

Modeling of multi-scale processes during plasma-assisted growth of carbon nanotubes

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ABSTRACT

Multi-Scale Computational Framework (MSCF) has been developed for modeling nanostructured materials fabrication. This framework integrates Computational Fluid Dynamic software for reactor-scale simulations, a Kinetic Monte Carlo simulator for atomic-scale surface modeling, and a Molecular Dynamic solver for computing rates of surface reactions, and other elementary processes. In this paper, the MSCF was used to investigate the catalytic growth of carbon nanotubes (CNT) in a C_2H_2/H_2 inductively coupled plasma reactor. It was shown that MSCF is capable of predicting paths for delivering carbon onto catalyst/CNT interface, formation of single wall or multi-wall CNTs depending on the shape of catalyst, and transition from nucleation to the steady growth of CNTs.

Keywords: multi-scale modeling, Computational Fluid Dynamics, Kinetic Monte Carlo, Molecular Dynamics, carbon nanotubes

1 INTRODUCTION

The rapid development of combinatorial techniques involving self-assembly of atoms into molecular structures has led to the discovery of a number of novel materials in technologically important fields [1]. The combinatorial techniques typically use multi-scale, highly coupled processes. Modeling of these processes complements experimental efforts by decreasing the number of trial-and-error experiments and offering better understanding of interactions between processes occurring on disparate spatial and temporal scales. Unfortunately, modeling of multi-scale processes is a challenging task [2, 3]. Purely atomistic models are clearly computationally intractable because of a huge gap between the length and time scales that can be studied in atomic simulations and those that are relevant for most industrial and biological processes. This gap will not disappear even when another thousand-fold increase in computing power will occur. Purely continuum models are also inappropriate as they neglect critical nanoscale phenomena. This issue has been recently addressed by developing a Multi-Scale Computational Framework (MSCF) that enables self-consistent modeling of processes occurring over the length and time scales that are a million times disparate [4, 5].

2 MSCF

Only a brief overview of MSCF is given here as the detailed description can be found in [4, 5]. Integration of computational solvers ranging from atomistic to continuum was achieved in MSCF by using Gap-tooth and Coarse Timestepper modules as shown in Fig. 1. The reactor-scale Computational Fluid Dynamics (CFD) simulator was used in large gaps where details of atomic motion are not important, while atomistic Kinetic Monte Carlo (KMC) and Molecular Dynamic (MD) solvers were applied to tiny regions, teeth, defined as areas where atoms self-assemble into molecular structures. Macroscopic fluxes from CFD solver were transferred to the Gap-tooth module for estimating microscopic fluxes towards the surface. These microscopic fluxes were used in KMC solver for prescribing velocity distributions of ions and neutrals at the source plane. The Gap-tooth module also accounted for the influence of KMC modeling in one tooth on those in the neighboring teeth by establishing relationship between incoming microscopic fluxes to each tooth and outgoing fluxes from the neighboring teeth. The Coarse Timestepper module projected in time the rates and probabilities of chemical reactions computed by MD solver. The implementation of the developed algorithms was performed for the reactor-scale CFD-ACE software with plasma simulation capabilities, NAMD simulator, and KMC-FILM solver.

3 PLASMA-ASSISTED GROWTH OF CNT

MSCF has been demonstrated for a plasma-assisted growth of vertically-aligned CNTs in a C_2H_2/H_2 inductively coupled plasma discharge operating at a gas pressure of 1 Torr and 200 W power [6, 7]. The substrate was patterned with Ni catalyst particles of 8 nm diameter and its temperature was kept at 700 C. The macroscopic fluxes of different radicals computed by CFD-ACE continuum solver were used to update on-the-fly KMC-FILM microscopic fluxes. Catalysts of two different shapes were used to investigate the growth of single-wall CNTs (SWCNTs) and multi-wall CNTs (MWCNTs).

Typical 2-d spatial profiles of electron temperature, T_e , gas temperature, T_g , electron density, $[e]$, and neutral concentrations $[C_2H_2]$, $[H_2]$ and $[H]$ are shown in Fig. 2. It

was observed that electron temperature peaks just below the dielectric window and maximum electron density is shifted from the center of the reactor. Gas temperature has a maximum of 700 C near the substrate, where gas densities

have minimum. [H] has a maximum close to the peak of electron temperature where rates of electron impact processes are large.

