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Densification of single-walled carbon nanotube films: Mesoscopic distinct element method simulations and experimental validation ^{EP}

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ABSTRACT

Nanometer-thin single-walled carbon nanotube (CNT) films collected from the aerosol chemical deposition reactors have gathered attention for their promising applications. Densification of these pristine films provides an important way to manipulate mechanical, electronic, and optical properties. To elucidate the underlying microstructural level restructuring, which is ultimately responsible for the change in properties, we perform large scale vector-based mesoscopic distinct element method simulations in conjunction with electron microscopy and spectroscopic ellipsometry characterization of pristine and densified films by drop-cast volatile liquid processing. Matching with the microscopy observations, pristine CNT films with a finite thickness are modeled as self-assembled CNT networks comprising entangled dendritic bundles with branches extending down to individual CNTs. Simulations of these films under uniaxial compression uncover a soft deformation regime extending up to an ~75% strain. When removing the loads, the pre-compressed samples evolve into homogeneously densified films with thickness values depending on both the pre-compression level and the sample microstructure. The significant reduction in thickness is attributed to the underlying structural changes occurring at the 100 nm scale, including the zipping of the thinnest dendritic branches.

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I. INTRODUCTION

Carbon nanotube (CNT) films exhibit a unique high porosity/low-density network structure with thickness values down to a few nanometers.^{1–4} Mechanical, electrical, and optical properties of the CNT films depend greatly on their microstructure, with the CNT orientation (aligned or random network) and density emerging as important parameters in addition to the CNT length and diameter. While manufacturing well-aligned films requires sophisticated synthesis⁵ and post-processing,⁶ the manipulation of the film density is a less technologically challenging process. After synthesis, one usually obtains sparse CNT “pristine” networks that can be densified even unintentionally, for example, during the sample transferring and doping procedures. In more controlled approaches, films and yarns are subjected to mechanical^{7,8} and liquid phase processing,^{9,10} where densification is viewed as an enabling step for developing CNT applications. For example, it was shown that the densification of the vertically aligned CNT forests can lead to significant improvements in mechanical properties.¹¹ It is also known that the CNT densification increases the CNT–CNT connectivity and decreases the contact resistance between CNTs,¹² which is very important for electrical properties. Thus, the manipulation of the intertube crossing points can be used for developing sensors or flexible electronics devices.^{13,14} In the optical domain, pristine films demonstrate antireflection properties, which are destroyed by densification.^{15,16}

Understanding the densification process at the microstructural level is a necessary step for establishing a structure–property relationship. One way to address the complexity presented by the microscale is through simulations.¹⁷ Unfortunately, the wide range of time and length scales encountered in CNT films makes the established all-atom molecular dynamics methods¹⁸ computationally prohibitive. Currently, the dynamical simulations of CNT films rely on numerical approaches, which are still under development and validation. In this respect, a recent theme in the development of numerical models is based on the idea of coarse-graining,^{19–22} where the goal is to develop computationally tractable models of reduced complexity, while preserving a set of target properties to a sufficient accuracy. One of the first developed models was based on the simple bead-and-spring (B&S) polymeric chain model,¹⁹ which is usually trained to reproduce elastic and adhesion properties of CNTs. Unfortunately, the impact of the very limited number of training parameters and (hence limited essential target properties passed to the mesoscale) afforded by the B&S model onto the simulated self-assembled CNT networks is not fully understood. This is important because the simplicity and ease of implementation into existing molecular dynamics codes¹⁸ make the B&S model a popular choice for studying CNT systems as well as other semi-flexible polymer networks.²³ So far, one significant deficiency of the B&S model associated with the large artificial barriers for relative displacements of interacting CNT,^{20,21} which limit the CNT–CNT sliding during the system evolution, was shown to strongly affect the bundling of the self-assembled CNT networks. The more complex mesoscopic CNT models,²⁴ including the mesoscopic distinct element method (mDEM)^{21,25} employed here, are placing a premium on the accuracy of the coarse-grained non-bonded²⁶ and bonded interactions.

For validation purposes, we have first examined with electron microscopy real pristine and densified films, which reveal multi-scale structural features comprising CNT bundles with thickness values down to individual CNTs. In benchmark simulation, a stable ultra-thin coupon with few-CNT branches and individual CNTs is regained with mDEM, but not with B&S, which gives instead an adhesion-dominated densified cellular structure formed by thick bundles. Therefore, the availability of the experimental microstructure for the validation step provides the opportunity to uncover another important deficiency of the B&S model, namely, its failure to properly capture the entanglement present in films formed by CNTs with low inclination angles and thus to more strongly usher in accurate mesoscopic models.

Once validated, mDEM is used to successfully generate low-density CNT samples, which comprise interacting CNT bundles with a dendritic structure, and to further simulate surface compression-driven densification. We note that while the mechanical response to uniaxial compression of vertically aligned CNT forests has been recently simulated and interpreted using the concept of a phase transformation,^{27,28} isotropic CNT thin films were previously considered only under compressive forces directed along the film direction.²⁹ The goal of this work is to simulate the compression response of the CNT microstructure over a large deformation range in order to shed some light into the film densification mechanism by liquid processing with a mesoscopic modeling method from the accurate class. Our simulations reveal the important role of the restructuring processes at the 100 nm scale and uncover the structural characteristics of the free-standing densified films. This is foundational knowledge for establishing the structure–property relationship, which is needed for the development of future technologies based on CNTs.

Our paper is organized as follows. Section II gives an overview of the two coarse-grained simulation methods used here: MDEM and B&S. Section III presents our electron microscopy results revealing the complexity of the structural organization of the pristine and densified CNT films, as well as results of express film thickness measurements by spectroscopic ellipsometry. The structural characteristics of the simulated samples, dynamical compression, and recovery simulations are presented in Sec. IV. Finally, the summary of this computational and experimental study is given in Sec. V.

II. COMPUTATIONAL METHODS FOR SIMULATING THE MESOSCALE DYNAMICS

A. B&S for CNTs

As already mentioned, the simple B&S polymeric chain multi-scale model¹⁹ inherits a very limited number of parameters from the atomistic scale. We briefly review this model to help relate the microstructure features observed in the simulation to the mesoscopic model. In B&S, a CNT of length L_{CNT} is represented as a linear chain of point masses. Each mass m is spaced apart by distance t . Massless linear springs between bonded pairs (k_s) and triples (k_t) are trained to capture the linear extension and bending behavior of individual CNTs, regardless of the size of the CNT segment represented by each spring. More specifically, $k_s = YA/t$ and $k_t = YI/t$, where Y is Young’s modulus, A is the

TABLE I. Parametrization of a B&S model with adhesion³⁰ for a (10,10) CNT.

m (amu)	t (Å)	k_s (eV/Å)	k_b (eV)	ε (eV)	δ (Å)
662	3.4	270	6,599	0.10	12.8

cross-sectional area, and I is the area moment of inertia of the CNT. Considering successive i , j , and k beads, the total potential energy is expressed in terms of two u_{ij}^t and three u_{ijk}^b body potential energy terms,

$$u_{ij}^t = \frac{1}{2}k_s(r_{ij} - t)^2, \quad u_{ijk}^b = \frac{1}{2}k_b(\theta_{ijk} - \pi)^2, \quad (1)$$

where r_{ij} stands for the distance between beads i and j , while θ_{ijk} is the angle between consecutive beads i , j , and k . Table I lists an example parametrization of a (10,10) CNTs, based on $Y = 1029$ GPa value. The dynamics of the CNT represented this way is dictated by the stretching and bending forces derived from these terms, along with the van der Waals forces described next.

