Multi-Scale Computational Framework: Theoretical approach and application for the growth of carbon nanotubes[1]

A. V. Vasenkov, A. I. Fedoseyev, and V. I. Kolobov
CFD Research Corporation, 215 Wynn Drive, Huntsville, AL 35805

Ki-Ha Hong, H. S. Choi, K. H. Kim, J. Kim, H. S. Lee and J. K. Shin
Samsung Advanced Institute of Technology, San 14-1 Nongseo-Ri, Kiheung, Yongin, Kyungki-Do 440-900, Republic of Korea

ABSTRACT

The rapid development of nanotechnology has created significant interest to predicting the behavior of materials from the atomic to the engineering scales. However, it was found that such a prediction is a very challenging problem because existing atomistic models are rather slow, while reactor-scale codes are not capable of capturing nanoscale effects. This paper addresses this problem by introducing a Multi Scale Computational Framework which couples a continuum model of reactor-scale processes, a Kinetic Monte Carlo (KMC) solver for the growth of molecular structures, and a Molecular Dynamics (MD) software for the self-assembly of atoms into molecular structures. Reactor-scale and atomistic KMC simulations were linked using a "Gap-tooth" algorithm, and KMC and MD were coupled by a "Coarse time-stepper" method.

Keywords: Atomistic to reactor scale modeling, stochastic time-steppers, gap-tooth, plasma-assisted growth, carbon nanotubes.

1 DESCRIPTION OF THE FRAMEWORK

The Multi Scale Computational Framework (MSCF) has been developed at CFDRC to enable self-consistent simulation of processes over the length and time scales that are a million times disparate (see Fig. 1). This was achieved by coupling computational tools of different types ranging from atomistic to reactor scale. The reactor-scale Computational Fluid Dynamics (CFD) simulation was used in large gaps where details of atomic motion are not important, while atomistic Kinetic Monte Carlo (KMC) and Molecular Dynamic (MD) simulations were performed in tiny teeth defined as areas where atoms self-assemble into molecular structures. The feasibility of the developed framework was shown using reactor-scale CFD-ACE software with plasma simulation capabilities [1], NAMD code designed for large molecular systems [2], and KMC-FILM software developed at CFDRC for the deposition of nanostructured films and growth of carbon nanotubes (CNTs).

The schematic of KMC-FILM software is shown in Fig. 2. The interactions between different KMC modules can be outlined as follows. The Interface control module receives initial data and transfers these data to other modules. For example, fluxes of different species are sent to the Transport module, reaction rates to the Surface module, and the surface morphology data to the FILM/CNT module. The Interface control module also calls other modules to perform simulations of different processes. The Transport module calculates the transport of gas species from the source plane to the surface. The surface kinetic module calculates surface reactions between gas and surface species. It also computes surface fluxes and fluxes of carbon absorbed on the surface of catalyst. The surface fluxes are used by the FILM/CNT growth module and the carbon fluxes are sent to the Catalytic Interface module. The Catalytic Interface module calls continuum solver to simulate the diffusion of absorbed carbon through the catalyst and compute fluxes of carbon atoms to be incorporated into CNTs. The CNT/FILM module simulates the growth of CNT on the surface of catalyst and the formation of crystal film on other surfaces. The Output module writes the growth and visualization data to output files.

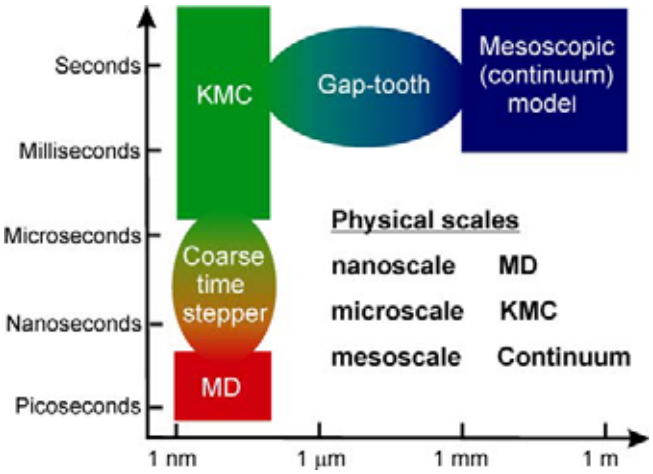

Figure 1: MSCF integrates reactor-scale model, atomistic KMC and MD using the Gap-tooth and the Coarse timestepper modules.