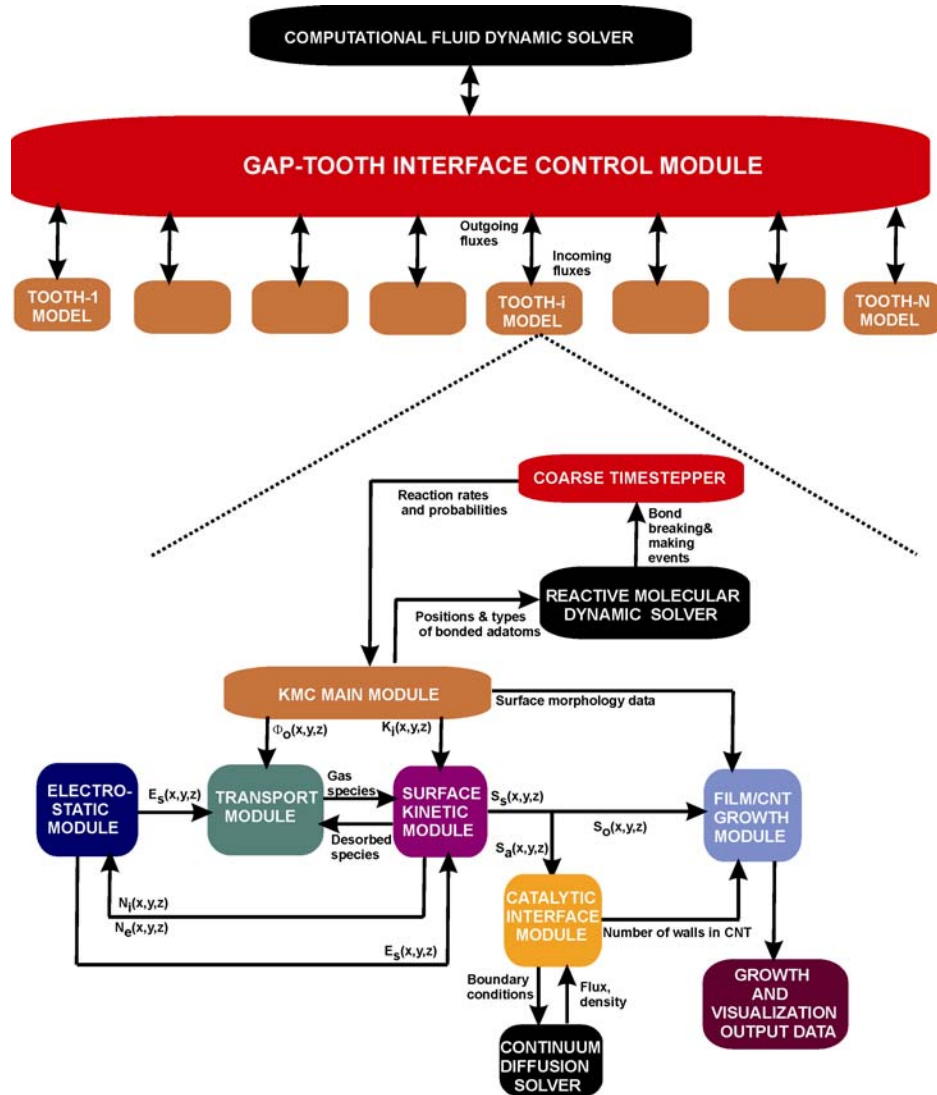


Figure 1: This diagram shows the interactions of three major solvers of MSCF: a CFD solver, a KMC software, and a MD solver. Gap-tooth interface control module calls CFD solver to get fluxes onto the surface, and KMC software to perform modeling in tiny teeth regions where atoms self-assemble in nanostructures. The Coarse timestepper module calls MD solver to get reaction rates and probabilities. These data are used by KMC software in modeling of CNT growth.

The computed distribution of [C]/[Ni] ratio for the “tall” and “short” catalysts are shown in Fig. 3. This figure also gives the spatial profile of carbon diffusion coefficients through the bulk of catalysts. The dependence of diffusion coefficients on carbon concentration was estimated by conducting an MD modeling using C-C and C-Ni linear bond potentials [8]. It was found that the diffusion coefficients peak at the minimum [C]/[Ni] ratio, where diffusion is mostly due to C-Ni interactions. Correspondingly, at the maximum [C]/[Ni] ratio, diffusion

coefficients were smaller because of the increased carbon concentration. It was determined that the flux outgoing from the tall catalyst peaked at catalyst/CNT interface and rapidly decreased with decreasing distance to the center of catalyst. In contrast, the flux outgoing from the short catalyst was relatively constant. Consequently, MSCF automatically determined that spatial profile of carbon fluxes from the tall catalyst promotes the growth of SWCNT, while the spatial profile of carbon fluxes from the short catalyst promotes the growth of MWCNT. The radius

of the outer wall of CNT was chosen equal to the radius of catalyst. The locations of inner walls of MWCNT were automatically selected during simulation assuming that the distance between walls was equal to the doubled carbon bond.

