Bending of nanoscale filament assemblies by elastocapillary densification

Zhouzhou Zhao, Sameh H. Tawfick, Sei Jin Park, Michael De Volder,* A. John Hart,† and Wei Lu‡
Department of Mechanical Engineering, University of Michigan, Ann Arbor, Michigan 48109, USA
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We report a mechanism by which nanoscale filaments self-assemble into asymmetric aggregates by elastocapillary action. Specifically, capillary rise of liquid into an asymmetric pattern of vertically aligned filaments causes the filaments to deflect laterally during elastocapillary densification. We quantitatively show that the lateral deflection can be controlled precisely by the pattern shape and the coupling strength among the filaments. We exploit this mechanism to fabricate asymmetric micropillars and multidirectional bridges of densely packed carbon nanotubes. Analogous behavior occurs as biological filaments interact with liquids, and these findings enable scalable fabrication of anisotropic filament assemblies for manipulating surface interactions between solids and liquids.

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I. INTRODUCTION

Self-assembly of filaments, ranging from actin to silk [1,2], is ubiquitous in nature. Biological filaments typically grow and assemble in a liquid environment, where capillary action plays a significant role. The arrangement and coupling of filaments determines their collective mechanical properties, and how forces are communicated through filament assemblies. Further, synthetic mimics of biological filaments, both in shape and chemistry, are widely sought for practical applications including smart surfaces, microelectronic interconnects, and electrode-cell interfaces [3,4]. However, while capillary forces have been shown to assemble synthetic nanostructures including nanoparticles [5], nanorods [6], micro pillars [7], and even wet hair [8], the formed structures are generally symmetric or uniform, showing a simple agglomeration of the components.

In particular, asymmetric assemblies of nanostructures are sought to mimic the function of biological structures such as cilia, and to create complex textures for uses including dry adhesives and directionally wetting surfaces. Importantly, such assemblies are difficult to fabricate by traditional methods such as photolithography and etching [9]. We report a mechanism whereby ensembles of nanoscale filaments self-assemble into asymmetric (bent) aggregates by infiltration and subsequent evaporation of a liquid. Quantitatively, we show that the lateral deflection of the filaments can be controlled precisely by the pattern shape and the coupling strength among the filaments. The finding provides insight into analogous behaviors in nature where biological filaments interact with liquids. In particular, bending filament assemblies are critical to mimic structures such as microhairs of insects [10]. More importantly, bending filaments can be combined to form dome shapes which are abundant in nature. The mechanism we discuss may present an enabling technique for scalable fabrication of asymmetric filament assemblies at a wide range of length scales.

Carbon nanotubes (CNTs) were chosen as an example system due to their outstanding mechanical, electrical, thermal, and chemical properties [11], along with the ability to fabricate patterns of vertically aligned CNTs [12] as starting templates for assembly experiments. Chemical vapor deposition growth of CNTs enables efficient production of vertical CNT “forest” microstructures having straight sidewalls and high aspect ratios, with dimensions ranging from micrometers to millimeters [13]. Despite the exceptional properties of individual CNTs, the bulk properties of CNT forests are typically poor due to the low density of CNT growth, rendering them inadequate for most applications. When a CNT forest is immersed in liquid, capillary forces densify the CNTs and significantly increase the mechanical robustness and bulk properties. Previous studies showed that nonpatterned CNT forests densify into clusters after liquid spreading and drying [14], creating uniform cellular foams. Similarly, patterned polymer nanopillars can aggregate into helical clusters [15].

For an ensemble of vertically aligned filaments, a critical cluster size is determined by a balance between elastic and capillary forces during densification. Any cluster having a larger size becomes unstable and forms internal voids. This critical size has been derived for various filament assemblies, like polymer micropillars and CNTs [14,16,17]. We consider filament assemblies smaller than the critical cluster size, which do not form internal voids during densification. Uniquely, while previous studies investigated the densification of nonpatterned CNT forests, or CNT forests patterned into shapes having rectangular or circular (azimuthally symmetric) cross sections, we study the behavior of bilaterally symmetric shapes. A shape with bilateral symmetry, such as a semicircle, has only one axis of symmetry. As discussed later, coupling between the local capillary forces and the geometry of these shapes causes a lateral deflection during the densification process.