The van der Waals inter-tube interactions are described by a pairwise Lennard-Jones (L-J) potential acting between the beads located on different CNTs. The two available parameters energy ε and distance δ are usually fitted to describe the equilibrium spacing and adhesion between two parallel CNTs. The CNT interactions at other distances than the equilibrium distance are not included in the training set. For (10,10) CNTs, adhesion is 0.23 eV/Å. Considering the tubes in contact with the inter-axis distance at 13.5 Å, one obtains the parameters listed in Table I.

Previous studies^{20,21} have shown that B&S chains can represent the shear strength of interacting CNTs when each bead represents only a small segment of a CNT. This is because the isotropic L-J potential between two infinite parallel chains favors a staggered over an in-line arrangement, a behavior that is not seen at the molecular level. Therefore, simulating the CNT dynamics requires the use of “small” beads, like the ones shown in Table I derived³⁰ for a (10,10) CNT, although coarser grains are required to achieve simulations of large enough network samples that exhibit representative behavior.³¹

Finally, it is important to note that the B&S model is a thermal model. After assigning velocities corresponding to the desired temperature, the beads can be evolved in time in the NVT ensemble with molecular dynamics codes, like LAMMPS.¹⁸ Dissipative forces can be added to this similar to those of Jacobs *et al.*³² for any application of the model in which energy is deposited or removed from the system.

B. mDEM for CNTs

The mDEM model for CNTs^{21,25} was introduced in our previous works in conjunction with its implementation in the popular distinct element code PFC3D.³³ More recently, the model was implemented^{31,34} in the code WaLBerla.³⁵ Relying on the scalable message passing interface technology, WaLBerla enables deterministic evolution of millions of distinct elements of given mass and moment of inertia. As discussed below, the model is now fully cast into a vector-based format.^{36,37}

Figure 1(a) illustrates the mDEM representation of a CNT (left), where each mesoscopic distinct element (center) lumps a finite number of atoms of the atomistic model. The distinct elements in direct contact interact via the enhanced vector model (EVM) potential,³⁷ which describes the resistance to stretching, shear, bending, and torsional deformation displacements of the CNT portion of length T and radius r_{CNT} as a Euler–Bernoulli beam.

Consider two equal-sized particles i and j with equilibrium separation T and orientation described with orthogonal vectors $\mathbf{n}_i^k$ and $\mathbf{n}_j^k$, $k = 1, 2, 3, \dots$ attached to each particle. The interaction potential is given as the function of invariant quantities associated with the inter-center normal $\mathbf{e}_{ij}$ and two set of vectors $\mathbf{n}_i^k$, $\mathbf{n}_j^k$. Let $\mathbf{n}_i^1$ be along the tube long axis. As depicted in Fig. 1(b) (left), in the undeformed state $\mathbf{n}_i^1 = -\mathbf{n}_j^1$, $\mathbf{n}_i^2 = \mathbf{n}_j^2$, and $\mathbf{n}_i^3 = \mathbf{n}_j^3$. The key components (for the present investigation) of the two-body EVM potential U_{ij} describe the resistance to stretching U_{ij}^t and bending U_{ij}^b deformation of the two elements, Fig. 1(b) right, as^{34,37}

$$U_{ij}^t = \frac{YA}{2T}(r_{ij} - T)^2, \quad U_{ij}^b = \frac{YI}{T}(\mathbf{n}_i^1 \cdot \mathbf{n}_j^1 + 1), \quad (2)$$

FIG. 1. (a) Coarse graining of the atomistic representation of a CNT into mesoscopic distinct elements connected by vector-based bond models. (b) Schematics of two distinct elements linked by an enhanced vector model (EVM) bond (left) and two modes of the bonded deformation (right). (c) Three deformation modes of the van der Waals interactions of elements located on different CNTs, for which only the axes are shown. The empty circles illustrate the position of the particles before deformation.

where Y is the CNT Young's modulus, A is the CNT cross-sectional area, and I is the area moment of inertia.

Unlike in B&S, the mDEM dynamics is dictated not only by forces but also by the moments arising from the employed EVM potential. For example, the components of force $\mathbf{F}_{ij}$ and moment $\mathbf{M}_{ij}$ on the center of mass of particle i due to particle j corresponding to terms (2) can be written as

$$\mathbf{F}_{ij} = \frac{YA}{2T}(r_{ij} - T)\mathbf{n}_r, \quad \mathbf{M}_{ij} = \frac{YI}{T}\mathbf{n}_i^1 \cdot \mathbf{n}_j^1. \quad (3)$$

Here, $\mathbf{n}_r = \mathbf{r}_{ij}/r_{ij}$.

EVM replaces the parallel-bond incremental model employed in the earlier approach.²¹ It can be parameterized to represent single- and multi-walled cylindrical and collapsed CNTs.³⁸ In this work, we coarse-grained a (10,10) CNT with a cylindrical cross section into a chain of spherical distinct elements with diameters $2r_{CNT}$ corresponding to CNT portions with $T = 2r_{CNT} = 13.56 \text{ \AA}$, i.e., four times larger than the in the B&S model shown in Table I. The values of the parameters of Eq. (2) are $Y = 1029 \text{ GPa}$, $A = 142.7 \text{ \AA}^2$, and $I = 3480 \text{ \AA}^4$.

