Electronic Supplementary Information: Aligned Carbon Nanotube Array Stiffness from Stochastic Three-Dimensional Morphology

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S1 Framework for Simulating Wavy Aligned Nanofibers in Three-Dimensions

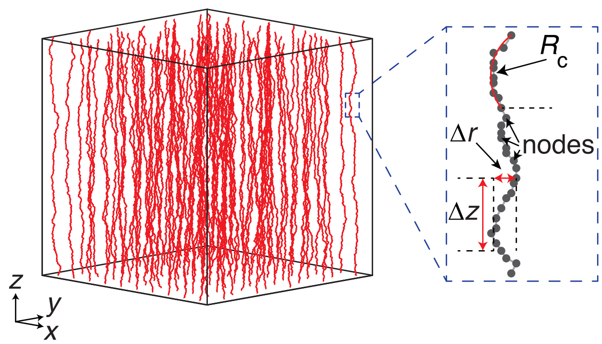

Fig. S1 Unit cell used in the analysis defined using the average displacement in the $x-y$ plane ($\rightarrow \Delta r$) and 10 nodes in the $\hat{z}$ direction ($\rightarrow \Delta z$). Δr and Δz are tied to the amplitude (a) and wavelength (λ) from the waviness ratio ($w = a/\lambda$) which is used to simulate the morphology of the CNTs in three dimensions. The radius of curvature (R_c) is evaluated using the unit cell, and is used to approximate the maximum CNT volume fraction that the simulation can be used to study.

To define the unit cell used in the analysis, one has to consider two displacements: the $x-y$ plane displacement ($\rightarrow \Delta r$), *i.e.* the two-dimensional random walk; and the displacement in the $\hat{z}$ direction ($\rightarrow \Delta z$), *i.e.* the nodal displacement. Each unit cell was comprised of 10 nodes whose $\hat{z}$ separation has a magnitude of 0.05λ ($\rightarrow 0.5\lambda$ for 10 nodes), where λ is the characteristic wavelength of the waviness from the waviness ratio (w). See Fig. S1 inset for illustration of the unit cell used in this analysis. Using the geometry of the unit cell shown in Fig. S1, Δr, Δz, and the local radius of curvature of the CNT (R_c) from the intersecting chord theorem can be defined as follows:

$$\Delta r = \chi(w)\lambda \tag{S1a}$$

$$\Delta z = \zeta(w)\left(\frac{\lambda}{2}\right) \tag{S1b}$$

$$R_c = 0.5\left(\Delta r + \frac{\Delta z^2}{16\Delta r}\right) \tag{S1c}$$

where $\chi(w)$ is a factor that relates the average of the displacement of the CNTs in the $x-y$ plane, a stochastic quantity, to the deterministic w, and $\zeta(w)$ connects the separation of the nodes that bound the unit cell in the $\hat{z}$ direction, a quantity that is varied to control the average stochastic tortuosity of each wavy CNT (see eqn S1), to the deterministic w. To approximate $\chi(w)$, the average displacement of a CNT in the $x-y$ plane is evaluated (see Fig. S2a) leading to the following functional forms:

$$\chi(w) = a_3 w \tag{S2a}$$

$$\zeta(w) = a_4(w)^{b_4} + c_4 \tag{S2b}$$

where $a_3 = 0.8794$ (coefficient of determination $\mathbb{R}^2 = 0.9999$); and $a_4 = -0.0748$, $b_4 = 0.6459$, and $c_4 = 0.4260$ ($\mathbb{R}^2 = 0.9962$). The fits in eqn S2 begin to deviate significantly from the simulation data at $w > 0.3$, an effect that originates from interactions with the simulation box that confines each CNT and prevents the CNTs from venturing outside of their confining box. This forces the CNTs to be non-interacting, and