II. EXPERIMENTS

Our process for creating bent CNT microstructures is as follows [Fig. 1(a)] [18]. First, a film of iron (1 nm thickness)
is deposited by e-beam evaporation on a silicon wafer coated with photoresist patterns having semicircular holes. After lift-off, the iron forms isolated islands each of which is designed to have an area smaller than the critical cluster size for a given forest height, thus forming a single aggregate upon densification. Then, the iron catalyst is annealed in a mixture of He and H2 at 775 °C followed by the CNT growth step where C2H4 is added to the gas mixture at the same temperature [13]. The process results in CNT forests with heights ranging from ten to hundreds of micrometers depending on the growth step duration [Fig. 1(b)]. Finally, the substrate with the CNT forests is placed upside down on a metal mesh covering a beaker containing a boiling organic solvent such as acetone. The condensed liquid wets the CNTs by rising independently within each CNT microstructure due to capillary pressure, and then the solvent evaporates when the substrate is removed from the vapor stream. After the structure is dried, the deflections are held by van der Waals force or mechanical interlocking. In particular, CNT forests grown from semicircular patterns deflect laterally, creating bent micropillars [Fig. 1(c)]. Unlike immersion, the condensation process is able to form small closely packed individual microstructures because the condensed liquid volume does not bridge neighboring structures.

III. THEORETICAL MODEL

A. Bending mechanism

The bending behavior of the assemblies poses interesting questions. What is the mechanism? How to control the bending angle? Since the collective properties of densely packed filament assemblies strongly depend on their morphology [19,20], the ability to predict and control the shape of the structures is critical. Imaging of the bent structures gives initial insights. First, we find that the filaments at the base are flattened onto the substrate [Fig. 1(c)] due to capillary pressure [17] on the perimeter of the microstructure. The lengths of flattened filaments are different, and the densified structure is located in close proximity to the centroid of the original cross section of the growth pattern. Further, the structure near the base is prone to bend toward the straight edge of the semicircle. In contrast, the upper portion of the structure, however, bends toward the opposite (curved) edge.

Based on these observations, we identified two major effects contributing to the bending behavior [Fig. 1(d)]. First, the filaments push against each other, introducing a distribution of lateral forces. The difference in population of filaments on both sides of the centroid results in the structure bending toward the straight edge. Second, the contraction of filaments creates a distribution of axial pulling forces that act asymmetrically on the upper portion of the forest. Based on the slip characteristics of filaments within the forest, this effect can lead to bending toward the curved or straight edge of the semicircle. The collective actions of the two effects determine the final bending angle of the densified structure.

B. Effect of lateral force

Now consider the first effect. Figure 2(a) shows the cross section of a semicylindrical filament microstructure with radius $R$. After densification, the radius reduces to $a = R/D$, where $D$ is the densification factor. We have assumed uniform densification, so that the cross section maintains the same shape after densification. The $x$ coordinate coincides with the symmetry line. The $z$ axis passes through the centroid, which does not move during the densification process. The whole structure bends within the $x-z$ plane by $\theta_l$, or $\beta = \pi/2 - \theta_l$. Consider the bending of an arbitrary filament, ABC, in Fig. 2(a). A magnified view is given in Fig. 2(b). To accommodate the bending of the whole structure, the filament bends by an angle $\gamma$ in plane ABC such that the portion BC is parallel to the $x-z$ plane and the angle between BC and the substrate equals $\beta$. To help visualize the relation, a line CD perpendicular to the substrate is shown. Denote the angle between the flattened portion AB and the $x$ axis by $\varphi$. The geometric relation gives $\cos \varphi = \cos \beta \cos \varphi$. 