The coarser mDEM modeling of CNTs is also enabled by a two-body vdW potential U , which nevertheless is of a more sophisticated form than the simple L-J expression. We recognize that the non-bonded interaction is also of a vectorial potential form,

$$U_{ij} = U(r_{ij}, \mathbf{n}_r \cdot (\mathbf{n}_i^1 + \mathbf{n}_j^1), \mathbf{n}_i^1 \cdot \mathbf{n}_j^1) = U(r_{ij}, \cos \theta_{ij}, \cos \gamma_{ij}), \quad (4)$$

where angles θ_{ij} and γ_{ij} describe mutual orientation of two elements i and j located on different CNTs and the precise expression for U is given in Ref. 21. It should be noted that this symmetrized form captures not only normal forces, but also shear forces and

aligning moments between distinct elements, Fig. 1(c),

$$\mathbf{F}_{ij}^r = -\frac{\partial U}{\partial r_{ij}}\mathbf{n}_r, \quad (5a)$$

$$\mathbf{F}_{ij}^\theta = -\frac{1}{r_{ij}}\frac{\partial U}{\partial \theta_{ij}}\mathbf{n}_\theta, \quad \mathbf{n}_\theta = \frac{\mathbf{r}_{ij} \times (\mathbf{r}_{ij} \times (\mathbf{n}_i^1 + \mathbf{n}_j^1))}{|\mathbf{r}_{ij} \times (\mathbf{r}_{ij} \times (\mathbf{n}_i^1 + \mathbf{n}_j^1))|}, \quad (5b)$$

$$\mathbf{M}_{ij}^\gamma = -\frac{\partial U}{\partial \gamma_{ij}}\mathbf{n}_\gamma, \quad \mathbf{n}_\gamma = \frac{\mathbf{n}_i^1 \times \mathbf{n}_j^1}{|\mathbf{n}_i^1 \times \mathbf{n}_j^1|}. \quad (5c)$$

The partial derivatives $\frac{\partial U}{\partial r_{ij}}$, $\frac{\partial U}{\partial \theta_{ij}}$, and $\frac{\partial U}{\partial \gamma_{ij}}$ are given in Ref. 21 and are, therefore, not repeated here.

To demonstrate this potential, Fig. 2(a) plots the vdW energy calculated between two parallel (10,10) CNTs, each represented by 10 distinct elements placed under periodic boundary conditions (PBCs). It can be seen that mDEM describes very precisely the narrow well obtained by the direct integration of the atomistic L-J interactions.^{21,39} At $d = 17.1 \text{ \AA}$, E_{vdW} has a minimum, where the force between CNTs is zero. At smaller d , the potential increases very rapidly and becomes positive for $d < 16.8 \text{ \AA}$. This behavior corresponds to significant repulsive forces between the elements located on the two CNTs, which prevent the interacting elements to interpenetrate. At larger d , the attractive dispersive interactions are dominating, and this will result in the clumping of the neighboring CNT's.

While the potential well description based on the simpler L-J potential of the B&S model captures similar adhesion energy, there are also some pronounced differences from the integrated well. By having the minima at $d = 13.5 \text{ \AA}$, the B&S allows for the CNT surfaces to physically overlap and even interpenetrate. On the attractive side, the potential approaches the horizontal axis with a lower curvature and even intersects the attractive part of the true integrated potential at $d \sim 20 \text{ \AA}$. Thus, we expect that, in the B&S model, the

FIG. 2. (a) The vdW energy E_{vdW} (per unit length) vs s the tube-tube center-to-center distance d , as described with mDEM (circles), B&S (triangles connected by lines), and direct integration (continuous line). (b) The mDEM model for non-bonded shear deformation of two distinct elements (left) leads to a constant E_{vdW} vs s , the relative shift between the two parallel infinitely long CNTs at $d = 17.1 \text{ \AA}$, where the potential depth has a minimum.

corresponding vdW attractive force between CNTs will have a much larger effective range than the underlying atomistic model.

Figure 2(b) illustrates another important quality of the mDEM model. Through the dependence of the non-bonding potential on the angle made by $\mathbf{n}_i^1 + \mathbf{n}_j^1$ and $\mathbf{r}_{ij}$ vectors, i.e., the shear deformation in Fig. 1(d), E_{vdw} is made invariant to relative shifts s of parallel CNTs separated by the maximal adhesion distance. Thus, despite the large T of the distinct elements, the mDEM inter-tube interaction is free of the artificial corrugation introduced by the B&S type of mesoscopic CNT models, and, therefore, provides realistic smooth sliding of aligned CNTs.

The *athermal* mDEM model overviewed above is augmented to capture the dissipative atomistic scale processes associated with the room temperature CNT zipping and sliding against one another.^{25,40,41} The representation of the bonded and non-bonded interactions with potentials allows for symplectic integration of the equation of motion instead of the incremental algorithm used for parallel bonds in PFC3D.³³ More specifically, the dynamics of distinct elements is described in terms of state variables—translational and rotational positions and velocities of distinct elements—that are evolved in time with an explicit velocity Verlet time integration scheme. The evolution of rotational degrees of freedom is analogous with the rotations stored as quaternions.⁴² (Note that the Verlet algorithm is non-symplectic for 3D rotations.)

III. EXPERIMENTAL METHODS AND CHARACTERIZATION OF PRISTINE AND DENSIFIED FILMS

To infer the structure of the experimental CNT films, we have first investigated with both SEM and TEM high-quality films produced by floating catalyst (aerosol) chemical deposition.^{43,44} These “pristine” films comprise μm -long 1.4–2.3 nm in diameter single-walled CNTs, which are randomly oriented in the film’s plane as they are collected onto cellulose membrane filters directly from the reactor. They have 10–200 nm in thickness and densities of $\sim 0.12 \text{ g/cm}^3$. In addition, the precise film thickness before and after densification was measured with spectroscopic ellipsometry.

A. Electron microscopy results

The combined SEM and TEM investigations evidence a hierarchical bundling pattern in the pristine CNT films. A typical few μm portion of the film surface can be observed in the SEM image presented in Fig. 3(a). The structure consists of wavy CNT bundles, which are branching out into thinner and bent bundles or merging into larger ones. On the 100 nm scale, Fig. 3(b), thinner bundles comprising few-CNTs and even individual CNTs can be observed with TEM. Figure 3(c) details few-CNT bundles, some branching out in fewer-CNT bundles and individual CNTs, coexisting with thicker $\sim 10 \text{ nm}$ diameter “medium” bundles. The TEM images show only the projection of the bundle on the two-dimensional plane and do not have information about the three-dimensionality of the structure. As such, the number of CNTs in these “medium” bundles can only be estimated based on the measured bundle thickness and the mean diameter $2r_{\text{CNT}}$ of individual CNTs. For example, an $\sim 10 \text{ nm}$ bundle with a hexagonal closed-packed $2r_{\text{CNT}} = 2.2 \text{ nm}$ single-walled CNTs⁴⁵ would contain about 14

CNTs. Figure 3(d) details the zipping of three “medium” bundles into a larger bundle. As in the previous images, individual CNTs and thin 2-CNT bundles are also present. Interestingly, these bundles and others are oriented perpendicularly onto the three “medium” horizontal bundles indicated by arrows. This orientation suggests that these bundles could play a role in arresting the zipping progression of the three “medium” bundles.

Significant densification can be achieved by the drop-cast volatile liquid processing of the pristine films.⁴⁵ As it can be seen in the SEM image shown in Fig. 3(e), on the few μm scale, such densified films preserve the branching characteristic observed earlier in pristine films. However, zooming in to the 100 nm scale, Fig. 3(f), the TEM images no longer show fewer-CNT bundles and individual CNT features. Additionally, this image shows the zipping (but not the full coalescence) the “medium” bundles located at different heights.