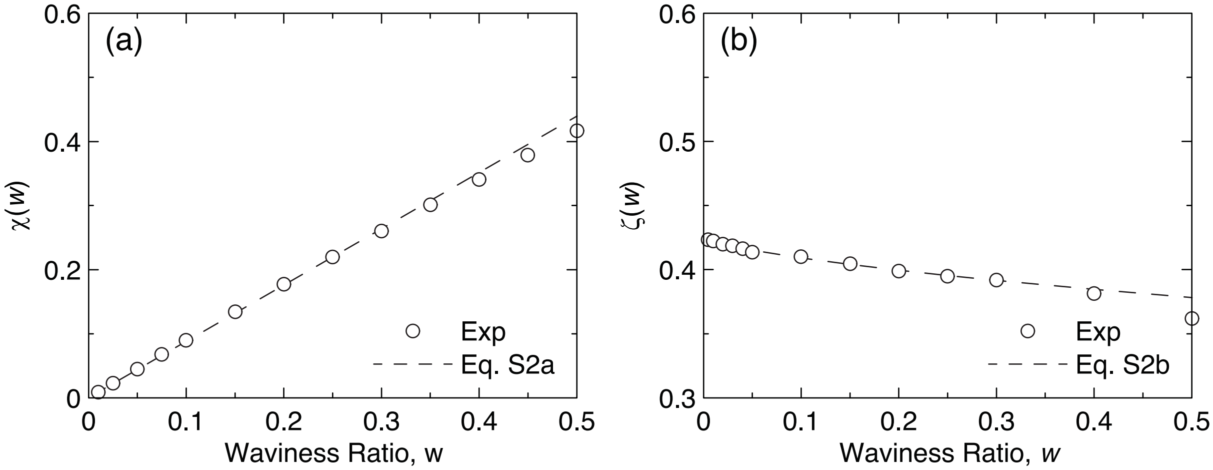

Fig. S2 Factors that link the average $x-y$ plane displacement ($\chi(w)$) and node separation in the $\hat{z}$ direction ($\zeta(w)$) to the waviness ratio (w). (a) $\chi(w)$ scaling with w demonstrating that CNT interactions with the hard boundaries that define the confining volume are significant at $w \gtrapprox 0.3$ where $\chi(w)$ transitions from a linear scaling (see eqn S2a) to a power scaling. (b) $\zeta(w)$ scaling with w demonstrating that CNT-boundary interactions are significant at $w \gtrapprox 0.3$ where $\zeta(w)$ transitions from a power scaling (see eqn S2b) to a linear scaling.

ensures that the system can be treated as dilute. Such an approximation is likely reasonable when the CNTs are not all in bundles, *i.e.* in CNT volume fractions that are far below the theoretical maximum of $\sim 83.45\%$ CNTs. Since the CNT-CNT electrostatic interactions are not well understood, and require further study to properly simulate and model, this study was limited to $w \lesssim 0.3$ where $\chi(w)$ is a constant and $\zeta(w)$ varies by $\lesssim 10\%$.

S2 Scaling of Waviness with Carbon Nanotube Volume Fraction

As discussed in the main text, the waviness ratio (w) of the aligned carbon nanotubes (CNTs) was approximated from scanning electron microscope (SEM) images of the cross-sectional morphology of CNT arrays at a variety of CNT volume fractions (V_f) for $1\% \lesssim V_f \lesssim 20\%$. At each V_f, w was approximated from 30 CNTs ($\rightarrow n = 30$), and the mean values of w (μ_w), the standard deviation of w (σ_w), and the uncertainty in μ_w ($\sigma_w/\sqrt{n}$) are included in Table S1. To convert from a deterministic waviness description (defined by w) to a stochastic one, tortuosity (τ) of the CNTs, which is discussed in the main text as the ratio of the true (arc) length of the CNTs to the measured height of the CNT array in the $\hat{z}$ direction, should be used instead of w. τ can be defined as follows for w that has a sinusoidal ($\rightarrow \tau(w)_{\text{sin}}$) and helical ($\rightarrow \tau(w)_{\text{helix}}$) functional forms (eqns S3a and S3b are simplified using $\rightarrow w = a/\lambda$ and setting $a = 1$):[1]

$$\tau(w)_{\text{sin}} = \int_0^1 \sqrt{\left(1 + (2\pi w \cos(2\pi z))^2\right)}\,\mathrm{d}z \tag{S3a}$$

$$\tau(w)_{\text{helix}} = \sqrt{(1 + (2\pi w)^2)} \tag{S3b}$$

See Fig. S3 for a plot of τ_{sin} and τ_{helix} evaluated via eqn S3a and eqn S3b. The mean (μ_τ), standard deviation (σ_τ), and uncertainty ($\sigma_\tau/\sqrt{n}$) of τ using both the sinusoidal ($\rightarrow \mu_\tau^{\text{sin}}$, σ_τ^{sin} and $\sigma_\tau^{\text{sin}}/\sqrt{n}$) and helical ($\rightarrow \mu_\tau^{\text{helix}}$, $\sigma_\tau^{\text{helix}}$ and $\sigma_\tau^{\text{helix}}/\sqrt{n}$) functional forms can be found in Table S1.

