

Zippering, entanglement, and the elastic modulus of aligned single-walled carbon nanotube films

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Reliably routing heat to and from conversion materials is a daunting challenge for a variety of innovative energy technologies—from thermal solar to automotive waste heat recovery systems—whose efficiencies degrade due to massive thermomechanical stresses at interfaces. This problem may soon be addressed by adhesives based on vertically aligned carbon nanotubes, which promise the revolutionary combination of high through-plane thermal conductivity and vanishing in-plane mechanical stiffness. Here, we report the data for the in-plane modulus of aligned single-walled carbon nanotube films using a microfabricated resonator method. Molecular simulations and electron microscopy identify the nanoscale mechanisms responsible for this property. The zippering and unzipping of adjacent nanotubes and the degree of alignment and entanglement are shown to govern the spatially varying local modulus, thereby providing the route to engineered materials with outstanding combinations of mechanical and thermal properties.

nanostructured materials | van der Waals | thermal interface materials | thermoelectrics | energy conversion

Nanostructured materials provide unique combinations of properties that promise performance breakthroughs for applications ranging from energy conversion to data storage and computation (1–4). In many cases it is the very unusual combination of two properties (2), neither of which is an extreme value when considered alone, that leads to adoption and major performance benefits. An example is the search for a mechanically compliant thermal conductor that can, for example, link semiconducting materials with the metals used for heat spreading and exchange. A particularly compelling case is thermoelectric waste heat recovery systems (3), for which the interfaces between the thermoelectric materials, electrodes, insulators, and heat exchangers must accommodate enormous, repetitive thermomechanical stress. However, nature does not provide a material combining the necessary high thermal conductivity with the required low elastic modulus (5, 6).

Vertically aligned carbon nanotube (CNT) films may combine mechanical compliance with high thermal conductivity (7–18), but there have been few reports of the in-plane modulus of these films and little physical explanation for the wide range for the data (2–300 MPa) (19–25). Our previous data for the thickness-dependent in-plane modulus of multiwalled CNT films indicated a strong dependence on the nanotube density and alignment (21), which are linked to the detailed growth details (26–28). Other approaches, such as mesoscopic simulations or atomistic models, found that CNT networks exhibit unique self-organization, including bending and bundling (29–31). Therefore, relating the nanoscale morphological details to the mechanical properties is critical.

Combined experimental, theoretical, and computational techniques applied to the more complex and fundamentally challenging single-walled CNT system are presented in this paper, along with the in-plane data for the modulus for single-walled CNT films. Because single-walled CNT films have higher densities and smaller tube–tube distances, these films exhibit more complex dynamics and tube–tube interactions than multiwalled CNT films. We present coarse-grained molecular simulations, and this

approach is consistent with a much simpler cellular model treating the films as foam. The coarse-grained simulations not only predict the modulus, but also describe the manner in which the nanotubes self-organize into bundles and highly entangled regions due to van der Waals forces. The computational results reveal the significance of deformation mechanisms in determining the mechanical response of the single-walled CNT films.

The microfabricated resonator depicted in Fig. 1*A* measures the effective in-plane modulus of single-walled CNT films ($E_{l,exp}$). The measurement method (21) and nanotube growth process (33) are described in *SI Text*. Fig. 1*A* shows that $E_{l,exp}$ decreases with increasing nanotube film thickness, which we attribute to inhomogeneities (with respect to the film-normal coordinate) in the density and alignment. The measured, single-walled CNT films have a disordered and dense crust layer on top of an aligned middle region. This is similar to observations of multiwalled CNT films in past work (21, 27, 34). Our single-walled CNTs have been observed to be denser and stiffer due to a smaller diameter as well as better quality. The theoretical curves, shown in Fig. 1*B*, capture the effect that as the film grows taller, the modulus of the middle layer becomes more dominant, and the overall modulus of the film decreases. The measurements and three-layer model (21) suggest that large differences between the modulus of the crust and middle layer are due to their morphological variations.