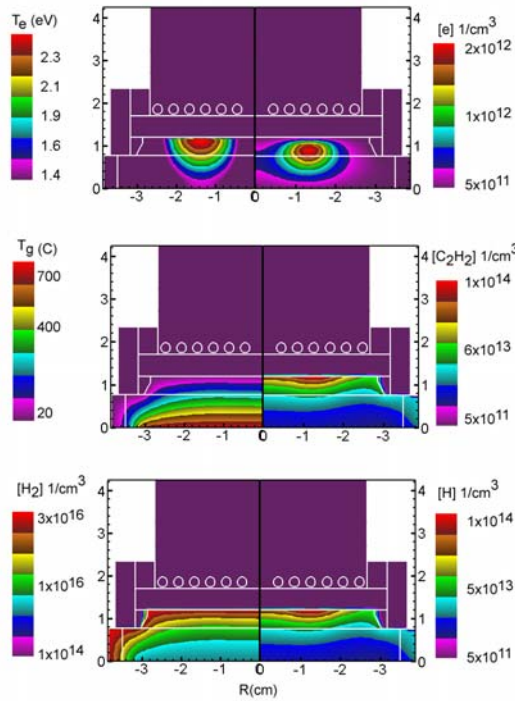


Figure 2: 2-D spatial profiles of plasma and gas properties in the inductively coupled plasma reactor used in the Center for Nanotechnology at NASA Ames Research Center.

The growth of CNT typically includes the nucleation and steady growth stages. During the nucleation, neighboring loose carbon atoms brake bonds with the atoms of catalyst and make bonds with each other in such fashion that the first structural units of CNT being formed. The probability of nucleation has to vary with time because the number of the loose carbon atoms changes with time. During the steady growth stage, CNT grows mostly when loose carbon atoms brake bonds with the catalyst atoms and make bonds with CNT atoms. One should expect that the probability of this process is fairly constant. The transition from the nucleation to the steady growth can be illustrated by analyzing time-dependent incorporation probabilities for the tall and short catalyst that are given in Fig. 4. In the case of the short catalyst, the probabilities are given for the formation of inner wall of MWCNT. It was observed that nucleation time interval for the tall catalyst is shorter than that for the short catalyst and incorporation probabilities increase with time for the tall catalyst considerably faster than those for the short catalyst. This is because the sides of the tall catalyst are almost flat at the catalyst/CNT interface and loose carbon atoms can easily nucleate the

structure of CNT. In contrast, the sides of short catalyst have curvature, which makes its difficult for loose carbon atoms to nucleate the structure of CNT. However, once a few first monolayers of CNT are formed and nucleation is replaced by the steady growth, the incorporation probabilities for the tall and short catalysts are similar indicating that the shape of catalyst do not substantially affect incorporation probabilities during the steady growth stage.

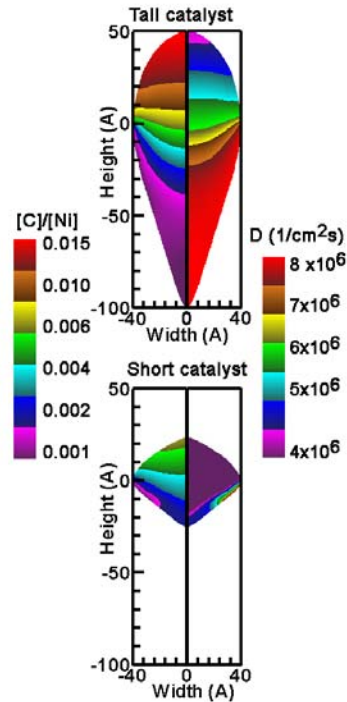


Figure 3: 2-D profiles of concentrations and diffusion coefficients of carbon for the catalysts of different shape.