The scaling of μ_w and σ_w with V_f is also presented in the main text (see Fig. 3 and eqn 1), and the role of μ_w and $\sigma_w/\sqrt{n}$ in modeling the wavy CNT stiffness is discussed in Sec. S3.

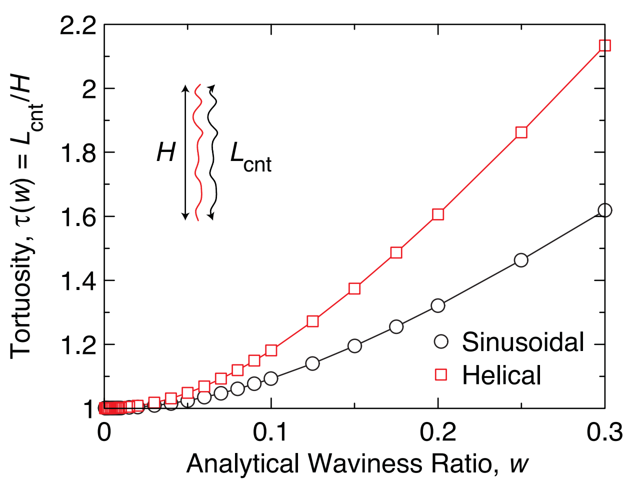

Fig. S3 Tortuosity (τ) as a function of waviness ratio (w) for sinusoidal (eqn S3a) and helical (eqn S3b) functional forms of the CNT morphology.

Table S1 Experimentally determined waviness ratio (w) and tortuosity (τ) from eqn S3 as a function of the CNT volume fraction (V_f). The mean values of w and τ (μ_w and μ_τ), the standard deviation of w and τ (σ_w and σ_τ) were approximated from 30 CNTs ($\rightarrow n = 30$).

V_f [%]	Experimental waviness (sinusoidal)		Sinusoidal tortuosity		Helical tortuosity	
	μ_w^{sin}	σ_w^{sin}	μ_τ^{sin}	σ_τ^{sin}	μ_τ^{helix}	σ_τ^{helix}
1	0.198	0.119	1.352	0.352	1.596	0.556
6	0.159	0.098	1.253	0.243	1.414	0.414
10.6	0.127	0.072	1.171	0.147	1.279	0.272
20	0.101	0.049	1.109	0.097	1.184	0.161

S3 Mechanical Behavior of Wavy Carbon Nanotubes

Using Δr and Δz as defined by eqn S1, the extension ($\xi_{\text{extension}}$), shear (ξ_{shear}), bending (ξ_{bending}), and torsion (ξ_{torsion}) contributions discussed in the main text can be derived from the correlations previously reported for a carbon nanocoil as follows:[2]

$$\xi_{\text{extension}} = \left(\frac{\Delta z^2}{\Delta r^2 + \Delta z^2}\right)\left(\frac{L}{YA}\right) = \left(\frac{\zeta(w)^2}{4\chi(w)^2 + \zeta(w)^2}\right)\left(\frac{L}{YA}\right) \tag{S4a}$$

$$\xi_{\text{shear}} = \left(\frac{\Delta r^2}{\Delta r^2 + \Delta z^2}\right)\left(\frac{L}{GA}\right) = \left(\frac{4\chi(w)^2}{4\chi(w)^2 + \zeta(w)^2}\right)\left(\frac{L\alpha}{GA}\right) \tag{S4b}$$

$$\xi_{\text{bending}} = \left(\frac{\Delta r^2 \Delta z^2}{\Delta r^2 + \Delta z^2}\right)\left(\frac{L}{YI}\right) = \left(\frac{\chi(w)^2\zeta(w)^2\lambda^2}{4\chi(w)^2 + \zeta(w)^2}\right)\left(\frac{L}{YI}\right) \tag{S4c}$$

$$\xi_{\text{torsion}} = \left(\frac{\Delta r^4}{\Delta r^2 + \Delta z^2}\right)\left(\frac{L}{GJ}\right) = \left(\frac{4\chi(w)^4\lambda^2}{4\chi(w)^2 + \zeta(w)^2}\right)\left(\frac{L}{GJ}\right) \tag{S4d}$$

where $L = \tau(w)\Delta z$ and represents the arc length of the CNT between the two nodes in the $\hat{z}$ direction (see Fig. S3 for the scaling of $\tau(w)$ with w), Y and G are the elastic and shear moduli of the CNTs, A is the cross-sectional area of the CNTs defined by the inner ($D_\text{i} \approx 5$ nm) and outer ($D_\text{o} \approx 8$ nm) diameters,[1] I and J are the area and polar (*i.e.* torsion) moments of inertia of a hollow cylinder, and α is the shear coefficient for a multiwalled CNT (MWCNT) that has the following form:[3]