The Gap-tooth module was used to couple KMC simulations in teeth with CFD simulations in large gaps Particularly, incoming microscopic surface fluxes (f) and number of particles to a tooth (N) at each tooth boundary were updated using the microscopic surface fluxes (q) and number of particles (M) outgoing from the nearest teeth as shown in Fig. 3. Two choices of flux interpolation were implemented in the Gap-tooth module: linear flux interpolation and quadratic flux interpolation. In both cases, incoming microscopic surface fluxes (f) and number of particles to a tooth (N) were computed using the microscopic surface fluxes (q) and number of particles (M) outgoing from the nearest teeth as described in [3]. For example, in the case of quadratic interpolation a left (L) incoming fluxes of rth species in the *i+1* tooth were given by

$$N^L_{r,i+1} = \frac{\alpha(1+\alpha)}{2} M^R_{r,i} + (1-\alpha^2) M^R_{r,i+1} - \frac{\alpha(1-\alpha)}{2} M^R_{r,i+2} \quad (1)$$

$$f^L_{r,i+1} = \frac{\alpha(1+\alpha)}{2} q^R_{r,i} + (1-\alpha^2) q^R_{r,i+1} - \frac{\alpha(1-\alpha)}{2} q^R_{r,i+2} \quad (2)$$

where *a* is a parameter that determines the distance between two nearest teeth. The right incoming fluxes were computed similarly, by using fluxes outgoing from the left boundaries of nearest teeth. It is important to notice that Eq. (1-2) contains both positive and negative coefficients. The negative coefficients mean that "anti-particles" capable of annihilating with regular particles must be sent to appropriate teeth. Consequently $q_{r,i}$ was redistributed so that $1-\alpha(1+\alpha)/2$ fraction was sent to $f_{r,i}$, α^2 to $f_{r,i+1}$, and $\alpha(1-\alpha)/2$ were cloned to be sent to $f_{r,i}$ and $f_{r,i+1}$, and one anti-particle to $f_{r,i-1}$.

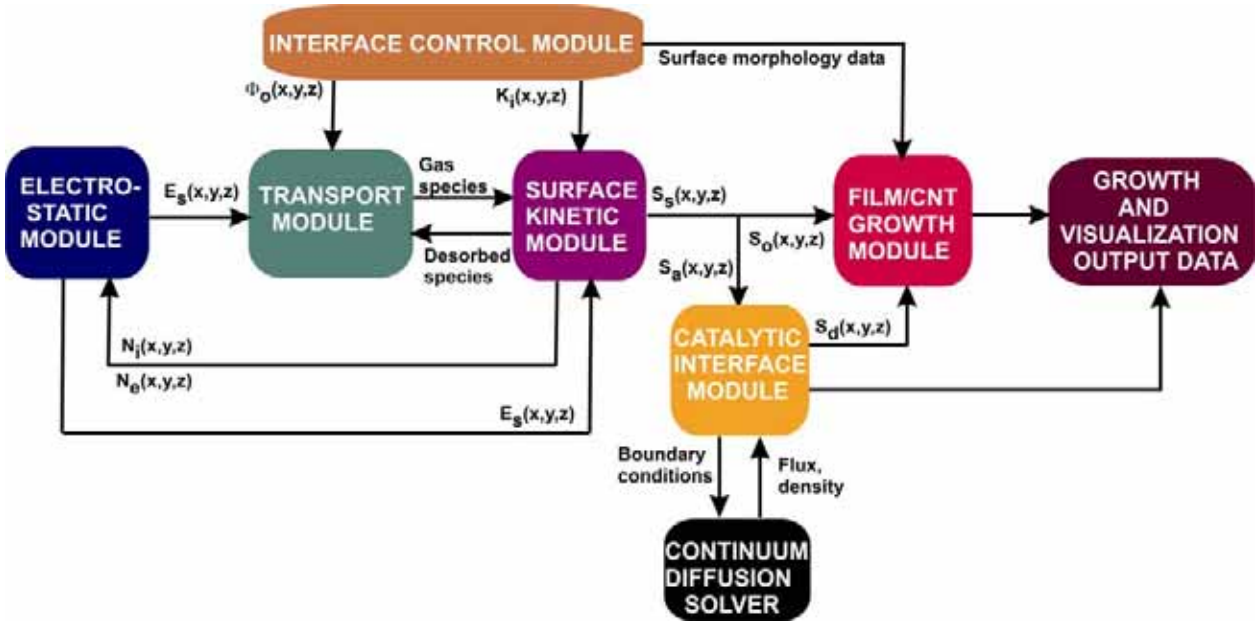

Figure 2: The schematic interaction between different modules of KMC-FILM software.

