Monte Carlo simulation of carbon nanotube nucleation and growth using nonlinear dynamic predictions

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Abstract

The computation time for Monte Carlo (MC) simulation of a nanostructure growth process was shown to be reduced by an order of magnitude compared to conventional atomistic and meso-scale models through the prediction of the structure evolution ahead of every growth step. This approach used to grow of one of the longest (~194 nm) reported carbon nanotubes (CNTs) from atomistic simulations. The key to the approach is the finding from simulation experiments that the CNT synthesis process exhibits nonlinear and recurring near-stationary dynamics.

1. Introduction

Due to the resolution and cost issues with physical experiments, Monte Carlo (MC) simulations are frequently employed to investigate the synthesis of nanometric structures, such as carbon nanotubes (CNTs). However, computational overhead limits these models to simulating mostly the initial stages of nanostructure growth. We present an approach to accelerate MC simulations of the synthesis of CNT and other nanostructures based on predicting the nonlinear, nonstationary evolution of the nanostructure growth. The growth increments from a meso-scale MC simulation of CNT synthesis from a chemical vapor deposition (CVD) process were found to exhibit nonlinear (likely chaotic) dynamics with a dimensionality of five, and a finite set of recurring near-stationary behaviors. The key feature of our approach is to predict the final structure ahead of every growth step from the local topological properties of the growth process dynamics, and use these predictions to initialize computations (the relaxation process) at each growth step. Simulation results indicate that the approach can reduce computation time by an order of magnitude compared to that with conventional meso-scale MC models. Such a reduction of computational effort vastly increases the power of MC methods in simulation studies.

Carbon nanotubes [1] and other nanostructures have multiple industrial applications. Typically, CNTs, including single and multi-wall nanotubes (SWNT/MWNT), are synthesized using CVD, laser ablation and arc-discharge processes [2]. Among these, the CVD process has received notable attention. In a CVD process, the carbon atoms decompose from a carbon source gas (e.g., C2H4) 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, the current production and yield rates remain rather low to permit wider industrial applications. Experimental [3–5] as well as atomistic MC/molecular dynamics (MD) [6] and continuum simulations [7] have been attempted to discern the pertinent growth mechanisms, which are considered paramount to improving the quality and yield in these processes. Due to high costs associated with experimentation, the effects of the chief process conditions influencing CNT growth cannot be effectively delineated. Also, the atomistic and short time-scale phenomena that drive CNT growth cannot be discerned due to sensing limitations and confounding effects present during experiments. Atomistic (predominantly MC), and to a lesser extent continuum simulations, have been attempted to gather information on the growth process that cannot be gleaned from experiments [6]. An MC simulation 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. The current atomistic MD/MC simulations are severely hampered by the huge computational overhead [8]. Continuum approximations [7] investigated as an alternative to MC models capture the concentration and growth variations but do not consider the complex potential functions about a CNT structure. Consequently, they do not track the growth trajectory and the
The majority (80–95%) of the computational overhead during an MC simulation is due to the relaxation process implemented after every growth step. The relaxation process 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 due to the carbon–carbon and carbon–catalyst interactions [6]. Methods reported in the literature for accelerating the relaxation process include the use of meso-scale aggregate particle nodes and atomistic clusters [6], blocking the retracing of realized trajectories [9], combining diffusion equations with atomistic representation, and parallelization of simulations in high-performance computing environments [10]. Despite these enhancements, the current MD/MC models are not computationally tractable for simulating CNT growth well beyond the nucleation stage. One of the longest reported CNT from atomistic/meso-scale simulations consists of some 10000 carbon atoms with a length of ~150 nm [10]. This is about an order of magnitude below the CNT sizes (500 nm to several μm in length) from experiments.