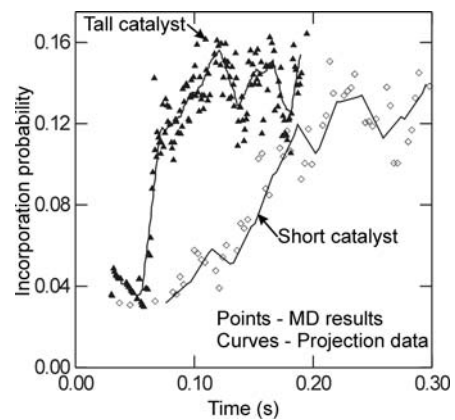


Figure 4: Transition from nucleation to steady growth of CNTs is illustrated by time-dependent incorporation probabilities for the tall and short catalyst.

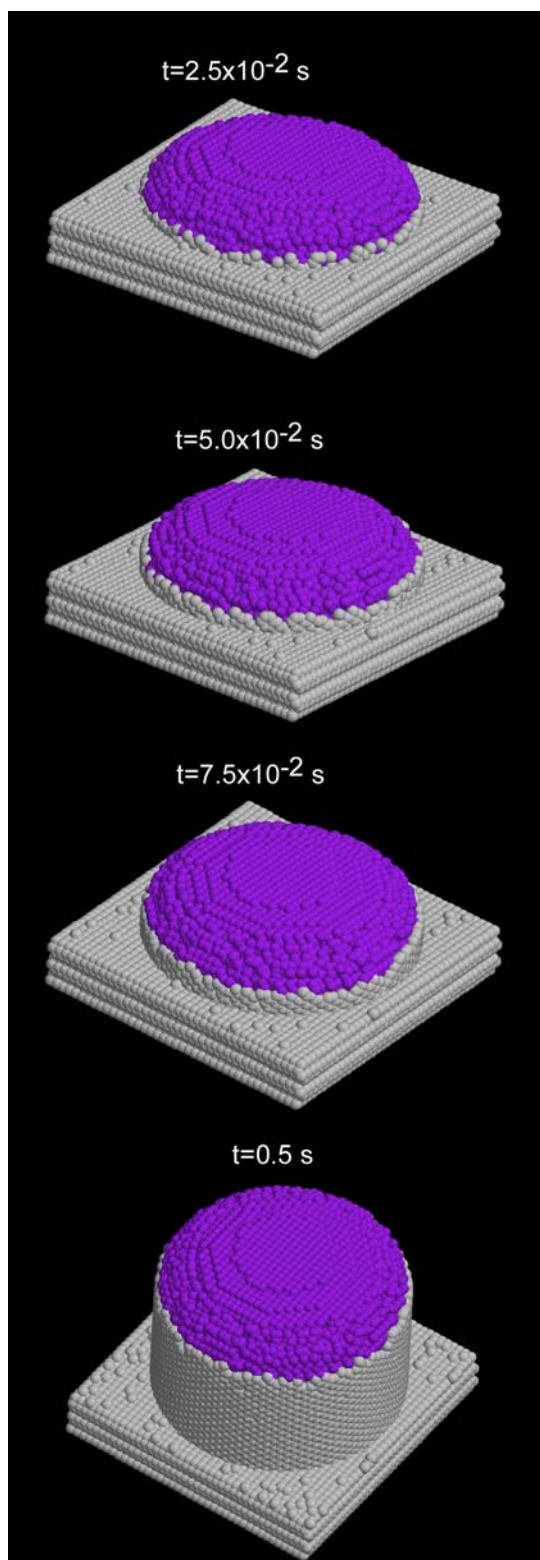


Figure 5: Visualization of KMC results for the CNT growth. Atoms of catalytic particle are shown in blue, and carbon atoms are grey.

Three snapshots of CNT growth during the nucleation at 2.5×10^{-2} s, 5.0×10^{-2} s, and 7.5×10^{-2} s, and one snapshot during the steady-growth stage at 0.5 s are given in Fig. 5. The catalytic particle is lifted during the growth according to, so-called, tip-type growth mode experimentally observed during plasma-assisted growth of CNTs [9].

4 SUMMARY

The Multi-Scale Computational Framework has been demonstrated for the catalytic growth of CNTs in the inductively coupled plasma reactor. It was shown that MSCF is capable of predicting paths for delivering carbon onto catalyst/CNT interface, formation of single wall or multi-wall CNTs depending on the shape of catalyst, and transition from nucleation to the steady growth of CNTs.

With further development, MSCF can be used to predict the growth of single-wall CNTs, multi-wall CNTs, or nanofibers for various gas mixtures and types of catalysts. Potentially, this framework could help in investigation of CNT alignment, tip-type and bottom-types modes of CNT growth, and chirality of CNTs.

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