![Fig. 1](https://example.com/fig1.png)
In this first effect, filaments are allowed to slide freely to each other, and we focus on forces locally perpendicular to the filaments, i.e., the lateral forces. The lateral force of a filament is the elastic restoring force due to its bending, which exerts on the microstructure. The total lateral forces from all filaments constitute a net force that depends on the overall bending of the structure. An initially vertical structure will bend until the net force equals zero to reach equilibrium. For each filament the lateral force is determined by its location and bending angle. We treat each filament as a beam. Consider beam bending under two perpendicular forces, \( P_1 \) and \( P_2 \), as shown in Fig. 2(b). These two forces are applied at the same location of a beam, but have different magnitudes and therefore produce different amount of bending. Denote the deflection angles by \( \gamma_1 \) and \( \gamma_2 \). The analysis of large beam deflection gives \( P_1 / P_2 = \lambda(\gamma_1) / \lambda(\gamma_2) \), where \( \lambda(\gamma) \) is a positive dimensionless monotonic function \(^{[21]}\). Note that the effect of force location and beam stiffness cancels out in the ratio. Each bent filament exerts an elastic force, \( P(\gamma) \), to the microstructure. Here \( P(\gamma) \) can be viewed as a concentrated force when two filaments have a narrow contact zone, or the resultant of a distributed contact force along the filament. The integration of \( \mathbf{P} = \lambda(\gamma) \mathbf{u}_p(\varphi, \beta) \) over all filaments gives the total lateral force, where \( \mathbf{u}_p(\varphi, \beta) \) is a unit vector in the force direction.

Due to the bilateral symmetry of the semicylindrical shape, the total lateral force component in the \( x-z \) plane is given by \( P_\perp = \lambda(\gamma)(\mathbf{u}_p - \mathbf{u}_p \cdot \mathbf{j}) \) with \( \mathbf{j} \) being the unit vector in the \( y \) direction, or

\[
P_\perp(\varphi, \beta) = \lambda(\gamma) \frac{\cos \varphi \sin \beta}{1 - \cos^2 \varphi \cos^2 \beta}.
\]

\( P_\perp(\varphi, \beta) \) is positive for filaments to the right of the \( y \) axis \((\cos \varphi > 0)\), meaning they push left. Those filaments to the left of the \( y \) axis push right. We use the shooting method to find the critical \( \beta_* \) which satisfies \( \iint P_\perp(\varphi, \beta) dA = 0 \). Note that a multiplier, i.e., the number of filaments per unit area in the as-grown forest has been dropped since it is uniform. The integration extends over the semicircular cross section of radius \( R \). Our calculation shows \( \beta_* < \pi/2 \), or the whole structure bends toward the straight edge. Note that \( \theta_* = \pi/2 - \beta_* \).

It is instructive to examine the resultant lateral force when the structure is vertical \((\beta = \pi/2)\). In this situation, \( P_\perp(\varphi, \beta) \sim \cos \varphi \) since all filaments have the same \( \lambda(\pi/2) \) coefficient. The total lateral force is proportional to \( \int_{\pi}^{\pi} \int_0^\pi \cos \varphi \, r \, dr \, d\alpha \approx -R^2/3 \). This net negative force pushes the whole structure to bend toward the straight edge until equilibrium is reached.
C. Effect of axial force

To understand the second effect which is due to axial forces, we begin with an introduction of the concept of differential length. Figure 3(b) shows two semicircles illustrating the cross section before and after densification. The origin of the $x$-$y$ coordinate coincides with the centroid. Consider a filament attached to the substrate at location $(r, \phi)$ before densification, where $r$ is the distance to the centroid and $\phi$ is the angle relative to the $x$ axis. After densification, the lower portion of the filament flattens on the substrate toward the centroid and the remaining portion bends upward to form the densified structure, as seen in Fig. 1. The flattened length, $\Delta_d(r, \phi) = (1 - 1/\sqrt{D}) r$, is shown by the blue segment in Fig. 3(b). The differential length is defined as the height reduction of each filament, $\Delta_d(r, \phi)$.