2. Research approach

We present here an approach based on tracking the local non-linear and nonstationary dynamics of CNT growth process to alleviate the associated computational overhead. Our simulation model captures the growth of CNT from a single Fe catalyst particle in a plasma enhanced PE-CVD process [3,4,11,12]. The process parameters, including temperature, catalyst geometry, and chemisorption rate are selected and time increments estimated based on our earlier experimental efforts on growing vertically aligned CNTs in a PE-CVD process [4] as well as related simulation studies [13]. As shown in Figure 1, a triangular mesh of carbon particle nodes [6] is used to represent the graphene sheet formed on the catalyst at the beginning of the synthesis process. At every growth step, new nodes are added to the base of the catalyst (shown with a light/red line1 mesh in Figure 1a) based on the dissociation rate of carbon atoms from the carbon source gas, and the probability of their chemisorption onto the existing CNT structure. Next, the resulting mesh structure is relaxed to a near-equilibrium state through a Metropolis Monte Carlo procedure. If this state can be predicted in advance, and the relaxation process initialized thereafter, the number of MC moves and hence the computation time can be greatly reduced.

We have simulated CNT growth at four catalyst particle base diameters (2, 2.5, 3, and 4.8 nm), and five temperatures (700, 750, 800, 850, and 900 °C). Since the CNTs generated from our earlier experiments [4] are aligned vertically with fairly homogenous height distribution (see Figure 2), we neglect the spatial distribution of the CNT growth, and focus on temporal growth of a single CNT under each condition. The forecasting of the equilibrium state of the structure to initialize the relaxation process therefore reduces to the prediction of the temporal evolution of the CNT length increments. At each condition, we generated five CNTs, each with a different random seed. A node of the triangular mesh used in the simulation represents eight carbon atoms2 with their relative positions consistent with the geometry of the graphitized material at the base of the catalyst and the synthesized CNT, as suggested by Elliott et al. [6]. The Metropolis MC simulation uses a potential function defined over this coarse-grained lattice [6]. It is superposition of four components, namely, bond stretching energy, surface curvature energy, and non-bonded carbon–carbon interactions, and catalyst cluster–carbon interactions. The parameters of the Boltzmann distribution were such that the acceptance–rejection ratio varied between

1 For interpretation of color in Figure 1, the reader is referred to the web version of this article.

2 For instance, each triangle element in the lattice shown in Figure 1a encapsulates four carbon atoms, and each of the four carbon atoms in a triangle element are shared equally by the three nodes of the triangular element. Since each node is shared by six such neighboring elements, one node can represent 1/6 ≈ 8 carbon atoms.
The simulation studies consistently indicate that growth increments over various carbon addition steps exhibit a nonlinear and nonstationary dynamics: a representative time portrait of growth increments (see Figure 3a) shows recurring oscillatory behavior, interspersed with some complex, aperiodic patterns in the growth increment time-series. 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 increments. The growth increments from a majority of the simulations exhibited these intermittent oscillatory time patterns. Even those simulated growth trajectories where the oscillatory behavior is not that apparent exhibit similar state space characteristics. For example, all simulated growth trajectories, despite the nonstationarities, were consistently embedded in a five-dimensional state space reconstructed using a delay embedding procedure [14]. Details of the delay reconstruction process may be gathered from the literature, including our recent work [15]. The dimensionality of the state space of the CNT growth process determines the size of the input vector for the local Gaussian process (LGP) model. The input vector consisted of the current and the m–1 previous realizations of the time-series, each shifted by a specified time-delay τ.

The recurrence plots3 (see Figure 3b) indicate that the CNT growth can be treated as a series of piecewise stationary evolutions. For example, in Figure 3 the evolution pattern over growth steps 92–106 is similar but distinctly different from the preceding and succeeding steps. Our earlier study 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 the time-series into near-stationary segments [15]. Furthermore, the recurrence plots contain extended regions with stacks of parallel (dark blue) diagonal lines of varying lengths and thicknesses. This pattern is quantified by high levels of determinism [14] (73–92%, i.e., the trajectories emerging from a neighborhood in the state space evolve in a fairly similar pattern over a short term, and repeatedly return to the same neighborhoods), and laminarity [14] (71–86%, i.e., the neighboring points in the state space often evolve gradually over a short term and exhibit similar spatio-temporal pattern). Interestingly, the values computed for each segment individually, as well as from merging similar segments (here, the similarity is determined based on the spatial correlation of recurrence patterns in the two segments considered for merger [15]) remain in the same range. Consequently, it should be possible to locally predict and track the evolution of the CNT growth trajectories through effective consideration of this nonlinear and nonstationary dynamics.