To understand the mechanisms governing the mechanical response of the single-walled CNT films, we use two separate simulation methods. The first is a simple model for cellular solids. Because carbon nanotubes are low-density solids, previous studies have shown that the mechanical response and nanostructure of films closely resemble those of a foam or cellular solid (10, 14). Gibson and Ashby introduced a rectangular cellular model that has

Significance

Aligned carbon nanotube films promise the unusual combination of high thermal conductivity and mechanical compliance. Here, the mechanical compliance of single-walled nanotube films has been measured and linked to their morphology and microscopic motions, including zippering, unzipping, and entanglement. The physical mechanisms governing the mechanical response include bending forces or van der Waals interactions, with the dominant mechanism depending on the nanotube density and alignment. The dependence of film morphology on mechanical modulus explored here provides the foundation for modeling of a variety of other properties including thermal and electrical conductivity.

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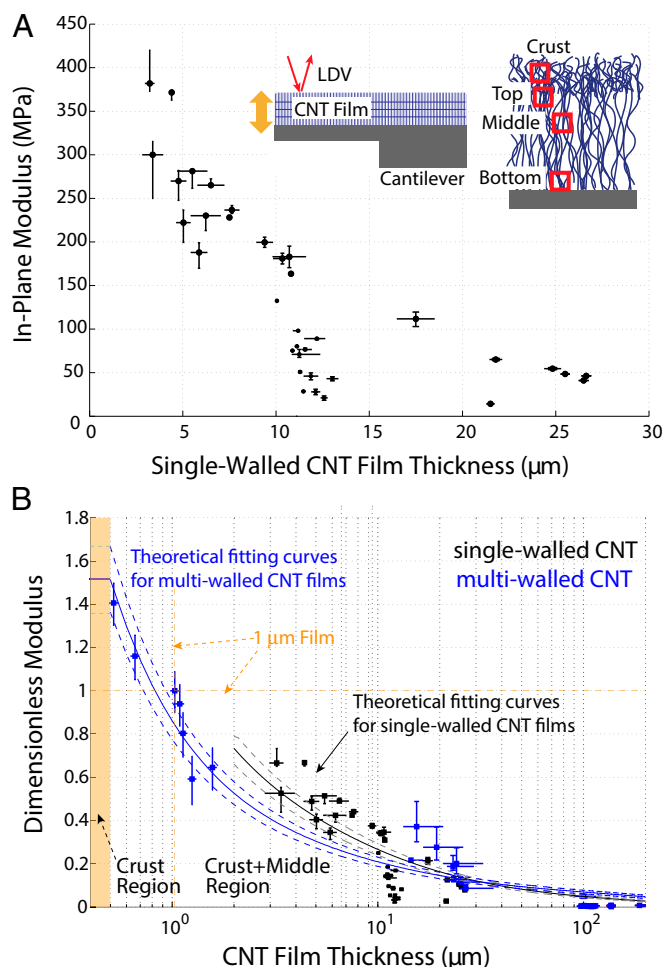


Fig. 1. (A) Effective in-plane modulus ($E_{1,exp}$) of vertically aligned single-walled CNT samples measured using a resonator technique. The thickness variations and the resulting modulus variations due to the nonuniformities in nanotube growth are illustrated by horizontal and vertical error bars, respectively. The samples are from several deposition batches. This can result in groups of samples that deviate from the trend. (Inset) Schematic of a resonator with a vertically aligned CNT film and a schematic showing the different layers in a film are overlaid on the plot. (B) Dimensionless modulus, $E^* = \frac{E_{1,exp}}{E_{1,theo}}$, including our past data on multiwalled CNT films (21, 32) and best-fit lines calculated using a three-layer analysis. Dashed lines indicate the effect of varying modulus of the crust (600 MPa) and middle (10 MPa) layers by $\pm 10\%$ on the effective modulus.

been widely used to estimate the modulus of foams (35). Because the film structure consists of angled tube segments rather than perfectly horizontal and vertical beams, we present a modified cellular model in which trusses connect the corners and the center of each unit cell, as shown in Fig. 24 (SI Text) (7). The aspect ratio (AR) of a unit cell is related to the angle made by the trusses with respect to the horizontal plane, where $AR = H/L = \sqrt{2} \tan \theta$. By considering the bending of the trusses in response to horizontal and vertical forces applied to the film, we can predict the in-plane modulus ($E_{1,cell}$) and out-of-plane modulus ($E_{2,cell}$) of the film as

$$E_{1,cell} = C \sin \theta \cos^4 \theta \cdot (2 - \cos^2 \theta)^{-1}, \quad [1]$$

