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A single degree of freedom 'lollipop' model for carbon nanotube bundle formation

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ABSTRACT

Current carbon nanotube (CNT) synthesis methods include the production of ordered, free-standing vertically aligned arrays, the properties of which are partially governed by interactions between adjacent tubes. Using material parameters determined by atomistic methods, here we represent individual CNTs by a simple single degree of freedom 'lollipop' model to investigate the formation, mechanics, and self-organization of CNT bundles driven by weak van der Waals interactions. The computationally efficient simple single degree of freedom model enables us to study arrays consisting of hundreds of thousands of nanotubes. The effects of nanotube parameters such as aspect ratio, bending stiffness, and surface energy, on formation and bundle size, as well as the intentional manipulation of bundle pattern formation, are investigated. We report studies with both single wall carbon nanotubes (SWCNTs) and double wall carbon nanotubes (DWCNTs) with varying aspect ratios (that is, varying height). We calculate the local density distributions of the nanotube bundles and show that there exists a maximum attainable bundle density regardless of an increase in surface energy for nanotubes with given spacing and stiffness. In addition to applications to CNTs, our model can also be applied to other types of nanotube arrays (e.g. protein nanotubes, polymer nanofilaments).

1. Introduction

Carbon nanotubes are among the most widely studied nanomaterials, with many potential applications that take advantage of their unique mechanical, electrical, thermal, and optical properties (Baughman et al., 2002). There are many concurrent investigations involving carbon nanotubes, ranging from experimental synthesis to atomistic and continuum modeling with focus on a variety of properties, behaviors, and applications. The superior mechanical properties of carbon nanotubes are appealing for their potential use in novel nanomaterials. For instance, the Young's modulus of a single-walled nanotube approaches a terapascal (10^{12} Pa) (Treacy et al., 1996), implying that CNT is one of the strongest known synthesized materials in terms of elastic modulus and ultimate tensile strength (Li et al., 2000b). For over a decade, attempts have been made to utilize the high strength of individual CNTs in an efficient manner. However, a well-known behavior of CNTs is inter-tube bonding due to weak van der Waals interactions, which results in formation of bundles that

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contain hundreds or thousands of individual nanotubes. The formation of these larger-scale structural features complicates investigations of the mechanical properties of nanotube materials, and challenges remain in understanding how to control and measure the properties of such large systems of CNTs. The study of the structural properties of larger-scale bundles of CNTs attached to a surface is the focus of this paper.

1.1. *Formation of bundles in nanotube arrays*

The interaction of individual CNTs in larger-scale structures often plays a critical role in the mechanical properties of CNT systems. At the nanoscale, weak van der Waals interactions govern the structural organization and the mechanical properties of CNT based materials. For example, the high axial strength of individual nanotubes is lost when nanotubes form bundles as the weak forces allow slippage of nanotubes within a bundle (Ajayan and Banhart, 2002; Kis et al., 2004). Such effects are also found in nanotube based fibers or ropes (Dalton et al., 2003; Zhu et al., 2002), as well as in vertically aligned nanotube arrays (Li et al., 2000a; Liu et al., 2008; Zhang et al., 2008). The importance of the interplay between adhesive forces and covalent bonding at the atomistic, molecular, and global material scales remains poorly understood for many CNT systems. Advancing our understanding of the structural arrangements and mechanisms resulting from such weak interactions is necessary for the development of materials and structures that take advantage of bundling of nanotubes, for example in self-organized CNT based surface materials. Fig. 1 shows snapshots of bundled polymer nanotube structures (Linares et al., 2009; Steinhart et al., 2002), illustrating the type of features and scales associated with bundle formation typically observed in nanotube systems, involving a very large number of nanotubes and structural features at tens and hundreds of nanometers. Modeling these systems requires time- and length-scales beyond the reach of conventional molecular dynamics, and the use of multi-scale approaches is critical to build simulation models of these structures.

The molecular level interactions of adjacent carbon nanotubes has been investigated using atomistic methods (Chen et al., 2003; Liew et al., 2005, 2006; Zhou et al., 2007; Zhu et al., 2004), but bundle formation and self-organization of a large number of CNTs becomes computationally expensive at the atomistic level for relatively long carbon nanotubes, or multiple nanotubes (the computational cost is proportional to the number of atoms in the simulation). Mesoscopic ‘‘bead–spring’’ methods have been proven a viable approach to simulate arrays of CNTs (Buehler, 2006; Cranford and Buehler, 2009) and graphene (Cranford et al., 2009), but these approaches are still limited to hundreds or thousands of nanotubes in a particular nanotube array. Synthesized samples of carbon nanotube arrays have shown bundles consisting of hundreds of thousands of individual CNTs (Bronikowski, 2006). Thus a new approach is required to investigate bundle formation of such large arrays of CNTs. The focal point of this paper is the multi-scale development of a single degree of freedom ‘‘lollipop’’ model for nanotube representation to enable the simulation of structural organization of very large bundles of CNTs. The development of this model is facilitated by a continuum elasticity model used to quantify the energy balance of adhered adjacent carbon nanotubes, where all parameters are identified by full atomistic simulation results. This simulation model has a twofold purpose: first, to confirm bundle formation of synthesized samples at a relatively large scale, and; second, to efficiently investigate the capacity to manipulate bundle formation within large nanotube arrays by introducing geometric changes to the geometry of constituting elements (e.g. patterning). Specifically, parametric investigations concerning nanotube length, spacing, diameters, and other structural and physical parameters can quickly be implemented to manipulate possible bundle formations and attain unique surface and mechanical properties of nanotube arrays. This approach can be used to engineer novel surface nanostructures.

1.2. *Outline*

The outline for the rest of this paper is as follows. In Section 2 the continuum theory governing nanomechanical bundle formation and equilibrium is described via an energy balance between bending strain energy, local deformation contact

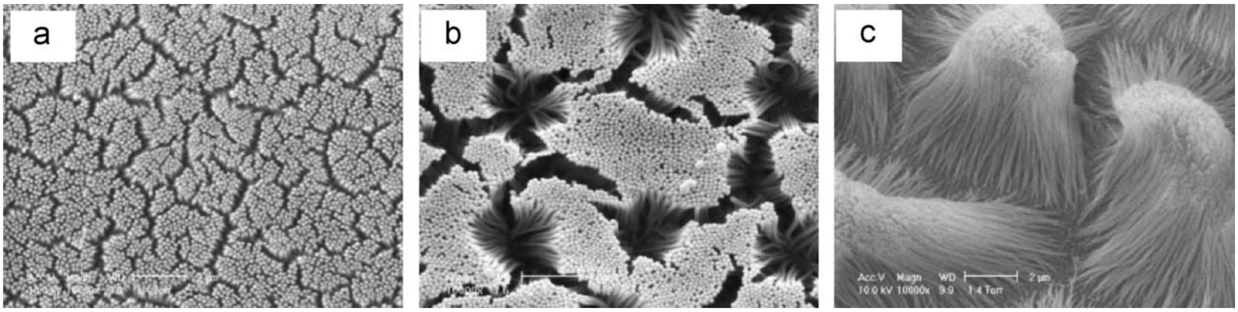

Fig. 1. Illustration of bundle formation in nanotube systems. The images show scanning electron microscopy (SEM) characterization of polymer nanofilament bundles (Linares et al., 2009). Image reprinted with permission from: Linares et al., 2009. Polymer films composed of surface-bound nanofilaments with high aspect ratios, molecularly imprinted with small molecules and proteins. Advanced Functional Materials 19, 1299–1303. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.