We applied a nonparametric local Gaussian process (LGP) [15] model that considers these local recurrence characteristics to estimate the CNT growth increment for the next addition step. An earlier study [15] has shown that LGP model can predict the nonlinear and (stochastic) nonstationary evolution patterns of CNT growth process. 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. Parenthetically, it may be noted that the CNT growth process dynamics drifts between multiple near-stationary regimes (see Figure 3) some of which may be previously encountered (revisiting). After the first 100 steps, we noticed that the system has experienced most the local regimes, and system trajectories essentially drift among these local regimes, and therefore no subsequent re-training of the LGP model was necessary. But, as the process evolves the definitions of these local near-stationary dynamic regimes in the state space are progressively updated. Also, should the system change to a new, previously unencountered regime, LGP model can define a new regime gradually, and the prediction accuracy is improved, usually within five growth steps.

Next, 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 initial condition. It is evident from Figure 4a that the LGP can capture the drifts and variations in the growth increment (one-step ahead prediction accuracy, R² > 0.6, and 85–90% of the observations were within the predicted 95% confidence interval). Among the prediction methods considered as possible alternatives, computationally intensive mixtures of Gaussian process (MGP) model can have prediction accuracy similar to that obtained with the LGP, but the second moment accuracy is not comparable. Prediction accuracies (R²) from other methods, including Autoregressive and Moving Average (ARMA) and global Gaussian process models, hovered between 0.3 and 0.45. It was also noted that the relaxation time was sensitive to the initial conditions, and therefore accurate prediction is essential. Inaccurate growth predictions could reduce the computational overhead only marginally at best. The initial conditions determined from LGP-predicted growth increments tend to be close to the equilibrium (relaxed) states of the structure, leading to a significant reduction in the computational effort.

The simulations also indicate that as the CNT grows vertically, the geometry near the cap remains almost invariant for growth steps >100. This is likely because the large separation between carbon atoms near the cap and catalyst weakens the interaction. Therefore, we evaluated the simulation of CNT growth assuming the material near the cap to be rigid.

Figure 3. (a) Variation of growth increments (nm) at each addition step; and (b) the corresponding recurrence plot with vertical lines partitioning the plot into near-stationary segments [15]. Here, dark blue colored points in the recurrence plot indicate 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.

3 A recurrence plot delineates the distribution of the distance between every pair of points in the state space. Each point in the recurrence plot is color coded according to the distance, indexed by the time at which they were realized. Here, the state space of CNT growth dynamics is reconstructed from the time-delays of the growth increments series [14].
3. Results and discussion

A comparison of the computational overhead of traditional MC simulation versus MC with LGP, and with additional rigid-body assumption (see Figure 4b) shows that LGP can save about 70% of the computational overhead in a traditional MC. The rigid-body assumption, along with LGP prediction can reduce the computational overhead by additional 10%.

The simulated CNT structures at different addition steps using MC with LGP and rigid-body assumption are shown in Figure 5. At the end of 300 steps, the CNTs were about 194 nm long, and consisted of about 12000 carbon atoms. This probably represents one of the longest simulated CNTs. More pertinently, in physical terms, the simulation time was reduced from about 3–4 weeks to about 2–5 days.

Also, the radial distribution of inter-particle distances was tracked at every step of the CNT growth simulation, and quantitatively compared with those obtained with traditional MC, and MC with LGP (without rigid-body assumption) using the Kolmogorov–Smirnov (KS) test [16]. Figure 6a shows a comparison of the radial distributions of the structures obtained with different simulation options at the end of addition step 125. The results indicate that the structures obtained with different options are statistically not distinguishable. Also, as shown in Figure 6b, the CNT growth rates estimated from simulation (based on the flow, decomposition, and chemisorption rates) increase from about 0.01–0.03 µm/s as temperature is varied over 700–950 °C range. This is because as temperature increases, the deposition and chemisorption rates, as well as the acceptance–rejection ratios of MC moves tend to increase. The simulation also indicates that, in consonance with the experimental results of Lee et al. [17], the average growth increment decreases at a geometric rate as catalyst particle size is increased from 2 to 4.8 nm. This is because as diameter increases the number of lattice nodes increases, causing the acceptance–rejection ratios to drop significantly.
4. Conclusions