B. Spectroscopic ellipsometry results

To characterize quantitatively the change in thickness under densification, we produced a free-standing CNT film by the dry-transfer method and measured its thickness before and after its densification by drop-casting of 200 μl clean ethanol. We use spectroscopic ellipsometry, a method that ensures that the film morphology is not affected by the measurement. For the measurement on the densified film, we have followed the methodology described in our recent work,³ where we successfully demonstrated that reflectance spectroscopic ellipsometry could alone determine the thickness and optical constants of the freestanding densified CNT films. For pristine films, we had to modify the method to measure in transmission [Fig. 4(a)] because the film reflection is suppressed to less than 1%. For both types of measurement, we use a variable-angle spectroscopic ellipsometer (VASE, J.A. Woollam Co.) within the wavelength range of 300–600 nm.

We have strong indications that pristine films exhibit optical anisotropy, which makes the simultaneous determination of optical constants and thickness a complicated task. However, as was shown by Hilfiker and co-workers,⁴⁶ the thickness could be determined from standard ellipsometry fitting of the change in polarization [i.e., Δ and Ψ in Fig. 4(a)] with effective optical constants. To verify the approach, we have retrieved the optical constants, i.e., the refractive index n and the extinction coefficient k as plotted in Fig. 4(b) and then calculated transmission predicted by the transfer matrix method.⁴⁷ We obtained excellent agreement with experimental values, Fig. 4(c). Employing these two approaches for a given film, we determined a thickness of $h_o = 122 \pm 5 \text{ nm}$ for the pristine case and an $h_d = 62 \pm 6 \text{ nm}$ thickness after densification. This means that the densification reduces the film thickness by about 50%.

IV. SIMULATION RESULTS

A. Spontaneous densification of an ultrathin “pristine” sample: mDEM vs B&S

Turning now to simulations, we have first tested the ability of the mDEM and B&S models to describe the microstructure observed on the sub- μm scale of the low-density pristine CNT films. In a benchmark example, Fig. 5, we find that the mDEM and

FIG. 3. Multiscale structure of the pristine (a)–(d) and densified (e)–(f) CNT film: (a) SEM showing an entangled structure of μm -long wavy bundles. (b) TEM of individual and 2-CNT bundles coexisting with “medium” ~ 10 nm diameter bundles (indicated with yellow arrow heads) on a 100 nm scale. TEM detailing (c) ~ 10 nm diameter bundles and (d) their merging into a thicker “large” bundle. Individual and 2–3 CNT bundles (indicated by black arrows) can be still observed. (e) SEM showing μm -long wavy bundles. (f) TEM of few-CNT bundles zipped on a 100 nm scale.

FIG. 4. (a) Scheme of ellipsometry measurement. (b) Obtained optical constants—refractive index (blue) and extinction coefficient (green), for pristine (dashed line) and densified (continuous line) CNT films. (c) Comparison of the transmittance spectra as obtained from the measurement (continuous line) and calculated (dashed line) from the measured optical constants.

FIG. 5. Comparison of the vdW and bending energy evolution in (a) mDEM and (b) B&S representation of a film network $700 \times 700 \times 11$ nm³ in size and density of $\rho = 0.176$ g/cm³. The film morphologies (top view) at the end of relaxation with (c) mDEM and (d) B&S; the number of CNTs in the selected bundles indicated by arrows is also given.

B&S models evolve into dramatically different structures. We have considered a network containing 450 CNTs, each with $L_{\text{CNT}} = 651$ nm. The starting structure for the mDEM simulations is a computer-generated network containing straight (10,10) CNTs, “grown” from “seeds” randomly placed in a $700 \times 700 \times 11$ nm³ cuboid. The CNT orientations were distributed isotopically in the CNT xy plane and uniformly distributed out-of-plane within the angle φ made by $\mathbf{n}_i^1$ vectors with the xy plane within the borders of 0° and 11°.

The initial van der Waals energy (E_{vdW}) of the sample originates in the crossed CNTs that form junctions. During cycling from a “cold” start (zero kinetic energy) with a 20 fs time step, the evolution is driven by the attractive vdW interactions which act to lower E_{vdW} at the expense of introducing strain energy (E_{strain}) in individual CNTs, Fig. 5(a), which practically coincides with the bending strain. The relaxation process is particularly fast during the first ns of the evolution. At the microstructure level, relaxation occurs through zipping,^{14,20} a topological transformation in which crossed CNTs bind locally on a sub-ns time scale.⁴⁰ The bundle aggregates generated this way contain only a few CNTs. After ~ 3 ns, the E_{vdW} lowering slows down significantly as the repulsive components of the vdW interactions and the CNT strain resistance are hindering the coarsening of the network into bundles. This “steady-state” structure contains “medium” size 5–10 CNT bundles, coexisting with thinner bundles and even individual CNTs, Fig. 5(c). As it can be seen in the inset, the 100 nm scale of the simulated sample exhibits important similarities, in terms of the variety of bundle sizes and branching, with the structure observed in the TEM images of the experimental film.

As the ratio between elastic and adhesion energy is well captured by mDEM and B&S, one may expect⁵⁰ that both models will give qualitatively similar network structures. In order to compare the outcomes of the mDEM and B&S treatments without introducing any sample bias, we have alternatively evolved the network structure obtained with mDEM after 6 ns of simulation time with the B&S treatment coupled with a Nose–Hoover thermostat at 300 K. When switched to the B&S model, the network structure becomes highly unstable. As it can be seen from Fig. 5(b), E_{vdW} instantly departs from the mDEM value and, during only 3 ns of evolution, it reaches a value which is about four times lower. E_{strain} presents a similar departure from its DEM value, reaching after 3 ns an about 30% larger value.

In both mDEM and B&S simulations, the network evolution is driven by the adhesive vdW forces. As CNT bending is well captured by the two models, it follows that the differences revealed in Fig. 5 originate into the inherent deficiencies of the L–J description of the non-bonded interactions. The B&S model fails to sustain the correct balance between the repulsive volume and dispersion interactions; the “input” CNT network disentangles and further evolves into an adhesion-dominated cellular structure under the long-range attractive forces which are overestimated in the L–J description [Fig. 2(a)]. During the B&S 3 ns of evolution, CNTs clump into bundles that further zip into very thick 50–70 CNT bundles, leaving behind large empty pores. The film acquires a qualitatively different cellular structure, Fig. 5(d), with CNTs characterized by $\varphi \sim 0$. Such a structural organization of the sub- μm scale disagrees

with the experimental observations of Figs. 3(b)–3(d) and is closer to the images of a few- μm scale.

Beyond the 3 ns time, we expect that the structures will further evolve into individual bundles weakly interacting with each other through bent CNT located at the bundle connectivity points.²⁰ Bending buckling⁴⁸ (not included here) is expected to play an important role²⁰ in further stabilizing these cellular networks. This effect does not play a role in the stabilization of the mDEM network of Fig. 5(c), which stores significantly less bending strain energy.

