Technical paper

Towards control of carbon nanotube synthesis process using prediction-based fast Monte Carlo simulations

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\begin{abstract}
Precise control of the lengths of carbon nanotube (CNT) and other nanostructures is important for various industrial applications. However, time-resolution (\textsim\,1 min) of current in situ measurements does not allow control of lengths to within 20 nm. We present an approach to combine intermittent in situ measurements with length estimates from a fast atomistic Monte Carlo (MC) simulation of CNT synthesis. The MC simulation time was reduced by >70\% through prediction of the nonlinear and nonstationary growth increments, and initialization of relaxation process (the most computationally intensive step in MC simulations) with the near-optimum predicted positions, leading to one of the longest (\textsim\,194 nm) CNTs from atomistic simulations. A utility function of growth predictions was defined so that its maximization specified the end-point of the synthesis process. Extensive simulation studies indicate that the approach can be used to control CNT lengths to within 1 nm of specifications.
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1. Introduction

The nanotechnology products market is projected arguably to exceed \$1 trillion in the next 10 years [1,2]. While some of these nanostructures and products are considered for niche applications in automotive, aerospace, construction, medical and defense industries [3–10], much of the synthesis processes, and related device development efforts mostly remain confined to labs [11–13]. Carbon nanotubes (CNTs) [14,15] are one of the promising nanostructure materials considered for industrial applications. Geometric features, such as the length and diameter, are known to be the major determinants of CNT properties for various industrial applications. While efforts have been made to address the optimization of the CVD and other processes used for CNT synthesis [16–18], the current production and yield rates remain rather low to permit wider industrial applications. Precise control of these features during atomistic-scale growth processes is considered essential towards improving the quality and yield rates [19]. Among these, control of CNT length is vital for many applications, such as composite elements [20] and electronic sensors [21]. However, precise control of CNT length during the synthesis process remains a major industrial challenge. Significant production efforts are taken for auxiliary process, such as sonication, oxidation, and alignment [22] to consistently realize the desired CNT lengths that lay within 10 nm of the specifications. Expenses on these processes often hinder the viability of using CNTs for broader engineering applications.

In order to achieve \textit{in situ} control of CNT lengths, one needs an effective end-point detection (EPD) method [23]. It involves \textit{direct measurement} or \textit{indirect estimation} of the CNT lengths (and their distribution) in real-time from various characterization and sensing methods, and comparison of the estimates with the specifications to establish a stopping criterion for a synthesis process. Alternative \textit{in situ} measurement techniques [24,25], such as those based on optical interferometry, atomic force microscopy (AFM) and scanning electron microscopy (SEM) [26–28] have attracted some recent attention. While \textit{in situ} measurement eliminates the need for elaborate sample preparation as in the \textit{ex situ} techniques, they are limited by the short and intermittent recording times, with sampling intervals of an order of 30–100 s, i.e., they are not suited for precise control of lengths to within 20 nm. These intermittent measurements need to be augmented with models capturing the growth process evolution in order to achieve the desired precisions.

Towards this end, various experimental and simulation approaches have been taken to model the CNT synthesis process for indirect estimation of lengths and other quality variables. Experimental studies [29–33], mostly of CVD process, have been reported to generate CNTs with lengths between 500 nm and 16 cm. But CNT synthesis experiments tend to be expensive and characterization...
of the synthesized structure tedious. Therefore, simulation modeling approaches, such as continuum modeling [34,35] and atomistic molecular dynamics (MD)/Monte Carlo (MC) simulation [36–42] of CNT synthesis may be pursued to capture the length variations at resolutions adequate for precise control of CNT lengths.

Continuum modeling [34,35] employs differential equations to describe the carbon concentration, but fails to track the growth trajectories, especially in short time scale. Atomistic simulations can explore the atomistic evolution during the synthesis process, and can explain the process not observed in experiments. However, the computational overhead involved in MD/MC simulations has limited the atomistic simulations only to the initial stage of CNT synthesis process. The longest CNTs obtained from atomistic simulation are less than 150 nm. Hence, there is a pressing need for methods to speed up atomistic scale models to investigate the synthesis mechanism, and to monitor the CNT length variation during a larger-scale synthesis process. Methods reported in the literature for accelerating atomistic simulation 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 environment [38,43–46]. Despite those efforts, one of the longest reported CNTs from atomistic simulations consists of some 10,000 carbon atoms with a length of ∼150 nm [45]. This is about an order of magnitude below the CNT sizes from experiments.

