 \right]_{D} \) as a function of \( D \) as

\[
\left[ \partial^2 \Delta \phi_{12} / \partial \Delta \phi_{12}^2 \right]_{D} = \frac{2(D - 1)^2 \left\{ \sqrt{\frac{3}{D-7}} - \frac{1}{4 - 2\sqrt{3}(D - 1)} \right\}}{6\sqrt{3}(D - 1) - 9}. \tag{14}
\]

For \( \Delta \phi_{13} \) to be a minimum as illustrated in Fig. 4(b), this second derivative has to be a real positive number with

\[
\frac{\sqrt{3}}{(D - 1)} - \frac{1}{4 - 2\sqrt{3}(D - 1)} > 0 \tag{15}
\]

and

\[
\sqrt{6\sqrt{3}(D - 1) - 9} > 0, \tag{16}
\]

which imply \( D < 1 + 4\sqrt{3}/7 \) and \( D > 1 + \sqrt{3}/2 \), respectively [the latter can also be obtained directly from Eq. (11)].

IV. DENSEST POSSIBLE DOUBLE HELIX

At \( D \in (1 + 4\sqrt{3}/7, 2) \), the densest possible structure is a double helix, the structure of which can be described as an alternation between two densest possible triplet configurations of mutually touching spheres, i.e., \{1, 2, 3\}, \{3, 4, 5\}, \{5, 6, 7\}, \cdots \) for one configuration, and \{2, 3, 4\}, \{4, 5, 6\}, \{6, 7, 8\}, \cdots \) for the other. Figure 6(a) depicts the relation between \( \Delta z_{13} \) against \( \Delta z_{12} \) for an arbitrary triplet of mutually touching spheres, \{1, 2, 3\}, at various values of \( D \) within this double-helix regime. Likewise, the triplet densities of the double-helix structure are maximized through a minimization of \( \Delta z_{13} \), and the unique minimum possible value of this vertical separation satisfies the relation \( \Delta z_{13} = 2\Delta z_{12} \).

FIG. 5 Plots of vertical position \( \Delta z \) vs angular position \( \phi \) for a triplet of mutually touching spheres at (a) \( \Delta z_{13} = \Delta z_{12,\text{min}} \) (solid lines) and (b) \( |\Delta \phi_{12}| = \pi \) (dashed lines). The value of \( \Delta z_{13} \) in (a) is smaller than that in (b), implying that, for sphere 3 to be placed at its lowest possible position, sphere 2 has to be shifted away from its lowest position \( |\Delta \phi_{12}| = \pi \) with respect to sphere 1.
we prove that this nontrivial solution is valid only for the regime of 
$D \in (1 + 4\sqrt{3}/7, 2)$.

Using the definition $\Delta \phi_{13} \equiv \Delta \phi_{12} + \Delta \phi_{23}$, the trigono-
metric identity $\sin(x + y) \equiv \sin(x) \cos(y) + \sin(y) \cos(x)$, as well as
Eq. (8), we first express $\sin^2(\Delta \phi_{13}/2)$ as a function of $\sin^2(\Delta \phi_{12}/2)$
follows:

$$\sin^2(\Delta \phi_{13}/2) = f_1/f_2,$$  \hspace{1cm} (20)

where

$$f_1 \equiv 1 - \sin^2(\Delta \phi_{12}/2) + \sin^2(\Delta \phi_{12}/2)\sqrt{D(2 - D)}\right)^2$$ \hspace{1cm} (21)

and

$$f_2 \equiv 1 - (D - 1)^2 \sin^2(\Delta \phi_{12}/2).$$ \hspace{1cm} (22)