In actuality, the slip between filaments such as CNTs is constrained by a top “crust” consisting of entangled filaments due to the self-organization mechanism of the initial stage of growth [22,23]. We define a sticking plane above which all filaments are connected. As is evident later, the location of the sticking plane does not affect the determination of the bending angle. Below this plane, filaments can slide to each other freely when they bend to compensate for the differential length. Above this plane, the structure does not bend since the differential length has been compensated by the bending below.

We use energy minimization to obtain the bending angle $\theta_d$ due to the axial forces, which pull down the structure and generate stretching energy in each filament. This energy is partially relaxed when the sticking plane moves down by $\Delta_0$ and rotates by $\theta_i$. The bending of the whole structure changes the differential length by $\Delta_d(r, \phi) = \theta_d r \cos \phi$, as shown in Fig. 3. The distribution of differential length is then given by $\Delta(r, \phi) = \Delta_d(r, \phi) - \Delta_0$. The stretching energy is $G = (SN/2) \int_0^L \int_0^{2\pi} \Delta^2 r dr d\phi$, where $S$ is the axial elastic stiffness of an individual filament, $N$ the number of filaments per unit initial cross-section area, and $R_{\text{d}}(\phi)$ the boundary of the initial cross section before densification. The values of $S$ and $N$ are insignificant as they drop out later. The high aspect ratio makes a filament very flexible, thus its bending energy can be neglected. Calculation shows that $R_{\text{d}}(\phi) = (4R/3\pi)[\cos \phi + (3\pi/4)^2 - 1 - \cos \phi]$ on the curved edge and $R_{\text{d}}(\phi) = -(4R/3\pi) / \cos \phi$ on the straight edge. Substituting the expressions of $\Delta_d$, $\Delta_b$ into $G$ and take $\partial G / \partial \Delta_0 = 0$, $\partial G / \partial \theta_d = 0$, we have

$$
\theta_d = (1 - 1/\sqrt{D}) \left\{ \frac{8 \left[ \int_0^{2\pi} R^2 d\phi \right] \left[ \int_0^{2\pi} R^3 \cos \phi d\phi \right] - 9 \left[ \int_0^{2\pi} R^3 d\phi \right] \left[ \int_0^{2\pi} R^4 \cos \phi d\phi \right]}{8 \left[ \int_0^{2\pi} R^2 \cos \phi d\phi \right]^2 - 9 \left[ \int_0^{2\pi} R^3 d\phi \right] \left[ \int_0^{2\pi} R^4 \cos^2 \phi d\phi \right]} \right\}.
$$

The expression suggests that $\theta_d$ increases with the densification factor, and vanishes when $D = 1$. Evaluation of Eq. (2) gives $\theta_d = -9.5(1 - 1/\sqrt{D})$ degrees, with negative sign for bending toward the straight edge.

D. Effect of slip

Now we consider slip of filaments from the sticking plane, which is likely to occur at the perimeter of microstructures where the axial forces are larger. We define a cutoff contour, $R_{\text{stick}}$, beyond which filaments can slip relative to one another and therefore do not contribute to the total axial forces. The contour is a circle centered at the centroid, since the flattened length, $(1 - 1/\sqrt{D}) r$, is independent of $\phi$. To calculate the stretching energy, the integral domain now reduces to the shaded intersection area of the circle with radius $R_{\text{stick}}$ and the original semicircle. We find a critical radius, $R_{\text{stick}}^c = 0.86 R_v$, where $R_v$ is the maximum distance from the centroid to a point on the semicircle. When $R_{\text{stick}} > R_{\text{stick}}^c$, i.e., the main aggregate (where slip is prohibited) equals the whole structure, the structure bends toward the straight edge.

In contrast, when $R_{\text{stick}} < R_{\text{stick}}^c$, i.e., the main aggregate is smaller than the whole structure and slip occurs at the corners, the structure bends toward the curved edge. $R_{\text{stick}}$ can be treated as a measure of the interfacial strength between filaments, as will be shown experimentally for CNTs later. The net deflection combines the two effects. As shown in Fig. 2, $\theta_i$ will induce an additional differential length, $\Delta_i(r, \phi) = r \cos \phi \tan \theta_i$. Under the constraint of sticking plane this length causes bending similar to that described in the second effect. The net deflection angle is $\theta = \theta_d - \theta_i + \tan \theta_i$, positive for bending toward the curved edge.

