Fast Monte Carlo Simulation-based Process Design and Planning for Carbon Nanotube Synthesis

Changqing Cheng¹, Satish T.S. Bukkapatnam²*, Lionel Raff³ and Ranga Komanduri⁴

¹Department of Industrial and Management Systems Engineering, University of South Florida, Tampa, FL
²Department of Industrial and Systems Engineering, Texas A&M University, College Station, TX
³Department of Chemistry, Oklahoma State University, Stillwater, OK
⁴School of Mechanical and Aerospace Engineering, Oklahoma State University, Stillwater, OK

Abstract

Although nanostructures have been considered for industrial applications, the current production and yield rate remains rather low, hovering in 10-20%. An effective process planning and design for nanomanufacturing is considered necessary to improve quality of nanostructures and consequently the yield rate. Key to quality assurance in nanomanufacturing is to derive desired geometric features, which are determinant to physical and chemical properties (e.g., Young’s modulus), of nanomaterials, such as carbon nanotubes (CNTs). While atomistic simulation models are widely used to study those nano-scale phenomena and consequentially the process design, they suffer from an overwhelming computational overhead. In this paper, we present a meso-scale fast Monte Carlo (MC) simulation approach to investigate large-scale CNT synthesis in chemical vapor deposition, and identify key parameters (here, catalyst diameter, temperature, and CNT length) to maximize the Young’s modulus.

Keywords: nanomanufacturing, process design, Young’s modulus, fast MC simulation

1 Introduction

Nanoscale structures and materials in the form of tube, film and wire are known to have novel physical, chemical, and biological properties. For instance, nanoscale translators have made computers faster, more powerful, and more energy efficient; recent advance in nanotechnology has made
high-efficiency and low-cost solar cells possible (Cui, Ruffo et al. 2009). In fact, nanotechnology is viewed as a paramount driver of future economic growth, through its impact in industries from aerospace and energy to healthcare. While many potential nanostructures have been identified and considered for industrial applications, they have often been synthesized using slow and costly methods in the research lab, not applicable for economical production at commercial scale. Therefore, there is a pressing need for economical nanomanufacturing to realize the potential of nanotechnology. Nanomanufacturing generally includes various synthesis and assembly techniques, including but not limited to chemical vapor deposition (CVD), physical vapor deposition, atomic layer deposition, molecular assembly and top-down miniaturization techniques, bio-assembly, networking at the nanoscale and multi-scale and hierarchical architectures (Chang, Uang et al. 2008, Ryckman, Liscidini et al. 2011). For example, carbon nanotubes (CNTs), with many outstanding properties, are one of the promising nanostructured materials considered for industrial applications (Iijima 1991, Iijima and Ichihashi 1993). CVD processes are widely used to synthesize CNTs (Kukovecz, Mehn et al. 2005), in which chemicals react to produce fairly pure and high-performance tube structures. In a CVD process, carbon atoms decompose from a source gas (e.g., C_2H_2) to nucleate and grow the CNT structure in the presence of a catalyst (e.g., Fe). While efforts have been made to address the optimization of these processes (Dasgupta, Ma et al. 2008, Vanyorek, Loche et al. 2011), the current production and yield rate remains rather low (hovering at 10-20%, often on the high side). Here, the yield rate is defined as the ratio between the amount of carbon atoms in the CNT structures and that in the CVD reactor. The low yield rate is also attributed to the amorphous carbon structures or impurities produced in the CVD processes. Translating these processes into viable scale-up manufacturing is an imperative to realize the market potential of nanotechnology.