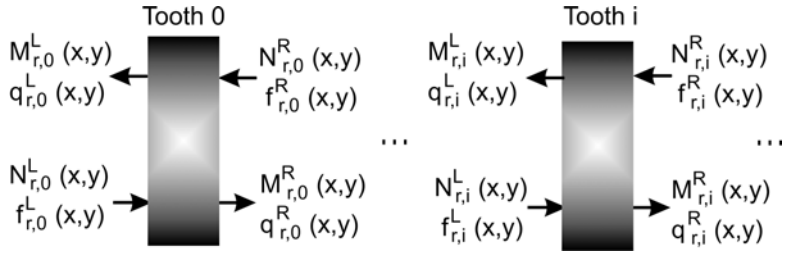

Figure 3: Incoming fluxes for each tooth estimated using outgoing fluxes from the nearest teeth.

The Coarse timestepper module was developed to bridge the differences in the time scales between KMC and MD. The major steps of the Coarse timestepper module are:

- Set initial configurations for NAMD simulations. Spatial coordinates of MD particles were cloned from those used in the corresponding KMC simulations so that initial ensemble in MD simulations is identical to that of KMC.
- Perform the evolutions of molecular systems. The evolutions were performed for the time T_{MD} long enough compared to MD time step τ_{MD} of 10 femtoseconds and short enough compared to KMC time step τ_{KMC} of a few microseconds. Each NAMD ensemble was at fixed volume, temperature, and the number of particles.
- Calculate rates, and their derivatives in respect to time. Accuracy required for the prediction of reaction rates was achieved due to the use of reactive MD approach. This approach employs pre-defined criteria in bond-breaking/bond-making routine and it has been successfully used for computing rates of thermal decomposition reactions in polymers [4].
- Project reaction rates to the time $t+\tau_p$ such that $T_{MD} \le \tau_p \le \tau_{KMC}$. The projection is achieved using the Newton-Raphson method.

The interactions between different modules of MSCF over a mesoscopic time step τ was conducted as follows. MD was performed in each tiny tooth to compute the rates of surface processes and their derivatives in time for a nanoscopic time. The MD results were transferred to the Coarse timestepper module which calculated the time-dependent rates using the Newton-Raphson method. The rates were used by KMC to model system evolution during a microscopic time step. Subsequent to each KMC iteration, the incoming fluxes for each tooth were updated by the Gap-tooth module from the fractions of outgoing KMC fluxes obtained in the nearest teeth and MD was called by the Coarse timestepper module for updating time-dependent rates. Once the simulation time in KMC reaches $t+\tau$, the CFD solver was called by the Gap-tooth module to simulate reactor-scale processes and compute the fluxes of absorbed species for KMC.

2 PLASMA-ASSISTED GROWTH OF CNT

MSCF was applied for the plasma assisted growth of aligned CNTs in an inductively coupled plasma reactor in a CH_4/H_2 gas mixture. In this reactors, plasma is sustained by radio frequency (RF) electro-magnetic fields created by an RF current in a coil [1]. The gas and plasma properties were obtained using CFD-ACE for a gas pressure of 100 mTorr, 100 W power adsorbed in plasma, and a driving frequency of 6 MHz. The substrate temperature was kept at 1000 K.

The fluxes of different radicals computed by CFD-ACE at selected monitor points were used to update on-the-fly KMC-FILM fluxes. The growths of CNTs of different diameters were calculated using these fluxes as shown in Fig. 4. For example, CFD-ACE fluxes at the 1st monitor point were used for the growth of two CNT of small diameter (35 A). At the same time, CFD-ACE fluxes at the 2nd monitor point were used for the growth of two CNT of small diameter (35 A) and one CNT of large diameter (58 A). Finally, CFD-ACE fluxes at the 3d monitor point were used for the growth of two CNT of large diameter (58 A).