B. mDEM simulations of spontaneous densification of “pristine” samples

The above results make mDEM the method of choice for studying film densification. Although mDEM has the necessary accuracy, developing faithful computational models for the CNT films described in Sec. III is still challenging. In addition to the difficulties associated with identifying the three-dimensionality of the film structure from the SEM and TEM images, we recognize that the multiscale structure observed by electron microscopy is the result of the vdW-driven CNT coagulation during synthesis, which involves direct CNT–CNT collisions in the gas phase,²² and during and after the collection onto the filter substrate. While the former involves the zipping of individual CNTs, the latter stage is likely dominated by the bundle–bundle interaction processes.⁴⁹ Additionally, there are computational challenges related to the film size.

Understanding the film densification requires a straight representation of the film thickness. In the in-plane direction, the sub- μm scale is reasonably accessible computationally with the current implementation of mDEM, while the few-micrometer scale still poses extreme computational demands.³¹ Without sacrificing the realistic representation of film thickness, we have focused our study on the sub- μm scale, where the accurate description of the mesoscopic interactions is able to describe individual and few-CNT bundles coexisting with “medium” size bundles. As suggested by the TEM images of Figs. 3(b) and 3(f), this scale undergoes significant restructuring during the liquid processing and, therefore, could be important for the densification process.

To this end, we have constructed a series of morphologically diverse models for the “pristine” CNT film, as summarized in Table II, with the goal of understanding how different parameters affect the film structure and densification, and to eventually project this understanding to the behavior of the larger scale. The sample films were generated in the same manner as in the example of Fig. 5, and all correspond to a low mass density of 0.12 g/cm³. With the exception of “FB,” all the sample models were constructed by “growing” individual CNTs at random locations inside the control volume listed in the first column of Table II. To get insight into the interaction of already formed bundles collected onto the filter substrate, in “FB,” 2-CNT pairs rather than individual CNTs were grown.

All CNTs considered here are of (10,10) type, which is a reasonable choice for our experimental films. The L_{CNT} values, listed in the third column of Table II, were selected in order to generate network structures with different cohesive energies.^{40,50}

TABLE II. Parameters and statistical information of five CNT samples with initial density of 0.12 g/cm^3 . The magnitude of the Herman orientation factor (HOF), average tilt ($\langle \varphi \rangle$) of elements, film thickness h_o , density ρ_o , van der Waals E_{vdW} , strain energy E_{strain} , and total energy E are listed for the sample structure generated at the end of the relaxation.

Film and size (μm)	N_{CNT}	L_{CNT} (μm)	φ_{max} ($^\circ$)	$\langle \text{HOF} \rangle$	$\langle \varphi \rangle$ ($^\circ$)	h_o (nm)	ρ_o (g/cm^3)	E_{vdW} (keV/CNT)	E_{strain} (keV/CNT)	E (keV/CNT)
FA $1 \times 1 \times 0.14$	5185	1	11	-0.48	4.4	140	0.12	-0.91	0.21	-0.7
FB $1 \times 1 \times 0.14$	5185	1	11	-0.49	3.8	108	0.15	-2.08	0.18	-1.9
FC $0.33 \times 0.33 \times 0.14$	1733	0.33	11	-0.48	4.9	127	0.13	-0.34	0.08	-0.26
FD $0.33 \times 0.33 \times 0.14$	1733	0.33	22	-0.46	7.1	133	0.13	-0.27	0.07	-0.20
FF $0.33 \times 0.33 \times 0.14$	1733	0.33	45	-0.35	15.4	209	0.08	-0.19	0.04	-0.15

In experiments, the collected CNTs are expected to have low inclinations with respect to the filter plane. Therefore, the constructed samples “FA,” “FB,” and “FC” used $\varphi_{\text{max}} = 11^\circ$. In “FD” and “FE,” larger φ_{max} values were considered in order to explore the impact of the inclination angle parameter, which, along L_{CNT} , are expected to couple to the network entanglement. All samples were subjected to PBC along the x and y Cartesian coordinates. As such, the simulated system exhibits two free surfaces, which are perpendicularly oriented onto the z Cartesian coordinate. Although the boundary conditions make it possible to represent films extending much further than the actual lateral dimensions of the computational system, they do not capture the patterns observed at the few μm scale, which consists of the self-similar branching realized with thicker CNT bundles.

To conduct parallelized simulations, the film domain is divided into cuboid subdomains, which are then distributed between computational cores and connected through the message passing interface. For each time step, every computational core resolves the portion of contacts associated with the elements that are inside the assigned subdomain. After each integration step, all processes synchronize their data, and distinct elements with updated positions can migrate from one subdomain to another. Although the selected domains are balanced throughout the simulations, the number of contacts is increasing with the film densification, and the numerical cycling slows down. Nevertheless, this parallelized framework allowed us to reach efficient simulation times for unprecedented CNT film sizes: for the most computationally intensive simulations, such as compression of the “FA” and “FB” CNT films, where 3.8×10^6 elements interact through up to 300×10^6 contacts, it took around 3 days of real-time when the simulation domain was distributed over 2240 processes on average. Simulations were performed on three computational clusters: Pleiades (NASA’s Advanced Supercomputing Division), Zhores (Skoltech University),⁵¹ and Mesabi (Minnesota Supercomputer Institute).

Figures 6(a) and 6(b) display images of the “FA” and “FB” film, as initially generated, and after 60 ns of cycling with a 20 fs time step from a “cold” start, while Figs. 6(c) and 6(d) display the evolution of E_{vdW} and E_{strain} , respectively. As in the benchmark example, E_{vdW} (E_{strain}) decreases (increases) fast during the first few ns and continues on at a much slower rate. As before, this behavior corresponds to zipping, a process that also bends the initially straight CNTs.

Since zipping occurs in the vicinity of the junction points, this mechanism is prevalent in the “bulk” part of the film, where the density of distinct elements is largest. Because of the small angle of inclination ($\varphi_{\text{max}} = 11^\circ$), the emerging bundles will be preferentially oriented in the film plane. Regarding the two film surfaces, we note that the computer-generated samples have rough surfaces. Many distinct elements on the surface belong to CNTs that are near the maximum inclination angle φ_{max} . During relaxation, most CNTs become nearly horizontal and zip with the “bulk” part of the film, thus creating relatively smooth surfaces. Because of the poor connectivity in the surface region, zipping of these CNTs among themselves is a rare event. When it occurs, surface bundles with a more vertical orientation are formed, as visible in Figs. 6(a) and 6(b).