Optimal design and planning of the nanomanufacturing processes is essential towards the quality assurance, and thereby to ensure the repeatability and scalability of nanomanufacturing processes so that nanostructures can be produced in a large scale. It involves determining how to set controllable parameters of processes, such that uncontrollable but very important variables are in tolerable ranges and product characteristics are optimized. To this end, an understanding of the process mechanism is required. In nanomanufacturing, due to complexity of the processes and huge cost of experimental study, simulations have played important roles to study the process. They can shed light on behaviors of product and performance of manufacturing processes. Macroscopic simulation approaches, such as continuum modeling (Pannala and Wood 2004, Naha and Puri 2008), have been investigated in literature to study the nano-synthesis process. Continuum models employ differential equations to model carbon concentration, but could not be used to track the growth trajectories especially in short time scale. Additionally, material properties require consideration of molecular structures. Therefore, atomistic Molecular dynamics (MD)/MC simulations (Ding, Rosen et al. 2004, Shibuta and Elliott 2006, Elliott, Hamm et al. 2009) of nanostructure synthesis are useful to capture atomic motion at resolutions conducive for effective process design of nanostructure characteristics.

However, previous studies on design of nanomanufacturing processes are largely based on macroscopic models (Lee, Yeoh et al. 2010, Vanyorek, Loche et al. 2011). Atomistic and meso-scale simulation-based process design and planning have not been successfully reported, as applications of MD/MC simulations are largely impedied by the computational cost. As a result, they are only applicable to investigate initial stages of the nano-synthesis processes, not suitable for real-world nanomanufacturing processes. For example, in the MC simulation of CNT synthesis in CVD process, 80-95% of the computational overhead is attributed to the relaxation procedure implemented at every growth step. Despite various attempts (Gentile 2001, Rocha, Coutinho et al. 2001) to increase computational speed, the current MC models are not computationally tractable for simulation of CNT and other nanostructures growth well beyond the nucleation stage. One of the longest reported CNT from atomistic/meso-scale simulations consists of some 10,000 carbon atoms with a length of ~150 nm (Tejima, Minami et al. 2008) using the earth simulator. This is about an order of magnitude below the CNT sizes (500 nm to several µm in length) from experiments.
Recently, we developed a prediction-based fast MC simulation approach (Cheng, Bukkapatnam et al. 2012) to model the growth of vertically-aligned single-walled CNT growth in a plasma-enhanced CVD process. It reduced over 85% of the computational cost, and led to one of the longest CNT structures from atomistic simulations. In this paper, we employ this fast MC simulation to explore design and planning of CNT synthesis in the above-mentioned CVD process, to investigate and quantify effects of factors on desired CNT properties. Here, the Young’s modulus of CNTs generated from the fast simulation will be derived from MD. Design of experiments is used to adjust process parameters to maximize Young’s modulus.

This rest of this paper is organized as follows: section II presents the research background; research methodology is introduced in section III; section IV presents the results of simulation-based process design, and section V concludes this report.

2 Background

Nanomanufacturing is referred to the new technologies that produces materials and creates artifacts with features having at least one dimension in nanoscale (Bukkapatnam, Kamarthi et al. 2012). The emergence of nanotechnology has led to materials with unprecedented physical, chemical and biological properties. Such nanomaterials are of vital interest to a variety of industries, ranging from aerospace engineering to healthcare. However, nanomanufacturing industries are facing a host of challenges, such as low yield rate and reliability, lack of process control, and high batch-to-batch variation, also known as repeatability and reproducibility. Those challenges have severely impeded scaling-up production of nanomaterials from the laboratory research to industrial applications. They could be addressed, at least partly, through process design that identifies and eliminates the fundamental limits to scaling. The nanosynthesis process design entails identification of robust settings of process conditions (e.g., temperature, pressure, gas flow rates) with minimal number of experiment runs to derive desired characteristics of nanomaterials.

Process design of nanomanufacturing is largely empirical (Kukovecz, Mehn et al. 2005, Casciato, Kim et al. 2012), and does not invoke a first-principle model. Instead, a simple model structure (e.g., polynomial function) is used to fit the experimental data. This type of process design usually failed to capture the highly nonlinear and nonstationary relationships between process parameters and system output in most nanomanufacturing scenarios. In contrast, fundamental law-based mechanistic models can provide insight into the complex processes (e.g., atomic reaction in CVD) to adjust process parameters. As such, they are more powerful than empirical models. Oftentimes, macroscopic models, such as finite element methods, are used (Harry, Amy et al. 2005). However, as dimensional scales of materials approach nanoscale, conventional rules and mechanisms governing behavior and properties of the components and systems change significantly. Lack of understanding on the fundamental mechanisms has prohibited the controllable mass production. Nonetheless, in nanomanufacturing, due to the physical constraints, effects of design parameters on the product characteristics usually cannot be known purely from phenomenological models. It often requires simulation studies. Thus, atomistic simulation models, including MD and MC simulations, are generally required to study the nanostructures and the corresponding synthesis process design.