We employed meso-scale MC simulation to study vertically aligned CNT synthesis in CVD process in this paper, and the majority (80–95%) of the computational overhead during the MC simulation is due to the relaxation process implemented at every growth step. This MC simulation can be accelerated through predicting the growth increment, which is based on our recent findings that CNT growth increment exhibits nonlinear and recurring near-stationary dynamics in the meso-scale MC simulation, and prediction models can be used to capture the nonlinear and nonstationary growth process evolution [47]. Our nonparametric prediction model, local Gaussian process (LGP) [48], uses the local recurrence and such topological properties to handle the nonlinearity and nonstationarity in CNT growth increment, and outperforms most traditional modeling techniques, including ARMA, Kalman filter, and neural network models [48] in terms of prediction accuracy. We have also investigated multi-step LGP prediction model to accelerate MC simulation for CNT synthesis process [49]. Consequently, the LGP based fast MC simulation model can be employed to monitor and predict CNT length variations in real time during the synthesis process. A utility function was defined to facilitate decision making (“continue synthesis” or “stop synthesis”) under the scenarios of “under-growth” and “over-growth” using the predicted growth increments. Maximization of the utility function specified the end-point for the synthesis process. Extensive simulation studies suggest that our approach can be used for control of CNT lengths to within 1 nm variation of the specifications.

The remainder of the paper is organized as follows: Section 2 explained the background of the meso-scale MC simulation; Fast MC simulation is presented in Section 3; Application of the simulation in CNT end-point detection (EPD) is discussed in Section 4; Section 5 concludes the reported research.

2. Meso-scale MC simulation

Our MC simulation model captures the growth of a CNT from a single Fe catalyst particle in a plasma enhanced PE-CVD process [33,50]. We employed spatial coarse-graining technique suggested by Elliott et al. [38] to reduce the computational efforts for regular MC simulation. As shown in Fig. 1(a), we used the triangle lattice structure to represent the graphene sheet formed on the catalyst surface. Note that, in each triangle we have 4 carbon atoms, and each of the 4 carbon atoms in a triangle element are shared equally by the 3 nodes of the triangular element. Since each node is shared by 6 such neighboring elements (provided it is not on the open end of the CNT structure), one node can represent (4/3) × 6 = 8 carbon atoms. At every growth step, new nodes will be added to the base of the catalyst (shown with a red line mesh in Fig. 1(a)) based on the dissociation rate of carbon atoms from the carbon source gas, and the probability of their chemisorption rate onto the existing CNT structure. The introduction of new nodes incurs strain into the triangle lattice structure. Next, the resulting mesh structure will be relaxed to a near-equilibrium state through a Metropolis MC procedure according to the predefined system Hamiltonian [38].

Fig. 1(b) shows the CNT mesh structure after relaxation at the 1st growth step (i.e., ∼4 ms of synthesis). As mentioned in the foregoing, the majority (80–95%) of the computational overhead during an MC simulation is attributed to the relaxation procedure here. If the near-equilibrium state can be predicted in advance, the relaxation process initialized therefrom, the number of MC moves and hence the computational time can be largely reduced. Since the CNTs from our earlier experiments were aligned vertically with fairly homogenous height distribution [33] (see Fig. 2), the length control reduces to the monitoring of temporal growth of a single CNT under different synthesis conditions. In this sense, the process is highly attractive from a control standpoint, and provides one of the most realistic opportunities to control the length and end pointing of CNT growth. Correspondingly, equilibrium state prediction problem is reduced to the forecasting of the vertical growth increment at every addition step.

3. MC simulation speedup

Accurate forecasting of growth increment is challenging due to the nonlinear and nonstationary nature of the CNT growth process.
Accurate prediction is crucial to achieve a significant acceleration of atomistic simulation. We employed LGP model [48] to predict the growth increment. LGP is a nonparametric model that uses certain topological properties of the nanostructure growth dynamics to effectively capture the nonstationaries and provide accurate initial conditions for relaxation. Among other prediction methods, LGP is attractive in that the Gaussian properties can be used to simplify the modeling efforts, and the model structure needs not be known a priori [51]. It seeks to establish a mapping between the instantaneous growth increment $y$ with an input vector $x \in \mathbb{R}^d$, composed of the historical realizations of $y$. Define $X = [x_1, x_2, \ldots, x_t]^T$ and $Y = [y_1, y_2, \ldots, y_t]^T$, then $Y \sim N(0, K(X, X) + \sigma^2_{\text{noise}}I)$, where $K(X, X)$ is the covariance matrix, whose elements are the covariance functions $k(x_i, x_j)$, usually expressed using a Gaussian-like kernel. The nominal (noise-free) predictions of $f^*$ at new input $X^*$ are given in terms of its first two moments [51] as

$$\hat{f}^* = K(X^*, X)\Sigma^{-1}y$$

$$\text{cov}(f^*) = K(X^*, X) - K(X^*, X)\Sigma^{-1}K(X, X) + \sigma^2_{\text{noise}}I.$$ 