Focusing now on the bulk part of the sample, Fig. 7(a) shows a typical dynamic leading to “medium”-size CNT bundles. The two simulation snapshots show three groups of initially crossed individual CNTs, which are located (for better visibility) just under the top film surface. These CNTs are subsequently zipping into bundles containing six and seven CNTs. The top view presented in Fig. 7(b) confirms that during relaxation, these bundles are branching out into thinner bundles and individual CNTs. The branches are sustained through their interaction with the film structure. For example, the callout in Fig. 7(b) identifies an entanglement mechanism in which the CNTs indicated with black arrows are filling the junction formed by two other CNTs (shown in green and maroon, respectively), thus helping prevent their zipping into bundles. In another mechanism, the purple arrow points to a CNT (shown in maroon) adhered to a side bundle. Such adhesion forces are helping to prevent the zipping of this branch to the main maroon bundle.

More generally, Fig. 7(b) proposes to conceptualize the film microstructure as a collection of entangled dendrimers, which are interacting through their branches. Without the repulsive volume interaction, van der Waals attractions, and dissipative frictional forces, the dendritic branches would quickly restructure into the main bundle.

Turning back to Fig. 6(c), it is important to clarify that while the “FB” sample exhibits a much lower E_{vdW} than “FA,” this difference does not imply the onset of an adhesion dominated structure. As “FA,” “FB” exhibits a similar branching pattern but with a 2-CNT bundle cutoff. The $\sim 1 \text{ keV/CNT}$ van der Waals energy advantage of the “FB” sample can be entirely attributed to the initial intra-bundle adhesion introduced by the initial construction

FIG. 6. mDEM relaxation simulations: The sample films (a) “FA” and (b) “FB” as computer-generated (left) and after 60 ns of mDEM relaxation (right). The color codes the magnitude of φ for each distinct element. The evolution of the (c) van der Waals and (d) strain energy.

and, in fact, “FA” and “FB” exhibit similar inter-bundle cohesive energy values. E_{strain} for “FB,” Fig. 6(d), is comparable to and slightly lower than the value found in “FA” because the 2-CNT bundles bend independently with inter-tube sliding. Bending with inter-tube sliding is a soft deformation mode captured⁵² by mDEM, in which the bundle bending rigidity scales with the number of constituent CNTs.

As pristine film thickness is an experimentally accessible parameter, we have monitored the evolution of this parameter in the simulated samples. Starting from the computer-generated networks, we noted that the zipping couples to a fast decrease in CNT film thickness. This is because bundling occurs mainly in the film direction. Nevertheless, as zipping slows down, the film thinning effect becomes negligible and the film acquires a finite thickness. In Figs. 6(a) and 6(b), elements are represented in color according to their orientation. Nevertheless, as zipping slows down, the film thinning effect becomes negligible and the film acquires a finite thickness. In Figs. 6(a) and 6(b), elements are represented in color according to their many elements located in the bulk region remain inclined ($\varphi > 0$) after relaxation. Based on this observation, we associate the initial arrest of the film thinning to the entanglement developed by inclined CNTs.

For a quantitative measure of the CNT orientation in the film, we have plotted in Figs. 8(a) and 8(b) the magnitude

of the Herman orientation factor (HOF), defined as $\text{HOF} = \frac{1}{2} [3 \langle \cos^2(90^\circ - \varphi) \rangle - 1]$. Here, the angle bracket $\langle \rangle$ denotes averaging over the distinct elements located in a “bin” layer with a thickness of 1 nm. HOF quantifies the extent of the orientation of CNT segments with respect to the xy plane and ranges from -0.5 to 1 , where the value of -0.5 corresponds to a perfect in-plane alignment. It can be seen that the HOF across the relaxed “FA” and “FB” thicknesses is not reaching the -0.5 value and in fact remains slightly above HOF of the computer-generated samples. The $\langle \text{HOF} \rangle$ and $\langle \varphi \rangle$ over the whole relaxed samples are listed in the fifth and sixth columns of Table II.

The film densification during relaxation can be analyzed in the density profiles shown in Figs. 8(c) and 8(d). Although “FA” and “FB” have the same volume filling factor, spontaneous densification is more pronounced in “FB,” which lacks individual CNT dendritic branches. This result already evidences the important role played by the individual CNT branches in maintaining the sparse film structure.

Based on the density profiles shown in Figs. 8(c) and 8(d), we define the film surface at the location where density becomes 0.01 g/cm^3 . In the seventh and eighth columns of Table II, we report the measured relaxed film thickness h_0 and the density values after relaxation (ρ_0). The ρ_0 values are in the experimental range and far different from the theoretical 0.9 g/cm^3 closed packed

FIG. 7. mDEM relaxation simulations: (a) a region located near the top surface of sample “FA” before (left) and after 60 ns of relaxation (right). The color (green, orange, maroon) is used to distinguish the CNTs that zip into the 3 bundles (green, orange, maroon). (b) Birds’ eye view of the top surface showing the branching structure of the bundles. The callout shows the arrest of zipping of the branches to the main one caused by excluded volume interactions (black ovals and arrows) and by zipping of these branches to other bundles (purple oval and arrow).

value. In addition to the limiting bundle-size cutoff, $\varphi_{\max}$ is another effective control parameter for the film structure. Confirming the direct impact of entanglement onto h_0 , films “FC,” “FD,” and “FE” with larger $\varphi_{\max}$ but the same volume filling factor, settle to h_0 values ranging from 127 nm to 209 nm and densities ρ_o ranging from 0.13 g/cm³ to 0.08 g/cm³. As a general trend, we observe that denser films are associated with lower E_{vdw} values.

C. mDEM simulations of compression-driven densification of “pristine” CNT Samples

In experiments, “pristine” films are further densified by liquid phase processing, as they experience the surface tension effect during liquid evaporation.³ To obtain insight into this process, we simulated the film compression process by evolving the CNTs interacting with two planar plates via a repulsive potential adopted

from Ref. 28. The plates are infinitely rigid and are applied to the entire two surfaces of the sample. The compressive strain ϵ is measured with reference to the 140 nm height of the film. Thus, the maximum compression strain of 85% considered in our simulations corresponds to a film thickness of 21 nm. The stress (σ) is defined as the sum of forces exerted by the indenter onto the interacting distinct elements divided by the surface area.

Figure 9 summarizes the results of the film compression simulations with the plates progressing at 10 m/s. The behavior of E_{vdw} and E_{strain} as well as σ vs ϵ , reveal two distinct deformation regimes: a soft regime, for $\epsilon < \sim 75\%$, and a hardening regime for $\epsilon > \sim 75\%$.