Atomistic MD/MC simulations have been widely adopted to study material transformation and chemical reaction dynamics (Raff, Komanduri et al. 2012) in nanomanufacturing, and they are essential to track the short-time (ps-scale) phenomena central to CNT synthesis and other nanomanufacturing processes. A MD simulation involves numerical integration of the classical equations of motion based on certain defined potential functions (Voter, Montalenti et al. 2002). Tracking of such atomic trajectories, for even 1 μs (equivalent to a few nm of nanostructure growth),
is difficult using today’s fastest processors. Direct parallel computation does not help since the integration is inherently sequential (Voter, Montalenti et al. 2002). Also, highly multimodal potential functions prevalent in large atomic systems impede the utility of most MD simulations, and confine them to simulating the nucleation stages of nanostructures, and to track a synthesis process for $10^{-7}$-$10^{-4}$ sec range (Voelz, Bowman et al. 2010). MC models have been widely used as alternatives to MD in atomistic simulations. They use statistical sampling methods to obviate the need of detailed trajectory computation. MC simulation of a nano-synthesis process consists of sequentially introducing atoms into a structure and relaxing the structure at every step until it nearly converges to a minimal-energy state. Computational overhead in the relaxation process is the main impediment to the scalability of MC simulations (Cheng, Bukkapatnam et al. 2012). The relaxation process in a nanostructure (e.g., CNT) growth simulation consists of making a series of random moves, and accepting or rejecting each of these according to a Boltzmann distribution so that the system arrives near an equilibrium state to minimize, at least locally, the total energy (the carbon-carbon and carbon-catalyst interaction energy in CNT) (Elliott, Hamm et al. 2009). Methods reported in the literature for accelerating the relaxation process include the use of meso-scale aggregate particle nodes and atomistic clusters, blocking the retrace of realized trajectories, combining diffusion equations with atomistic representation, and parallelization of simulations in high-performance computing environments (Rocha, Coutinho et al. 2001, Tejima, Minami et al. 2008, Elliott, Hamm et al. 2009). Despite those attempts, one of the longest reported CNT from atomistic/meso-scale simulations consists of some 10,000 carbon atoms (~150 nm) (Tejima, Minami et al. 2008), which is about an order of magnitude below the CNT sizes (0.5-10µm in length) from experiments. Therefore, the use of atomistic simulations has not been extensively investigated for nanomanufacturing process design owing to their formidable computational overhead.

Therefore, the conventional atomistic simulation models need to be accelerated to model the large-scale nanomanufacturing process. Our recent simulation study (Cheng, Bukkapatnam et al. 2012, Cheng, Bukkapatnam et al. 2012, Cheng, Bukkapatnam et al. 2012) of the growth process of vertically-aligned CNTs indicated that growth increments over various carbon addition steps exhibit nonlinear and nonstationary dynamics, and a recurrence-based predictive model was then used to accelerate MC simulations. 194 nm long CNTs (with ~ 12,000 atoms) were obtained from the prediction-based fast MC. This represents one of the longest simulated CNTs, and can potentially enable extensive off-line exploration of the process parameters to optimize settings to realize desired geometric or physical properties.