A representative time portrait of the growth increment over various carbon atom addition steps from our simulation is shown in Fig. 3(a). It exhibits recurring oscillatory behaviors, interspersed with some complex, aperiodic patterns. The autocorrelation function showed significant positive correlation at lag 1, negative correlation at lags 2 and 3, and some long-term dependency. These patterns, taken together, indicate the presence of strong local correlations in the growth increment time series. We studied the growth increment using nonlinear time series approach, including recurrence analysis [52]. The recurrent plot (see Fig. 3(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 increment realized at the corresponding growth steps (e.g., growth steps 23 and 40) are neighbors in the state space, and possibly have similar evolution pattern over growth steps. Our earlier study [48] has shown that the changes in the recurrence patterns (i.e., distance distribution) between successive time steps in a recurrence plot can be used to partition a time series into near-stationary segments. Furthermore, the recurrence plots contain extended regions with stacks of parallel dark (blue) diagonal lines of varying lengths and thicknesses, indicating that the CNT growth increment trajectories repeatedly return to the same neighborhoods in the state space, and the trajectories emerging from nearby state space points evolve gradually and exhibit similar spatio-temporal pattern [52].

Our methodology towards the MC simulation speedup is summarized in Fig. 4. The growth increment realizations at each of the first 100 addition steps were used to fit the LGP model. The trained LGP model was used to predict the growth increment ahead of every subsequent addition step. Then all nodes of the lattice structure were lifted up vertically by this predicted growth increment amount, new nodes added at the base, and the strained structure relaxed from this predicted initial condition.

As indicated in Fig. 5 that LGP can capture the drifts and variations in the growth increment ($R^2 > 0.6$ for one-step-ahead prediction accuracy, $R^2 > 0.45$ for three-step-ahead prediction in most cases, and 85–90% of the observations were within the 95% confidence interval). The LGP prediction accuracy outperforms traditional modeling techniques, including ARMA, Kalman filtering, and neural network models. Our extensive simulation studies showed that the relaxation time was sensitive to the initial conditions, and that is why accurate prediction is essential to accelerate MC simulation model. The initial conditions determined from LGP-predicted growth increment tend to be close to the equilibrium

**Fig. 2.** SEM image of vertically aligned CNTs with uniform length grown on a silicon substrate in our PE-CVD process [33].

**Fig. 3.** (a) Variation of growth increment (nm) at each addition step; and (b) the corresponding recurrence plot with vertical lines partitioning the plot into near stationary segments.

**Fig. 4.** Flow chart of LGP prediction-based CNT growth synthesis simulation.
(relaxed) states of the structure, leading to a significant reduction in the computational efforts.

As the CNT grows vertically, the separation between carbon atoms near the cap and catalyst weakens the interaction, and the geometry near the cap remains almost invariant for growth steps > 100. Therefore, we can assume the structure near the cap to be rigid during the simulation. Comparison of the computational cost of conventional MC simulation versus MC with LGP, with LGP three-step-ahead prediction and with additional rigid-body assumption shows that LGP prediction modeling approach can save over 70% of the computational overhead in a conventional MC. The rigid-body assumption, along with LGP can reduce the computational overhead by additional 10% (see Fig. 6).

The simulated CNT structures at different addition steps using MC with LGP and rigid-body assumption are shown in Fig. 7. At the end of 300 steps, the CNTs were about 194 nm long, and consisted of about 12,000 carbon atoms. This probably represents one of the longest simulated CNTs. The simulation time was reduced from 3 or 4 weeks to about 2–5 days.

We tracked the radial distribution of inter-node distances at every growth step, and the Kolmogorov–Smirnov test indicates that the structures obtained with classical MC and fast MC simulations are statistically not distinguishable. We also validated our simulation against prior experimental research [47], and found that the growth rates of CNTs are of the same order of magnitude, and have the similar trend with respect to temperature effect [32,33]. The study of catalyst diameter effect indicates the geometrically decreasing trend of growth rate with increasing diameters. This is consistent with earlier experimental findings of Lee et al. [53].
4. CNT end-point detection

The fast MC simulation enables us to monitor the CNT length variation over a relatively large scale, so that these models can be coupled with intermittent measurements. The current in situ measurement techniques are expensive, and mostly provide intermittent (~1 min) recordings. Fast atomistic Monte Carlo (MC) simulation of CNT synthesis process can be used to supplement these intermediate measurements with continuous growth estimates, necessary for precise control over lengths and other geometric features. Data-driven model can be used to predict the CNT length variation in advance.