$$\alpha = \frac{7 + 6\nu\left(1 + (D_\text{i}/D_\text{o})^2\right)^2 + (20 + 12\nu)(D_\text{i}/D_\text{o})^2}{6(1+\nu)\left(1 + (D_\text{i}/D_\text{o})^2\right)^2} \tag{S5}$$

where ν is the Poisson ratio with an assumed value of $\nu \sim 0.3$ ($\rightarrow \alpha \approx 1.3$ for the CNTs studied here), and D_i and D_o are the inner and outer diameters of the MWCNTs. Using these correlations, the mechanical behavior of CNTs with waviness defined by the mean and uncertainty in w (see Sec. S2) is studied via an array of 10^5 simulated CNTs, and the physical origin of the scaling of the CNT array stiffness as a function of CNT proximity is evaluated (see Figure 4 in the main text).

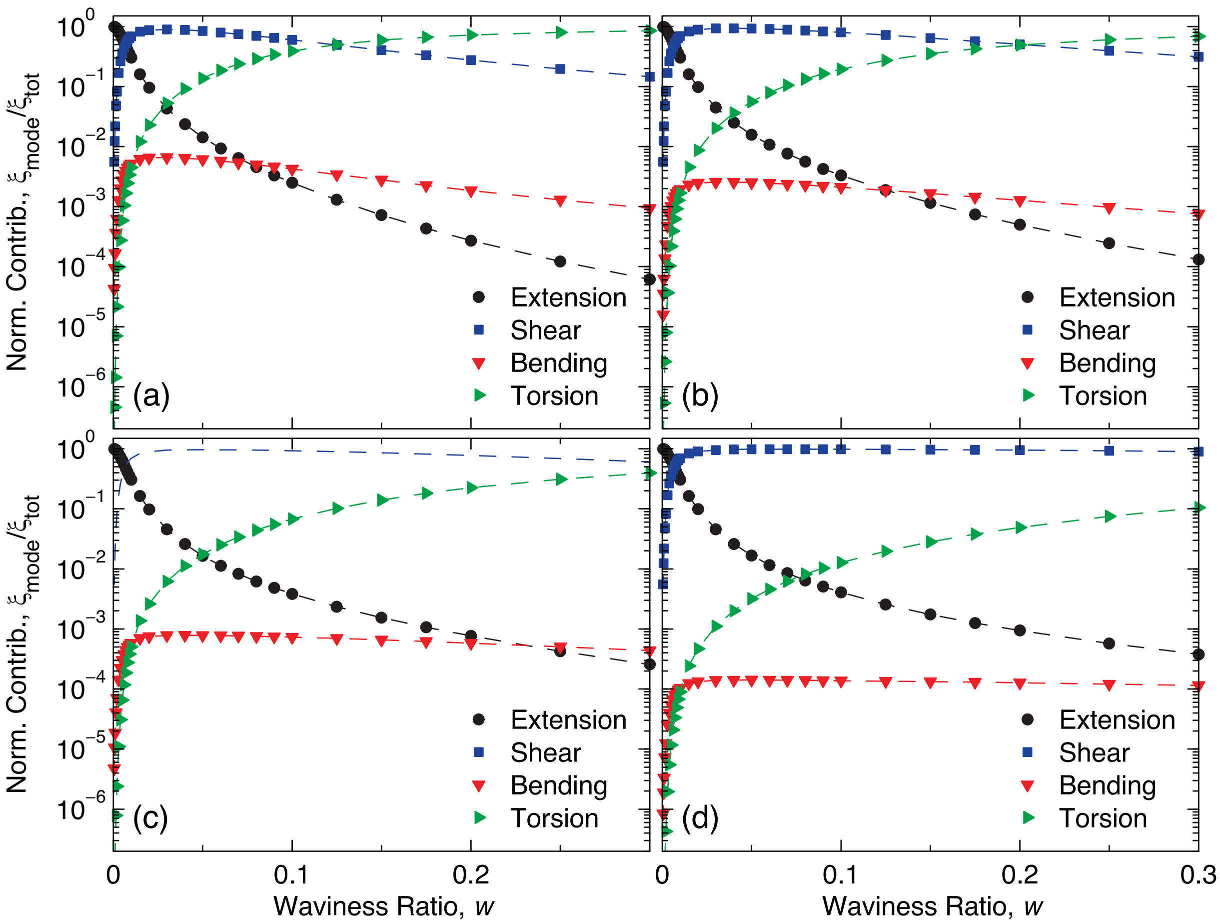

Fig. S4 Contribution of extension, shear, bending, and torsion deformation mechanisms (see eqn S4) to the effective compliance ($\rightarrow \xi_{\text{mode}}/\xi_{\text{tot}}$ where $\xi_{\text{tot}} = \sum \xi$) of wavy CNTs as a function of the waviness ratio (w) and CNT volume fraction. (a) Deformation mode contributions for CNTs with $V_{\text{f}} \approx 5\%$. (b) Deformation mode contributions for CNTs with $V_{\text{f}} \approx 10\%$. (c) Deformation mode contributions for CNTs with $V_{\text{f}} \approx 20\%$. (d) Deformation mode contributions for CNTs with $V_{\text{f}} \approx 40\%$.

See Fig. S4 for the contributions of extension, shear, bending, and torsion to the stiffness of CNTs arrays as function of w and V_{f} (see Figure 4b in the main text for a plot of the stiffness scaling).

S4 Guide for Applying This Simulation Framework to Other Nanofiber Arrays

The 3D morphology and mechanical behavior of aligned nanofiber (NF) arrays can be predicted using the simulation framework presented here by following the steps outlined below:

Part I 3D morphology initialization

1. Determine the NF geometry (*i.e.* inner and outer diameters), and the value and/or range of the NF array volume fraction (V_f) that will be used in the study. These parameters can either be assumed, or be experimentally/theoretically evaluated.
2. Evaluate the average minimum and maximum inter-NF separations. This can be done by assuming a packing coordination (either square or hexagonal close packing), or preferably using the model previously developed for quantifying the packing morphology of NFs.[4,5] These values are evaluated using the NF outer diameter and V_f, and will be used to define the confining area of each NF.