Exceptional Young’s modulus is one of CNT’s many outstanding properties. In any micro-system design, knowledge of nanostructures’ mechanical properties, especially its elastic modulus, is usually crucial. Generally, CNT morphology and hence the corresponding Young’s modulus varies dramatically according to process parameters. Despite the immense research efforts on the process design and optimization (Iyuke, Mamvura et al. 2009, Lee, Yeoh et al. 2010, Löffler, Häffner et al. 2011, Vanyorek, Loche et al. 2011), CVD process is not yet completely understood and the far from optimized (Ohmori, Saito et al. 2010). Also, due to confounding effects during physical experiments, the effects of the major process variables influencing CNT growth cannot be effectively delineated in the optimization design. Thus, this study provides a framework, through a design of experiments technique-enhanced fast MC, for simulation, quality control and design of nanomanufacturing processes.

3 Research Methodology

In our previous investigations (Cheng, Bukkapatnam et al. 2012, Cheng, Bukkapatnam et al. 2012), we studied vertically-aligned CNT growth in a plasma enhanced CVD process (see Figure 1 (a)), in
which CNT growth was oriented perpendicular to the substrate surface with fairly uniform length distribution (see Figure 1 (b)). This process is attractive from the standpoint of length control of CNT and other nanostructures. The length of CNTs is critical in determining the Young’s modulus (Agrawal, Sudalayandi et al. 2006). The overall flowchart of the proposed approach is illustrated in Figure 2. The fast MC simulation was first used to describe CNT synthesis process. Due to limitations of the simulation models, we only consider here the synthesis temperature and catalyst diameter as process variables. The simulation result will be validated against our previous experimental studies in terms of temperature and catalyst effects on CNT growth rate. The simulated CNT structures will be fed into a MD simulator to estimate the Young’s modulus. Last, in the process design, we will investigate key variables towards determining Young’s modulus.

![Figure 1: (a) plasma-enhanced CVD apparatus; (b) highly-vertically aligned CNTs (Nidadavolu 2005)](image)

**Figure 1:** (a) plasma-enhanced CVD apparatus; (b) highly-vertically aligned CNTs (Nidadavolu 2005)

![Figure 2: Flowchart of fast MC simulation-based process design](image)

**Figure 2:** Flowchart of fast MC simulation-based process design

### 3.1 Fast Monte Carlo simulation

The fast meso-scale MC simulation model aims to mimic CNT growth with Fe catalyst particles in the plasma-enhanced CVD process in Figure 1. Instead of studying atomic motions, a meso-scale model was introduced (Cheng, Bukkapatnam et al. 2012). As shown in Figure 3 (a), the black dot represents carbon atoms, connected by bonds between them (gray lines), in the graphene sheet structure on top of the catalyst particles at the beginning stage of the synthesis process. A triangle mesh was generated for a coarse-grained representation, such that each node can represent multiple carbon atoms. Correspondingly, the equivalent potential function in terms of nodes can be reconstructed (Elliott, Hamm et al. 2009, Cheng, Bukkapatnam et al. 2012). The continuous supply of carbon atoms, which are deposited to the base of the catalyst particles, will induce strain in the triangle mesh (red lines). MC simulation is then executed to relax the structure to grow CNTs upwards (see Figure 3 (b)).
The key to our fast MC simulation is the recurring oscillatory behaviors embedded in the growth increment time portrait (Cheng, Bukkapatnam et al. 2012, Cheng, Bukkapatnam et al. 2012). One realization of the growth increment series is shown in Figure 4 (a). The complex and aperiodic patterns in the time series indicate the presence of strong local correlations (Bukkapatnam and Cheng 2010). The recurrence plot (see Figure 4 (b)) of the growth increment indicates that the CNT growth can be treated as a series of piecewise stationary evolutions. Here, the dark blue shade in the recurrence plot indicates that the growth increments realized at the corresponding growth steps (e.g., growth steps 23 and 40) are neighbors in the state space, and possibly have similar evolution, and dark red indicates that the points are far apart in the state space. Also, CNT growth rate trajectories repeatedly return to the same neighborhoods in the state space, and trajectories emerging from nearby points in the state space evolve gradually and exhibit similar spatio-temporal pattern (Marwan, Carmen Romano et al. 2007). Exploring these key properties of growth patterns, we implemented a recurrence-based predictive model to forecast the relaxation state after each addition step. The prediction model initializes relaxation process at every growth step, such that the structure can be relaxed therefrom, to reduce the computational overhead.