$$E_{2,cell} = C \sin^3 \theta, \quad [2]$$

with $C = \alpha E_{truss} I_{truss} f_{truss}^2 A_{truss}^{-2}$, where E_{truss} , I_{truss} , and A_{truss} are the Young's modulus, moment of inertia, and cross-section

area of each truss, respectively, and α is a numerical constant. The volume fraction occupied by the nanotubes is $f_{truss} = A_{truss} l / HL^2$, where l is the length of the truss. Because nanotubes tend to bundle together, the trusses in our cellular model do not necessarily represent individual nanotubes. Hence, I_{truss} and A_{truss} in our model are unknown, and constant C in Eqs. 1 and 2 is treated as a fitting parameter. Fig. 2B plots the predicted dependence of the moduli on the AR at different volume fractions (f) of nanotubes. Our model predicts the f_{truss}^2 dependence of the film moduli as the Gibson and Ashby model, but shows a stronger dependence of the film moduli on the AR. The prediction is largely consistent with our experimental data on the film moduli as well as SEM estimates of the AR and f . The ratio between the predicted $E_{1,cell}$ of the middle and crust layer is consistent with the measurements, which is in the range of 30–60. The cellular model provides insight into the overall mechanical behavior of the CNT array. This model assumes that the elastic deformation of the film is entirely caused by truss bending, which is not precisely correct in accounting for the complex morphology in the CNT array. Nonetheless, we apply the cellular model here owing to its simplicity and the possibility, when combined with the coarse-grained approach also developed in this paper, to provide insight into nanotube alignment by means of the AR parameter. In reality, the nanotubes are held together by weak van der Waals forces, and zipping of nanotube bundles may play a role in the elastic compliance of the film. To remove the empirical fitting parameter C and to gain a deeper understanding on the realistic structure and dynamics of the nanotubes in the films, we use a coarse-grained molecular simulation.

In the coarse-grained molecular simulation, each nanotube is modeled as a fiber discretized into a chain of nodes. Neighboring nodes on the same fiber interact to give the bending and stretching stiffness of the nanotube, whereas nodes on different fibers interact through van der Waals forces (31) (SI Text). In this model, the range of AR (1.4–4.2) and f (2–12%) of interest are determined from the characterization results including image processing (7, 9, 11, 13). The moduli calculated using the simulation $E_{1,sim}$ and $E_{2,sim}$ are shown in Fig. 2B. Fig. 3 shows that the molecular simulation is qualitatively similar to the SEMs, where the middle layer is more aligned compared with the crust. The average tube orientation θ in the relaxed structure is determined for comparison with the cellular model. A consistency is observed between the molecular simulations, the cellular model (with a fitting parameter $C = 60,000$), and our experimental measurements, as shown in Fig. 2B. Better agreement is observed particularly at $AR < 3.0$, where bending is dominant rather than van der Waals forces. However, due to the cancellation effect of the van der Waals interaction and bending energy, the overall trend of the curve (Fig. 2B) remains qualitatively the same. The simulation predicts that the moduli in both directions scale with $f^{1.5-2.0}$, depending on the AR, consistent with the f^2 dependence predicted by the cellular model. A better-aligned film with greater AR has not only lower in-plane modulus, which is preferable for the interface applications, but also higher out-of-plane modulus (SI Text). This is because longer beams are weaker in bending, so as the AR increases, the lengthened beams bend more easily in the direction perpendicular to their axis (Fig. 24). If the beams are aligned better, they are more difficult to stretch in the out-of-plane direction.

The molecular simulations also provide more details about the mechanisms of nanotube deformation when the film is subjected to an elastic strain. There are many complex deformation modes not considered in the cellular model. For example, bundles of nanotubes may move together, a bundle formed by several nanotubes may partially zip (Fig. 4A) or unzip, two nanotubes or bundles may rotate around a contact point (Fig. 4B), and nanotubes within a bundle (oriented perpendicular to the straining direction) may slide relative to each other.