3. Approximate the waviness ratio (w) of the NFs. This can be done by either assuming the value and/or scaling of w with V_f, or by experimentally evaluating the evolution of w with packing proximity (as done here). If the average tortuosity (τ) of the NFs is known instead of w, τ can be converted to w using eqn S3.
4. Initialize the confining box of each NF starting at the first node. For simplicity, place the first node in the middle of the confining area.
5. Place the second node using the position of the first node, and a small $x-y$ plane displacement evaluated using the the waviness amplitude λ (λ is set as the average inter-NF separation here), w, and a normally distributed random number with a value ranging from 0 to 1 (*e.g.* 'rand' in MATLAB). The displacement of the second node in the $\hat{z}$ direction should be evaluated using the number of nodes that comprise each λ (*i.e.* the simulation resolution, where 20 nodes for each λ was used in this study).
6. Repeat this process until all the nodes for each NF are generated. If a node falls outside of the confining area, place that node at the boundary.
7. Evaluate the average arc length ($\equiv \tau$) of each NF in the array, and adjust the node displacement in the $\hat{z}$ direction until $\tau = \tau(w)_{\sin}$ from eqn S3.
8. Sample and record the average $x-y$ ($\rightarrow \Delta r$) and $\hat{z}$ ($\rightarrow \Delta z$) displacements for $\lambda/2$, and use eqn S1 to evaluate the coefficients $\chi(w)$ and $\zeta(w)$.

Part II effective elastic modulus prediction

1. Input the NF geometry, intrinsic moduli, and morphology parameters into eqn 2 and eqn 3 in the main text.
2. Solve numerically at each V_f by sampling the stiffness of each NF (*i.e.* using the unit cells that comprise the NF and their respective τ), and average over the entire NF array.
3. Repeat for the entire V_f range.

References

[1] J. Lee, I. Y. Stein, M. E. Devoe, D. J. Lewis, N. Lachman, S. S. Kessler, S. T. Buschhorn, and B. L. Wardle, Appl. Phys. Lett. **106**, 053110 (2015).

[2] X. Chen, S. Zhang, D. A. Dikin, W. Ding, R. S. Ruoff, L. Pan, and Y. Nakayama, Nano Lett. **3**, 1299 (2003).

[3] X.-L. Wei, Y. Liu, Q. Chen, M.-S. Wang, and L.-M. Peng, Adv. Funct. Mater. **18**, 1555 (2008).

[4] I. Y. Stein and B. L. Wardle, Phys. Chem. Chem. Phys. **15**, 4033 (2013).

[5] I. Y. Stein, N. Lachman, M. E. Devoe, and B. L. Wardle, ACS Nano **8**, 4591 (2014).