Our extensive studies show that this approach can reduce over 85% of the simulation time, and thus make the fast and large-scale simulation possible.

### 3.2 Young’s modulus simulation

MD simulation is powerful for investigation of structures and Young’s modulus of CNTs. The key is to choose the appropriate potential energy function to describe the bonding and nonbonding interaction between carbon atoms. The effects of CNT’s tube diameter (here, the same as catalyst diameter), length and process temperature (it could have affect the growth rate and tube chirality) on Young's modulus are examined.
Based on the simulated coarse-grained representation of CNTs, the all-atom CNT structure was then obtained from retrieving the average atom positions. Tersoff potential energy was then employed to evaluate the Young’s modulus on the large-scale atomic molecular massively parallel simulator (LAMMPS) platform developed by Sandia National Laboratories. The CNT was fixed at one end, and subject to a small extension by pulling atoms at the free end at a given strain rate. Afterwards, the tube structure was relaxed, with atoms at both ends fixed to reach equilibrium state. The force exerted on each atom at equilibrium state can then be calculated to determine the external force required for the predefined strain (Agrawal, Sudalayandi et al. 2006). The same procedure was applied with more extensions, and Young’s modulus can be fitted from the observed force-strain relationship. To avoid end effect, only CNTs longer than 20 nm are used in this study.

3.3 Process design

Atomistic simulation-based process planning approach is a new paradigm to provide fundamental understanding of the nanoscale process, and is necessary to control and optimize those processes to realize scalable nanomanufacturing. Principles obtained from simulations provide foundation to design and optimize processes systematically. On the other hand, effective process design offers guide and insight of physical experimental studies. Further, it enables efficient implementations of experiments.

We employed design of experiments technique to explore the effect of variations in process parameters on Young’s modulus, identify optimal process settings, and validate these settings through confirmatory production runs.

4 Results and discussion

Fast MC simulations were executed at various process parameter combinations, and validated against previous studies. We found that there was a lower- and upper-limit of the catalyst diameters to support CNT growth. This is consistent with previous experimentation and simulation studies, indicating limiting size of catalyst particles for CNT synthesis (Demczyk, Wang et al. 2002, Maruyama, Kojima et al. 2002, Elliott, Hamm et al. 2009). It is noteworthy that CNT growth rate tends to decline as the diameter increases, owing to the relatively low chemisorption rate with larger diameters. This inverse relationship resembles that reported in experimental research (Lee, Lyu et al. 2001). Further, CNT growth rates are of the same order of magnitude with prior experimental investigations under similar synthesis conditions (Lee, Park et al. 2001, Nidadavolu 2005), and have the similar trend with respect to temperature effect. Note that our simulation generated one of the longest CNTs from atomistic simulation study (see the representative structure in Figure 5).

![Figure 5: CNT structure obtained from meso-scale fast MC simulation](image-url)

Next, we investigated the variation of Young’s modulus of CNTs with different length obtained at different catalyst diameters and synthesis temperatures. Previous studies suggested that CNT Young’s
modulus increases as the length increases, and level off when the length reaches 15 nm, and it can vary dramatically according to the process parameters, such as catalyst diameter and synthesis temperature (Yao and Lordi 1998). The parameter range is indicated in Table 1. Note that, here again due to simulation overhead, we could not explore a dense representation of the parameter space. MD simulation is sequential by nature, and could not be accelerated using our recurrence-based predictive models.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter ($D$)</td>
<td>2, 3, 4 (nm)</td>
</tr>
<tr>
<td>Temperature ($T$)</td>
<td>700, 800, 900 ($^\circ$C)</td>
</tr>
<tr>
<td>Length ($L$)</td>
<td>25, 50, 75 (nm)</td>
</tr>
</tbody>
</table>

Table 1: Parameter levels for process planning to optimize CNT Young’s modulus

CNT structures obtained with each variable combination were fed into MD simulation from LAMMPS. For instance, with catalyst diameter of 3 nm and synthesis temperature of 600 $^\circ$C, stress-strain relationship of CNTs with length 50 nm is shown in Figure 6. Hence the Young’s modulus is estimated as 610 GPa. Comparatively, the Young’s modulus for CNTs reported in literature is in the range of 600 -1200 GPa (Yao and Lordi 1998).