The growth rates of CNTs in seven teeth are shown in Fig. 5. It was observed that the growth rates of CNTs in the 1st and 2nd teeth with small catalyst are larger than those in the 6th and 7th teeth with large catalyst. In contrast, the growth rate in the 4th tooth with large catalyst is larger than that in the 3d and 5th teeth with small catalyst. The reason for the described trends is as follows. The light hydrocarbon specie can react on both catalyst surface and substrate surface, while heavy hydrocarbon radicals dominantly react on the surface of catalyst. Consequently, in the teeth with small catalyst, the ratio of heavy species to light species increases with time since heavy species react only on a portion of the tooth's surface. As the fraction of heavy species increases, the growth rates of CNT in 1st and 2nd teeth also increase compared to those in the 6th and 7th teeth. This is due to the thermal decomposition of heavy hydrocarbon radicals on the surface of catalyst. At the same time, data exchange between 3d, 4th, and 5th teeth increases the ratio of heavy species to light species in the central tooth and decreases this ratio in the side teeth.

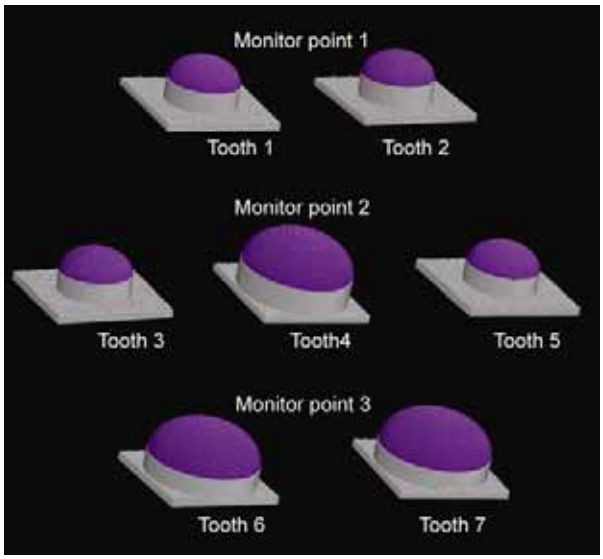

Figure 4: The growth of CNTs on the catalyst of different size at chosen monitor points.

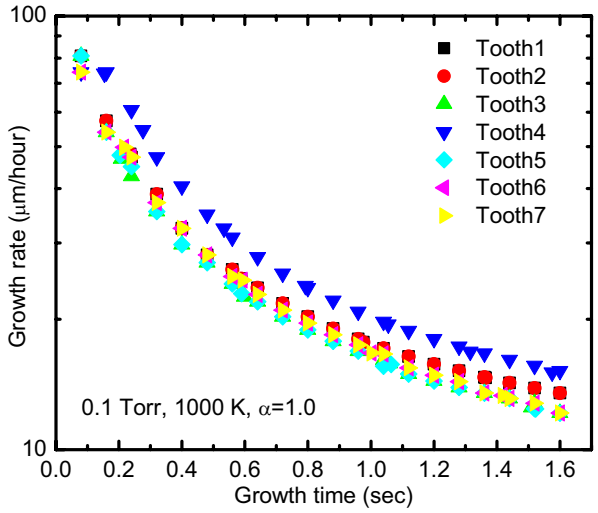

Figure 5: The growth rates. The largest growth rate is in the 4th tooth due to data exchange between 3d, 4th and 5th teeth. The growth rates in 1st and 2nd teeth are slightly higher than those in the 6th and 7th teeth.

3 CONCLUSIONS

The multi-scale computational framework has been developed for nanostructured materials' fabrication. The validation was performed for the plasma-assisted growth of vertically aligned CNTs in a realistic CH_4/H_2 ICP system. It was found that boundary data exchange between regions where atoms self-assemble into CNTs of different size substantially affected the simulation results.

REFERENCES

[1] V. I. Kolobov, Comput. Materials Sci. **28,** 302, 2003.
[2] L. Kale, R. Skeel, N. Bhandarkar, R. Brunner, A. Gursoy, N. Krawetz, J. Phillips, J. Shinozaki, K. Varadarajan, and K. Schulten, J. Comput. Physics **151,** 283, 1999.
[3] C. W. Gear, J. Li, and I. G. Kevrekidis, Phys. Lett. A **316,** 190, 2003.
[4] S. I. Stoliarov, P. R. Westmoreland, M. R. Nyden, and G. P. Forneyb, Polymer **44,** 883, 2003.

[1] This work was supported by the Samsung Advanced Institute of Technology and by the National Science Foundation (DMI-0441412).