In summary, while MC simulation is a useful tool to study the synthesis of CNT and such nanostructures at atomistic scales, it is limited by the computational overhead resulting from the elaborate relaxation process. Our simulation studies indicate that CNT growth dynamics over atomistic scales exhibits a nonlinear and piecewise near-stationary behavior. Nonparametric local Gaussian process (LGP) models can be used to predict these increments. Using the LGP model predictions, the computational overhead can be reduced by 70%, thereby improving the scalability of MC simulations to capture the real-scale CNT growth process. Thus far, we have simulated isolated CNTs of 194 nm in length, having about 12000 carbon atoms, which is one of the longest CNTs reported from atomistic/meso-scale simulations. This approach can also improve the scalability of MC simulations to capture the synthesis of a variety of nanostructure elements (e.g., films, wires, tubes, honeycombs, and composites) from processes, such as atomic layer deposition (ALD), chemical/physical vapor deposition (CVD/PVD), self organization and assembly, mainly because nucleation and growth of these nanostructures are noted to exhibit recurring oscillatory patterns over certain time scales. We anticipate that these findings would spur further modeling and experimental studies on the complex growth dynamics of nanostructures, and scale-up atomistic and meso-scale simulations to capture the real-world nanostructure synthesis processes. Our ongoing investigations are aimed at using more accurate potential energy surfaces together with high performance computing facilities to capture the carbon deposition and the resulting CNT growth about a cluster of catalyst particles at multiple nodes of the lattice.

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Appendix A

We adapted Elliott et al.’s [6] coarse-grained potential function, which consists of the following four components defined over the nodes of the lattice:

A.1. Bond stretching energy

The interaction between bonded nearest neighbor nodes is expressed as

$$E_b = \frac{1}{2} K_b (l - l_0)^2$$

Here, $K_b$ is the internode Hookean bond stretching constant, $l$ and $l_0$ are the actual and reference bond length, respectively, with $l_0$ set to 0.49 nm, $K_b$ for the node representation system was estimated to be $\sim$27 eV Å$^{-2}$ node$^{-1}$. It may be noted that a node represents an elemental surface composed of multiple carbon atoms as shown in Figure 1.

A.2. Surface curvature energy

$$E_c = \frac{1}{2} K_s J^2 + \sum_{j=1}^{6} \frac{1}{2} K_j J_j^2$$

Here, $K_s$ is the surface bending stiffness parameter for a single node, $A$ is the triangle area associated with each node, and $l$ is the curvature at each node. The subscripted quantities, $A_j$ and $J_j$, refer to the same properties for each of the neighboring nodes, and $K_s$ for the node representation system was estimated from the graphene sheet bending stiffness to be $\sim$0.23 eV node$^{-1}$.

A.3. Carbon–carbon interaction energy

This component considers the interaction between non-bonded nodes as

$$E_{cc} = \sum_j E_{cc,j}$$

where

$$E_{cc,j} = \begin{cases} \infty & d < d_1 \\ \frac{A_j A_l E_{cc,1}}{d_1 < d < d_2} & d_1 < d < d_2 \\ \frac{A_j A_l E_{cc,2}}{d_2 < d < d_3} & d_2 < d < d_3 \\ 0 & d \geq d_3 \end{cases}$$

Here, the cutoff distances $d_1$ ($=0.16$ nm), $d_2$ ($=0.28$ nm), and $d_3$ ($=0.8$ nm) define the range for hard repulsive, soft repulsive, and soft attractive and zero interactions, respectively. $E_{cc,1}$ (24 eV Å$^{-4}$) is obtained as the average value of the energy between $d_1$ and $d_2$, and $E_{cc,2}$ ($-1.5$ eV Å$^{-4}$) is the average between $d_2$ and $d_3$.

A.4. Carbon–catalyst interaction energy

The interaction between a node of the nanostructure, and the metal atom cluster. It is negative valued, corresponding to the favorability of the carbon–catalyst particle interaction. Also, $d_0$ ($=7$ nm) is the cutoff distance for carbon–catalyst interactions, and $E_{ct,1}$ is determined from the energy of adsorption of a graphene sheet on the catalyst nanocluster, which is estimated from MD simulations as $\sim$21.4 eV Å$^{-4}$ node$^{-1}$.

References