IV. RESULTS

The model can be readily extended to other cross-section shapes, and is verified by experiments. Specifically, we have considered the elastocapillary densification of solid and hollow semicylindrical filament assemblies parametrized by $r = R_i / R_v$, with inner radius $R_i$ and outer radius $R_v$. Figure 4 gives representative results, showing that the total deflection is highly sensitive to $r$ and to the parameter $k = 1 - R_{\text{stick}} / R_v$, which describes the amount of slip.
Figure 4(a) shows that when slip is absent \(k=0\), the densified structure always bends toward the straight edge \(\theta<0\). With increasing \(r\), the microstructure becomes a thin “C” shape and bends more. With slip among the filaments, the structure can bend toward the curved edge \(\theta>0\). Take \(k=0.4\) as an example. At \(r=0\), i.e., a semicircular shape, the bending angle is 13°. While the angle is −7° when \(k=0\). This interesting transition can be understood as follows. As shown in Fig. 3, when there is slip, those filaments whose base is outside the \(R_v\) circle lose grip on the sticking plane and do not contribute to creating a differential length. As \(k\) increases, more filaments in the corners to the left side of the centroid lose grip. As a result, those filaments to the right of the centroid win, and the resultant axial pulling force bends the structure toward the curved edge. This explains the possible reversal of the bending direction as \(r\) increases, and the further increase of the bending angle when \(k\) changes from 0 to 0.4. This effect becomes more important as \(r\) increases because a greater proportion of the filaments are near the corner of the shape. Consequently, the net bending angle toward the curved edge is larger. The \(k=0.1\) curve shows that when the interfacial strength of slip is fixed, changing the shape factor \(r\) can tune the bending from toward the straight edge to the curved edge. This intriguing behavior is captured by the experimental data.

We have validated these trends in experiments with CNT microstructures. Figure 4(b) shows two sets of CNT structures, confirming the capability to tune the bending angle based on the initial pattern of filaments prior to elastocapillary densification. Each row shows a series of shapes with different \(r\), and the measured bending angles are represented by the solid squares in Fig. 4(a). The different trends are created by varying the intensity of plasma etching of the CNTs in \(O_2/Ar\) prior to densification. We find that plasma etching efficiently reduces the main aggregate size by reducing the CNT density at the top and outer surface of each structure. Therefore, plasma etching enables more slip around the edges of the CNT structure, and causes more bending toward the curved edge which agrees precisely with the model. The upper image matches the \(k=0.3\) curve while the lower one is close to the \(k=0.1\) curve. Nonuniformity in densification changes the cross-section shape, which may partially account for the discrepancy between prediction and experiments.

Understanding of the bending mechanism also allowed us to create complex arrangements of CNT structures as shown in Figs. 4(c)–4(f). These include flowerlike architectures made from circular arrangements of structures that bend toward a common point; and large arrays of bending structures that resemble microhairs on the skin of insects. Notably, these structures range in size over two orders of magnitude, from a few microns to hundreds of microns in height. These special geometries, coupled with the attractive mechanical, electrical, and chemical properties of CNTs provide a promising foundation for future work.

V. CONCLUSION

In summary, we introduced a mechanism by which nanoscale filaments form laterally bent assemblies during elastocapillary densification of filament assemblies. This bending occurs due to the distribution of lateral and axial forces.
which result in competition between bending in opposite directions. The initial arrangement of the filaments, the densification ratio, and the amount of slip influence the final bending angle. Therefore, coupling of capillary effects and internal sliding among filaments can produce a rich pattern of complex morphologies. From a practical point of view, these findings can enable a class of approaches to form complex and biomimetic microstructures that harness the attractive properties of synthetic nanostructures such as CNTs.

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