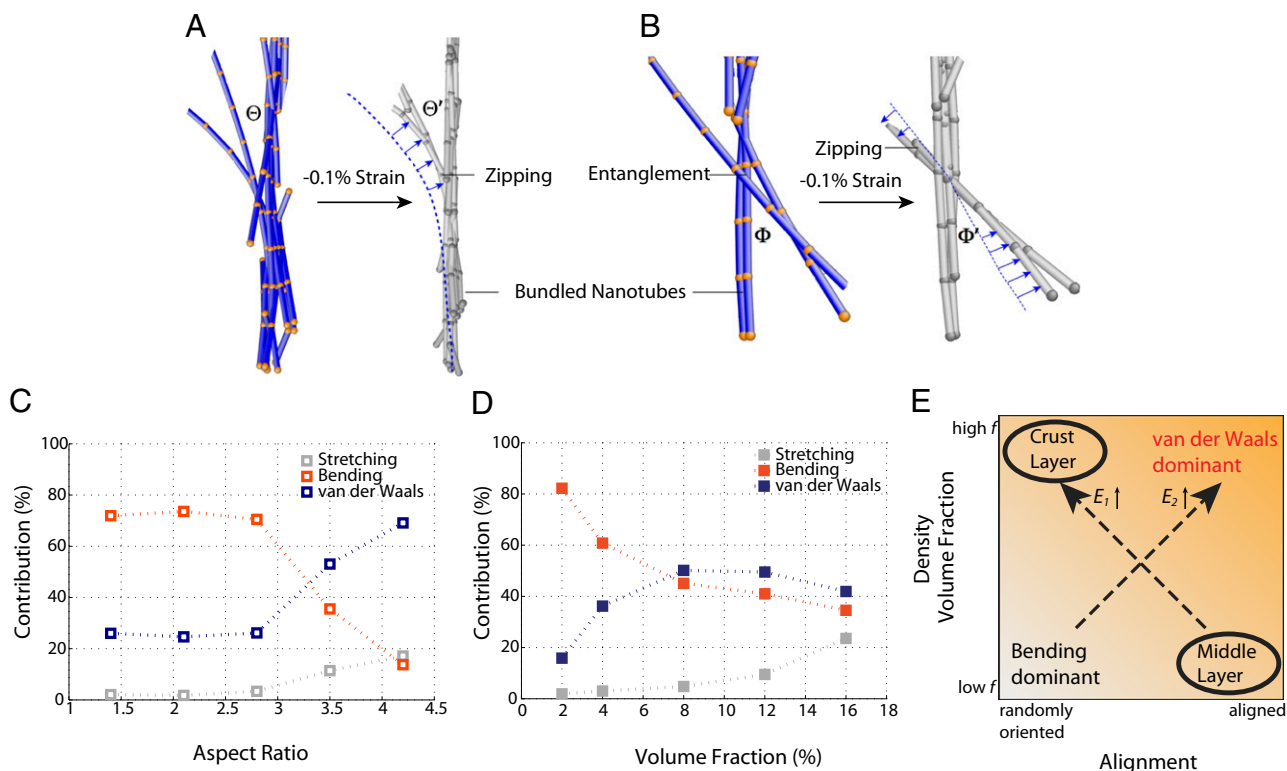


Fig. 4. Nanotube interactions when a compressive 0.1% strain is applied to the film ($f = 2\%$, $AR = 3.5$). Snapshots from the molecular simulation illustrate the different types of nanotube displacements under strain, including (A) zipping and unzipping (governed by van der Waals forces) and (B) crossed nanotubes. The blue lines show the nanotubes in the initial relaxed structure. The gray lines represent the new positions of the nanotubes when the cell is compressed. The contribution of bending, stretching, and van der Waals energy in the calculation of elastic modulus for varying (C) AR and (D) volume fraction. (E) Phase diagram to show the governing physics to decide the modulus of nanotubes with varying nanostructures.

their nanostructure, which can be achieved by altering the synthesis conditions or by adding surfactant molecules. The development of self-consistent simulations and the experimental data can provide guidance on detailed simulation of other material properties including the effective thermal and electrical conductivities. The approach presented here is also applicable to a wide range of films with a fibrous nanostructure, such as films made of nanowires and microwhiskers.