We applied LGP model based on the fast atomistic MC simulation to detect the end-point (EPD) of CNT synthesis for desired length, as indicated in Fig. 8. We assumed 3 more addition steps (each addition step is about 4 ms) will occur after we stop the synthesis process based on our experimental conditions, i.e., stop feeding in carbon source gas. Hence we implemented three-step-ahead LGP prediction at each addition step. Here, we defined the following utility function that maps the various decisions taken under different scenarios ($\phi_{1,2}$) to real values in the range of $-1$ (minimum utility) to 1 (maximum utility): $c_{11} = 1$ for “continue synthesis” if the CNT is “under-growth” ($\phi_1$), $c_{12} = -0.8$ for “continue synthesis” if the CNT is “over-growth” ($\phi_2$), $c_{21} = -1$ for “stop synthesis” if the CNT is “under-growth” ($\phi_1$), and $c_{22} = 1$ for “stop synthesis” if the CNT is “over-growth” ($\phi_2$). It may be noted that $c_{22} < c_{21}$ needs to hold because under-growth is less desirable than over-growth, since post-processing can generate CNTs with specified length for over-grown CNTs. Also, $c_{12}$ is a tunable parameter, representing one’s expected utility of “continue synthesis” under the situation of “over-growth.” With this specification of utility function, the issue of real-time end-point detection can be addressed based on determining the decision alternative $i$ (“stop synthesis” versus “continue synthesis”) that maximizes the expected utility as $\max \sum_{j=1}^{2} c_{ij} P(\phi_j|y) [54]$, where $y$ is the CNT growth increment time-series recorded from a measuring instruments or estimated using the present LGP-based fast MC simulations, and $P(\phi_j|y)$ is the probability of under-growth or over-growth for a given growth increment time series $y$.

The utility function plot at different addition steps of a synthesis process to realize CNTs of length 90 nm is shown in Fig. 9. The red (light shade) curve shows the variation of the utility over time (addition steps) as one decides to continue synthesis, and the blue (dark shade) curve captures the variation of utility when the synthesis process is stopped at different times (addition steps). The time (specified in terms of the addition step) at which the two curves in the utility plot intersect is considered as the end-point for realizing desired CNT length. For this representative case, one should stop the synthesis at addition step 185, i.e., ~750 ms of synthesis time to realize CNTs of length 90 nm.

We ran this model with 50 different CNT length specifications in the range of 80–130 nm, and the 95% confidence interval of length specifications is defined by the second moment of the LGP prediction model. The CNT synthesis process is stopped when the utility function is maximized. Our studies showed that CNTs generated through the EPD procedure here are within the 1 nm variation of the specifications. Over 88% of the generated CNTs are within the 95% confidence interval of length specifications. Such effective control of the CNT length variation can be helpful for consistent synthesis of CNTs of various lengths and spatial patterns, as shown in Fig. 10. The CNT growth was oriented perpendicular to the substrate surface with fairly uniform length distribution (see Fig. 10(a)). Controlled growth of CNTs only at the specified sites is also possible (see Fig. 10(b)).

5. Conclusions

In summary, length control of CNTs and other nanostructures is critical for various engineering applications, and remains a major industrial challenge. An end-point detection method is essential towards the precise control of CNT lengths, which involves direct measurement or indirect estimates of CNT length in real time, and comparison of the estimates with the specifications. The current in situ direct measurement techniques cannot control CNT lengths to within 20 nm due to the low time-resolution (~1 min). While atomistic MC simulation methods can explore CNT synthesis in CVD process not observable in the experimental studies, they are limited by the computational overhead, and can only study the early stage of the synthesis process. We have developed an approach to accelerate the MC simulation by predicting the nonlinear and nonstationary growth increment using LGP model, and initializing the relaxation process with the near-optimum predicted positions. As a result, the simulation time can be reduced by >70%, thereby improving the scalability of MC simulations to capture the synthesis of CNTs, and we obtained one of the longest CNTs (~194 nm) from atomistic simulations. We combined the fast MC simulation model of CNT synthesis with intermittent in situ direct measurements for real-time length control. A utility function, that maps different decisions (“continue synthesis” or “stop synthesis”) taken under different scenarios (“over-growth” or “under-growth”) to real values in the range of $-1$ (minimum utility) and 1 (maximum utility), was defined, and its maximization specified the end-point for the CNT synthesis process to achieve length variations within 1 nm of the specifications. Statistically, over 88% of the synthesized CNTs
are within the 95% confidence interval of the length specification, indicating our model is effective for the process quality control.

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