Taking square of both sides of Eq. (2) and incorporating Eqs. (8) and
(20) into the new equation, we arrive at the following quadratic
equation for $\sin^2(\Delta \phi_{12}/2)$:

$$C_4 \sin^4(\Delta \phi_{12}/2) + C_5 \sin^2(\Delta \phi_{12}/2) + C_6 = 0,$$ \hspace{1cm} (23)

where $C_4 \equiv 2(D - 1)^2\sin^2(\Delta \phi_{12}/2)$, $C_5 \equiv 3(2 - 1)^2$ and
$C_6 \equiv 1 + 2\sqrt{D(2 - D)}$. Equation (23) yields two quadratic roots for
$\sin^2(\Delta \phi_{12}/2)$,

$$\sin^2(\Delta \phi_{12}/2) \equiv \frac{1 - \cos(\Delta \phi_{12})}{2} = f_{3,3}/f_4,$$ \hspace{1cm} (24)

where

$$f_{3,3} \equiv 3(D - 1) - \sqrt{8[1 - \sqrt{D(2 - D)}] - 7(D - 1)^2}$$ \hspace{1cm} (25)

and

$$f_4 \equiv 4(D - 1)[1 - \sqrt{D(2 - D)}].$$ \hspace{1cm} (26)

The relative positions between any two consecutive spheres are then
given by the double roots

$$\Delta \phi_{12,\pm} = \frac{\cos^{-1}[1 - 2f_{3,3}/f_4]}{2},$$ \hspace{1cm} (27)

and

$$\Delta z_{12,\pm} = \sqrt{1 - \left[(D - 1)^2f_{3,3}/f_4\right]}$$ \hspace{1cm} (28)

such that we have

$$2(\Delta z/\Delta N) = \Delta z_{12,+} + \Delta z_{12,-} = \sqrt{1 + \sqrt{D(2 - D)} - \frac{1}{2}}$$ \hspace{1cm} (29)

where, as shown in Fig. 6(a), the numerical values computed from
Eqs. (28) and (29) are in agreement with values computed from the
existing volume-fraction data.

Since all vertical separations of the double helix are real, nonzero quantities, we have $D(2 - D) > 0$, i.e., $D < 2$, according
to Eq. (17). On the other hand, by definition, the double-helix
structure corresponds to the existence of two different real roots of 
\( \sin^2(\Delta \phi_{12}/2) \) such that

\[
8(1 - \sqrt{D(2-D)}) - 7(D-1)^2 > 0, \tag{30}
\]

which implies \( D > 1 + 4\sqrt{3}/7 \) as in agreement with the existing results.\(^{15,20,21,24}\) As illustrated in Fig. 7, the critical diameter ratio \( D = 1 + 4\sqrt{3}/7 \) can then be interpreted as a bifurcation point at which the number of density-maximized configurations in any triplet of mutually touching spheres changes from unity for a single helix to two for a double helix as the value of \( D \) increases.

V. DISCUSSION AND CONCLUSIONS

The work presented here is complementary to an aforementioned analytic theory\(^{2,24,25,26}\) that accounts for the emergence of a range of densest possible helical structures at \( D > 2 \). Our theoretical analysis, which relates two densest possible helical structures of equal-sized hard spheres at \( D < 2 \) to the density maximization of repeating microconfigurations, helps us understand why these helical structures can be constructed from a method of sequential deposition\(^{21,22}\) where each sphere is dropped to its lowest possible position for a local maximization of the packing density: (1) A global maximum of the packing fraction is achieved when the densities of such local configurations are all maximized. (2) The overlapping of each triplet configuration with its neighbors (e.g., the pair \( [2, 3] \) is shared between the adjacent triplets \( [1, 2, 3] \) and \( [2, 3, 4] \)) ensures that the same type of handedness is propagated across each helical structure. (3) A transition of helicity occurs at the critical diameter ratio \( D = 1 + 4\sqrt{3}/7 \) because there is a change in the number of optimal microconfigurations for any triplet of mutually touching spheres. As to potential applications of our results, the analytic expressions obtained for the positions of spheres in these two helical structures could serve as a theoretical basis for developing novel rodlike chiral molecules of different lengths and helicities, where a subject of great interest would be the liquid-crystalline properties of such systems.

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