Methods

Coarse-Grained Nanotube Simulation. We adopt a coarse-grained molecular model in which each nanotube is represented by a set of nodes. The interaction between neighboring nodes on the same chain is designed to reproduce the bending and stretching response of an elastic tube with Young's modulus E_{tube} , inner radius r_{in} , and outer radius r_{out} . A Lennard-Jones (LJ)-type interaction is introduced between nonneighboring nodes to account for the van der Waals attraction and steric repulsion between nanotubes. The potential energy as a function of nodal positions $\{r_i, r_j\}$ can be written as (36)

$$V(\{r_i, r_j\}) = \sum_i \frac{1}{2} k_s (|r_{i+1} - r_i| - l_0)^2 + \sum_i \frac{1}{2} k_B \left(\frac{(r_{i-1} - r_i) \cdot (r_{i+1} - r_i)}{|r_{i-1} - r_i| \cdot |r_{i+1} - r_i|} + 1 \right) + \sum_{ij} \left(\frac{C_{12}}{|r_i - r_j|^{12}} - \frac{C_6}{|r_i - r_j|^6} \right). \quad [3]$$

The first summation is over all neighboring nodal pairs on the same nanotube; the second summation is in which i is the neighbor of nodes $i-1$ and $i+1$ on the same nanotube; the third summation is over all nodal pairs that do not belong to the same nanotube (where $j \neq i \pm 1$). $k_s = E_{tube} A_{tube} / l_0$ and $k_B = E_{tube} l_{tube} / l_0$, where $l_{tube} = \pi(r_{out}^4 - r_{in}^4) / 4$ is the moment of inertia of the tube cross-section, and l_0 is the discretization length of the nanotubes. Here we adopt $r_{out} = 5 \text{ \AA}$, $r_{in} = 4.4 \text{ \AA}$ by using the effective tube thickness (37). The LJ coefficients between the nodes are proportional to the LJ coefficients describing the interaction between individual carbon atoms. Specifically,

$C_{12} = N_c c_{12}$ and $C_6 = N_c c_6$, where N_c is the number of carbon atoms represented by each node (36), $c_{12} = 2,516,582.4 \text{ kcal} \cdot \text{mol}^{-1} \cdot \text{\AA}^{12}$, and $c_6 = 1,228.8 \text{ kcal} \cdot \text{mol}^{-1} \cdot \text{\AA}^6$ (38). For single-walled CNTs, we estimate N_c to be $2\pi r_{out} l_0 / A_c$, where A_c is the average area covered by each carbon atom. The nanotubes are initialized as straight lines randomly positioned in the simulation cell. The number of nanotubes and the length of each nanotube are selected to achieve the desired density. The initial nanotube orientations are parallel to vector $t = (x_1, x_2 + p, x_3)$, where x_1, x_2 , and x_3 are random numbers uniformly distributed in $[-0.5, 0.5]$. A larger p value corresponds to a stronger alignment to the y axis. The structure is then allowed to relax by minimizing the potential energy using the conjugate gradient algorithm. During the relaxation, the nanotubes bend and bundle together. The relaxation algorithm stops when the potential energy change in one iteration is smaller than 10^{-4} eV .

After the structure has been relaxed, the components of the elastic stiffness tensor (C_{ij}) connecting normal stress (σ_i), and normal strain (ϵ_j) (where $\sigma_i = C_{ij} \epsilon_j$) are computed by stretching the simulation cell along the x , y , and z axes, respectively, relaxing the structure again, and computing the stress change. The maximum strain applied to the simulation cell is $\pm 0.1\%$, which is also the maximum applied strain in our experiments. The effective modulus of $E_{1,sim}$ and $E_{2,sim}$ is computed from the components of the elastic stiffness tensor. For example, $E_{1,sim}$ corresponding to the equivalent value of $E_{1,exp}$ in the current work is

$$E_{1,sim} = C_{11} - (C_{11}C_{12} - C_{12}C_{13})(C_{11}C_{22} - C_{12}^2)^{-1}C_{12} - (C_{12}^2 - C_{13}C_{22})(C_{12}^2 - C_{11}C_{22})^{-1}C_{13}, \quad [4]$$

where σ_y and σ_z are assumed to be zero because of the free surfaces of the single-walled CNT films. Because vertically aligned CNT films have entangled morphologies showing foam-like behavior (10, 15, 17, 18), we assume that the film has a Poisson's ratio of zero. Thus, the $E_{2,sim}$ is assumed to be C_{22} .

The model accounts for the nanotube morphology by incorporating various density and alignment parameters (i.e., AR and f). The coarse-grained molecular simulation predicts the mechanical response of single-walled CNT films depending on the film nanostructures and the intrinsic mechanical behavior of nanotubes.

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