In the soft regime, the film compression corresponds to a rather slow energy increase, in which the drop in E_{vdw} , Figs. 9(a) and 9(c), is accompanied by a monotonic increase in E_{strain} [Figs. 9(b) and 9(d)]. For example, at $\epsilon = 50\%$, we find that

FIG. 8. mDEM relaxation simulations: Herman orientation factor (HOF) across z in (a) “FA” and (b) “FB” samples before and after relaxation. Density ρ across z in (c) the “FA” and (d) “FB” sample before and after relaxation.

sample FA lowered its E_{vdW} by -0.12 keV/CNT, while E_{strain} increased by 0.47 keV/CNT, giving a total energy increase of 0.28 keV/CNT, Fig. S1 in the [supplementary material](#). Furthermore, the compression of films “FC,” “FD,” and “FE” shows that the separation between the two regimes, which is defined by the minimum of E_{vdW} , depends very little on ϕ_{max} , a parameter that controls the initial degree of bundling in these films. The threshold strain separating the two regime exhibits a weak dependence on the applied strain rate. [Figures 10\(a\) and 10\(b\)](#) quantify E_{vdW} and E_{strain} vs ϵ for sample “FC” compressed with different indenter velocities. The slowest 2 m/s case is linked to lowest E_{vdW} and E_{strain} curves, and to the shifting of the E_{vdW} minima to about 80% .

In the soft regime, the computed stress strain curves presented in [Figs. 9\(e\) and 9\(f\)](#) resemble those obtained from aerogel-spun and dry-spun CNT fibers subjected to transverse compressive tests.⁵³ The stress initially increases very slowly. The initial sub-MPa regime, lasting until $\epsilon \sim 4\%$, reflect the resistance to flattening of the surface CNT bundles with a more vertical orientation. Next, σ increases more rapidly. We find that 29 MPa is required to compress the FA film by 50% (the experimental reduction value in drop-cast volatile liquid processing) and 529 MPa to reach 75% compression, Fig. S2 in the [supplementary material](#). Note that these σ values are smaller than the GPa stress range required to

stretch CNT fibers but consistent with those applied in transverse compressive tests.⁵⁴ In the hardening regime, σ is increasing more abruptly, reaching few GPa values. It can be also seen that, in this regime, both E_{vdW} and E_{strain} are dramatically increasing for all film samples.

At the microstructural level, the applied compression alters the entanglement established in the original low-density film, opening new possibilities for CNTs to restructure under the action of vdW forces. In this respect, the simulation snapshots presented in [Fig. 11\(a\)](#) evidence two E_{vdW} lowering processes identified in sample “FA:”

- (I) At $\epsilon = 50\%$, we observe a *new bundle* formed by the zipping of the individual CNTs depicted in yellow. The applied compression brought close enough these entangled CNTs to trigger their zipping. The inherent bending introduced by such zipping events explains the initial increase in E_{strain} , as quantified in [Fig. 9\(b\)](#). Note that, at these higher densities, most bundles have flatten instead of circular cross sections.
- (II) Furthermore, by $\epsilon = 75\%$, the new bundle zips with an existing bundle shown in orange. The *bundle–bundle zipping* can be also inferred from the TEM image of [Fig. 3\(f\)](#).

FIG. 9. mDEM compression simulations: (a) vdW energy and (b) strain energy vs strain in samples "FA" and "FB." (c) vdW energy and (d) strain energy vs strain in samples "FC," "FD," and "FE." Stress-strain curves in samples (e) "FA" and "FB," and (f) "FC," "FD," and "FE." In (e), the inset presents the rise in σ on a logarithmic scale.

By defining the available volume that can accommodate CNT rearrangements, density becomes an important control parameter for zipping. As density increases uniformly under compression, zipping is hindered and the response is dominated by entanglement. An important response mode of the microstructure is the development of nm-scale waviness under large ϵ . This is evidenced in Fig. 11(b), where a CNT of initial 11° inclination (before relaxation), remains tilted during compression but acquires significant bending. The bending deformation, which contributes to the

increase in E_{strain} , is not caused by zipping but by the transversal loads exerted onto CNTs at the junctions through repulsive volume interactions.

In the hardening regime, the repulsive volume interactions overcome the attractive ones to the extent that E_{vdW} becomes positive at the largest considered strains, Figs. 9(a) and 9(c). The sharp increase in stress observed in this regime, Figs. 9(e) and 9(f), originates in the resistance to interpenetration of the mDEM-represented CNTs.

FIG. 10. mDEM compression simulations: (a) vdW energy and (b) strain energy vs strain in samples "FC" at three different compression rates.

FIG. 11. mDEM compression simulations: (a) A region located near the top surface and (b) a CNT of sample "FA" at different stages of compression and in the recovered film, as indicated for each frame. In (a) the color is used to distinguish the evolution of existing bundles (green, orange, maroon,) and formation of a new bundle (yellow) and bundle-bundle zipping (yellow and orange). In (b) the color gives the bending strain energy in the EVM bonds. The background is a portion of the substrate illustrating the shown CNT location in the film.

D. mDEM models of free-standing densified CNT Films

The last set of simulations considered the release of the loads applied to the pre-compressed sample. Figures 12(a) and 12(b) present the evolution of E_{vdW} and E_{strain} for “FA” and “FB,” both

pre-compressed to an $h_c = 40$ nm thickness (soft regime.) Unlike in the relaxation of the computer-generated samples (Sec. IV B), here the relaxation dynamics is driven by the lowering of E_{strain} . During the first 250 ps, the samples undergo spontaneous thickening with a significant release of E_{strain} . The initial increase in E_{vdW} reflects

FIG. 12. mDEM release stage simulations: (a) vdW energy and (b) strain energy vs time in samples “FA” and “FB.” Density ρ across z in (c) the “FA” and (d) “FB” sample before and after relaxation. (e) Birds’ eye view of sample “FB” after relaxation. The callouts shows examples of 2-CNT bundles (indicated by arrows) at the junctions that help maintain the branching structure.

TABLE III. Parameters and statistical information of CNT samples after recovery from thickness h_c . Film thickness h_d , density ρ_d , magnitude of the Herman orientation factor (HOF), average tilt $\langle\varphi\rangle$ of elements, van der Waals E_{vdW} , strain energy E_{strain} , and total energy E .

Film	h_c (nm)	h_d (nm)	ρ_d (g/cm ³)	$\langle\text{HOF}\rangle$	$\langle\varphi\rangle$ (°)	E_{vdW} (keV/CNT)	E_{strain} (keV/CNT)	E (keV/CNT)
FA	25	75.6	0.22	−0.48	5.7	−1.31	0.58	−0.73
FA	40	80.0	0.21	−0.48	5.4	−1.20	0.49	−0.71
FB	40	62.5	0.27	−0.48	4.9	−2.26	0.36	−1.90
FC	40	74.9	0.22	−0.47	6.1	−0.46	0.19	−0.26
FD	40	75.6	0.22	−0.47	6.7	−0.40	0.18	−0.22
FE	40	76.3	0.22	−0.45	8.3	−0.38	0.20	−0.19

the increase in spacing between CNTs rather than a de-bundling effect. After this initial stage, the increase in thickness slows down as the film evolves to lower both E_{vdW} and E_{strain} energy terms. By increasing the film thickness, the inclined tubes are lowering their waviness, as it can be seen in the last simulation snapshot of Fig. 11(b).