![Figure 6: Stress-strain relationship obtained from MD simulation for CNTs of length 50 nm, diameter of 3 nm and synthesis temperature of 600 $^\circ$C](image)

A full factorial design is implemented to investigate the effects of process variables on the Young’s modulus. Our analysis indicated that all three variables are significant, and length is the most important variable towards determining Young’s modulus ($p$ value < 0.0001). That said, diameter and length will affect CNT mechanical properties. Temperature is likely to affect carbon atom deposition patterns, and hence the molecular structure, which will affect the Young’s modulus. Through response surface design, the empirical model that describes the relationship between Young’s modulus (GPa) and the 3 variables is expressed as

$$E = -0.18 - 0.05D + 0.0008T + 0.0192L - 0.0002L^2$$

Visualization of the response surface is shown in Figure 7. Note that catalyst diameter and synthesis temperatures have only approximately linear effect in the response (Figure 7 (a)). CNT length has nonlinear effect (Figure 7 (b) and (c)). Young’s modulus increases first as CNT length increases, then declines after CNT length reaches 48 nm. This nonlinear effect is also observed in previous studies on atomistic simulation of Young’s modulus (Yao and Lordi 1998). Note that, although we only kept CNT longer than 25 nm for the Young’s modulus simulation, the length-to-diameter ratio is still rather low. Therefore, as CNT lengths increase, end effect on the stiffness will decrease gradually. However, kinks (or defects, see Figure 5) will be introduced in the structures for longer CNTs, which will definitely affect the stiffness negatively. All the interaction terms are nonsignificant. The maximal Young’s modulus 900.8 GPa is achieved at $D = 2$ nm, $T = 900 ^\circ$C and $L = 48$ nm.
Figure 7: Contour plot of Young's modulus with respect to: (a) catalyst diameter $D$ and synthesis temperature $T$, with CNT length $L$ fixed at 50 nm; (b) catalyst diameter $D$ and CNT length $L$, with synthesis temperature $T$ fixed at 800 °C; (c) synthesis temperature $T$ and CNT length $L$, with catalyst diameter $D$ fixed at 3 nm

To verify this optimized process design, we run multiple confirmation runs with the optimized parameters, and the obtained 95% confidence interval of the Young's modulus is given as [860, 990] GPa, compassing the optimized Young's modulus. Statistical $t$ test indicates that the average Young's modulus from confirmation runs is statistically indistinguishable from the optimized stiffness.

5 Conclusions

Effective process design of nanomanufacturing is necessary towards improving quality and hence the scale-up production of nano-products. In this paper, meso-scale fast MC simulation model, perhaps for the first time, is used in the design of CNT synthesis process to identify the critical parameters that maximize Young's modulus. This is of great significance for nanomanufacturing industries in that specific nanostructure properties (e.g., Young’s modulus) can be obtained by tuning the parameters, thus reducing reliance on experiments that are often prohibitively expensive.

We note that while this work exemplified synthesis process design of CNTs in CVD, it could be generalized to a variety of nanostructures from a host of novel processes, including physical vapor deposition and self-assembly. An extension of the reported study could be the robust design based on variable uncertainty. Further, nanomanufacturing is a complicated process, and many factors can jointly affect the geometric features of structures and properties of synthesized nanostructures, such as the purity of the precursor, poison effect of the catalyst and gas-feed pressure, etc. Those factors may not be quantified accurately. Therefore, a robust process design formulation will be pursued in our future study.

Acknowledgements

The authors would like to acknowledge the support of the National Science Foundation (Grants No. CMMI-1432914 and CMMI-1437139) and Rockwell international professorship.
References


Voelz VA, Bowman GR, Beauchamp K and Pande VS. Molecular simulation of ab initio protein