Figures 12(c) and 12(d) show the mass density profiles in the compressed and released states for both “FA” and “FB” samples. Similar simulations considering the compression and bending buckling⁴⁸ of vertically aligned CNTs, reported the formation of a top dense layer near the indenter plate.²⁸ Our simulations show that when the constituent CNTs have low inclination angles, this surface effect becomes negligible. Remarkably, we find that the density of the compressed film is uniform over the bulk part of the film and remains uniform after release, while the surface density develops a smooth drop over a ~ 10 nm distance. In good agreement with the experiment, the sample “FA” (“FB”) settles to a thickness value h_d which is 43% (42%) smaller than h_o of the pristine form.

The parameters of all the released densified samples, including E_{vdW} and E_{strain} , are summarized in Table III. We note that the total energies of the released films are very close to the ones of the corresponding pristine films, which are listed in Table II. Thus, there is no thermodynamic drive for the densification process to occur naturally. However, the E_{vdW} and E_{strain} energy components are differently distributed. Reflecting the irreversible coarsening of the bundles during compression and the partial waviness stored by entangled CNTs, all densified films have lower E_{vdW} energies but larger E_{strain} .

While the densified films models obtained here are stabilized to a greater extent by adhesion, the dendritic branch model still holds, and thus the film structure is still far from a cellular one. For example, Fig. 12(e) shows that the “FB” densified microstructure maintains the branching pattern. A small 4-CNT “small” bundle (shown in yellow) and a 16-CNT “medium” bundle (shown in green) split into thinner bundles with the help of the repulsive volume interactions with the bundle crossing. Additionally, the averaged HOF and φ listed in Table III are showing that the densified films still contain CNTs that are held inclined by their entanglement.

The pre-compression level is an important parameter for densification. Larger excursions into the soft regime and above it lower irreversibly E_{vdW} but also introduce more bending strain, which nevertheless can be significantly lowered upon release. In agreement with this picture, our simulations show that larger pre-compression levels result, upon release, into better densified

and lower energy films. For example, the data presented in the first lines of Table III indicated film “FA” with $h_c = 25$ nm (40 nm) gives $h_d = 75.6$ nm (80 nm) thickness and -0.73 keV/CNT (-0.71 keV/CNT) total energy upon release.

The angle of CNT inclination φ_{max} is unknown experimentally. As we have seen in the pristine sample models, this parameter impacts the initial film thickness and density. To check the robustness of our results we have also investigated the free evolution of samples “FC,” “FD,” and “FE” after being pre-compressed at $h_c = 40$ nm. Because in their pristine forms, these model films are less energetically stable than the “FA” one, they are more susceptible to densification under compression. As can be seen from the data listed in the last three lines of Table III, the h_d values are smaller than those of the “FA” sample released from the same h_c values. The three thicknesses are within 2 nm, and, therefore, φ_{max} appears not to be a key parameter, as long as $\varphi_{max} < 45^\circ$.

By comparing the evolution of samples “FA” and “FB” both pre-compressed at $h_c = 40$ nm, we can see that the h_d and ρ_d values are not uniquely defined by h_c : while sample “FB” evolves toward a 62.5 nm thickness, sample “FA” settles instead to 80 nm thickness. This result clearly evidences the hindering role of the individual CNT branches present in the experimental film; achieving their restructuring by zipping under compression, as evidenced, for example, in Fig. 11(a), represents an effective mechanism for the film densification. Because of the monodisperse construction manner of sample “FA” (as opposed to the two-step formation of the pristine films discussed above) and the inherently large applied strain rate used in the simulation (as opposed to slower densification process by liquid evaporation), the densification levels obtained for “FA” should be viewed as lower limits. The densified “FB” sample with no individual CNT branches emerges as our best representation of the densified film characterized in Sec. II.

V. SUMMARY AND CONCLUSIONS

Motivated by the advances in CNT simulation, synthesis, processing, and characterization, we used mesoscale simulations, electron microscopy, and spectroscopic ellipsometry to understand and characterize densification by volatile liquid drop-casting. SEM and TEM characterization indicated that the pristine films exhibit multiscale structural features comprising CNT bundles down to single CNTs and suggested a coarsening of these bundles in the densified films. The spectroscopic ellipsometry measurements in transmission (pristine film) and reflection (densified film) revealed a nearly 50% change in the film thickness during ethanol evaporation.

To understand the connection between the reduction in film thickness and microstructural changes, we have simulated the mechanical response of the sub- μm scale to extensive compressive deformations on an ensemble of computer-generated samples with different cohesive energies but with common density and thickness values. We employed mDEM, an accurate coarse-grained simulation method, that describes the microstructure of the pristine and densified CNT films as a collection of interacting dendritic bundled CNTs. These simulations reveal significant structural changes occurring at the 100 nm scale and indicated that the simulated samples undergo homogeneous densification in a two-stage regime comprising a sub-GPa plastic compression followed, at above $\sim 75\%$ strain, by a sharp rise of stress. In the first regime, the film is lowering irreversibly its van der Waals cohesive energy by zipping, while increasing the bending energy of those CNTs joining into new bundles and of other entangled CNTs, which develop nm-scale waviness. In the second deformation regime, the application of few GPa stress values is required. These large values reflect the resistance to interpenetration of the mDEM-represented CNTs. Note that compression in the hardening regime is not studied here in much detail. As thin-walled structures, small diameter CNTs may undergo a transformation from circular to hexagonal cross section at about 1.5–1.7 GPa.^{55,56} Therefore, the rigid distinct element model employed here is not fully valid in this regime.

When removing the compressive loads, the pre-compressed samples partially released the bending strain associated with the nm-scale waviness and evolve into densified films with thickness values depending on both the pre-compressed strain and the sample micro-structure. Compared to the original pristine films, the free-standing densified films have lower van der Waals adhesion but larger bending strains.

Although the considered computational samples do not include dendritic bundling above the μm scale, the recovery simulations are in good agreement with the experiment with respect to the changes in film thickness. This suggests that the structural restructuring occurring at the 100 nm scale is responsible for the densification process to a great extent. The mesoscopic models for pristine and densified films obtained here can be further used to investigate the changes in mechanical, electrical, and optical properties driven by densification.

We emphasize that the dendritic microstructure of the pristine films proposed by our mDEM model differs qualitatively from the usual adhesion dominated cellular structure obtained by the simpler B&S mesoscopic model.³⁰ Our simulations indicate that accounting for the thinnest branches and individual CNTs is important for describing the densification process. Unfortunately, these microstructural features are not captured by the popular B&S model for CNTs. Since the realistic description of the microstructure ties directly to the mesoscale interactions, our work points to the need for accuracy in the coarse-grained modeling of CNT and of semiflexible polymer self-assembled networks²³ in general.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for total energy, bending, and van der Waals energy for sample FA shown until 50% compressive

strain (Fig. S1). Figure S2 shows stress–strain curves for samples FA and FB up to 75% strain.

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DATA AVAILABILITY

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

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