

# MOLECULAR DYNAMICS MODELING OF TEMPERATURE, POROSITY AND TORTUOSITY INFLUENCES ON DIFFUSION INSIDE CNT FORESTS

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## Introduction

Research and spread of CNT has gone a remarkable way, while CNT composite materials seem to reach market capability at first, where the addition of CNT can have high impact on material properties [1]. Carbon/carbon composites are used in such fields, where high mechanical stability and thermal conductivity even at higher temperatures are needed, e.g. in aircraft braking systems. To fulfill these criteria, the composite must consist of only high textured carbon morphology and minimal porosity [2]. Recently it has been shown that high textured carbon can be deposited around CNT inside vertically aligned CNT (VANTA) [3]. Modeling of the infiltration process can help to understand transport, gas phase and surface reactions of synthesizing carbon composites [4], with the current effort consisting of modeling the deposited texture based on phase field approaches.

The micro porous VANTA network is inaccessible for common fluid dynamics and macro scale modeling, where molecular diffusion is the only mechanism for transport in the gas phase. Theoretical relations for diffusion in confined space, like Knudsen [5] or extended models could be used to estimate diffusivities. For CNT however, these models either strongly underestimate diffusion or are insufficient [6,7].

In this work we present a broad study of geometric and process parameters on the gas transport, exemplarily for a simple case of CNT infiltration. We consider not only temperature and pressure influences, but more importantly CNT tortuosity and VANTA porosity.

## Experimental

Classical equilibrium and non-equilibrium molecular dynamics are performed with the LAMMPS package (7 July 2009) [8]. All simulations are performed with a time step of 0.5 fs and are thermostated under the canonical ensemble (NVT) using Nosé-Hoover method. Initial atom velocities are given using a Maxwell distribution according to the chosen temperature. Intermolecular interactions between the fluid-fluid particles and fluid-carbon atoms are modeled with the united atom approach and the truncated Lennard-Jones (LJ) 12-6 potential, with a cutoff radius of 15 Å with common parameters from. Self-diffusion coefficients are calculated with the mean square displacement (msd) using Einstein's relation, where msd are recorded for at least 12mio time steps (corresponding to >600 ps) and values are only considered above 50 ps. CNT are simulated with flexible carbon atoms

using the second-generation reactive empirical bond order potential (REBO) [9], although these are by far more computationally demanding than rigid carbon atoms. The periodic cell contains two 5 nm long CNT with diameters between 7 – 18 Å, which is shown in figure 1. The EMD simulations are performed at the zero loading limit [7], with the advantage of much less CPU expenses and better statistics, where the simulations are performed with 140 fluid atoms simultaneously.

## Results and Discussion

Molecular diffusion inside the VANTA is of great importance for an understanding of the molecule distribution along and across the CNT. The temperature dependency of our simulations show that the diffusion coefficient of hydrogen compared to methane is about 50 % higher for axial diffusion and 300 % higher for radial diffusion. This means that diffusion perpendicular to the CNT is much more sensitive to the molecule mass and size due to its undirected pore geometry. The directed geometry of the axial pores is also the reason for the, with about 2 orders of magnitude, enhanced diffusion coefficients compared to radial (perpendicular) diffusion coefficients. An Arrhenius fit is consistent for temperatures up to roughly 900 °C, while the correlation with a power fit (close to the Chapman-Enskog relation) is further consistent for temperatures above round about 800 °C.

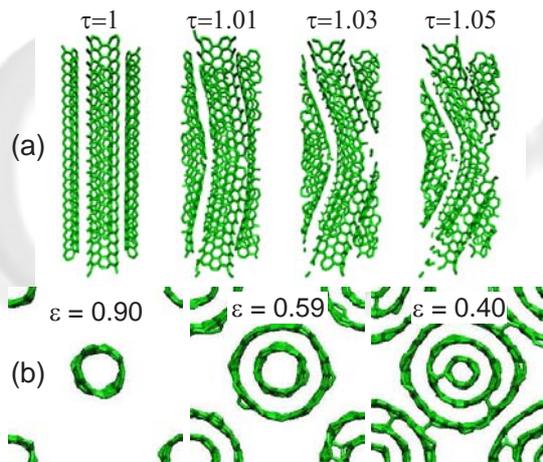
During the transient CVI process, the change of VANTA porosity has the strongest influence on the gas phase transport, which is shown in figure 2. Here, the diffusion coefficient is reduced at a factor of about 10 between the initial porosity (0.9) and the final porosity (0.4) at which the gas phase transport breaks down. The break down of the transport is indicated by a sharp decrease of the diffusion coefficient. The simulation results also reveal that gas phase transport of hydrogen and methane is possible until porosities as low as 0.4. Within these porosities, the decrease of the diffusivities can be correlated with a power fit. Elevated exponents for the porosity dependency of roughly 2.5 for axial diffusion and 5 for radial diffusion are determined, showing that the radial transport is more sensitive towards changes in the pore geometry. For hydrogen, the exponent of the porosity influence is about 0.6 smaller than the exponent of methane, due to its reduced mass and size.

Finally, the tortuosity influence of transport through VANTA is reported. For a better understanding, the tortuosity dependency is analyzed for different porosities. A strong sensitivity of the CNT tortuosity on the self diffusion is found for both axial and radial diffusion. For methane, the axial diffusion coefficient between a tortuosity of 1.00 and 1.03 is reduced at a factor of about 5, while the radial diffusion coefficient is reduced at a factor of around 1.5. In contrast to the porosity influence, with the radial transport showing higher sensitivity, the axial transport is found to have a higher sensitivity on the tortuosity influence. Our simulations reveal that VANTA have a strongly enhanced tortuosity influence with exponents up to 63. The reason of this strong increase is

on one hand, the small tortuosity values corresponding to changes on the micro scale. On the other hand, the pore geometry of straight and unidirectional pores in VANTA is already changed at small CNT tortuosity values to curved pores with edges and knees (figure 1). Differences between hydrogen and methane exist, showing slightly higher sensitivity of the tortuosity influence for the heavier and larger molecule. A comparison of the tortuosity influence at different VANTA porosities reveals similar exponent values with a variance of roughly 10 around the median value. Therefore, it can be assumed that the tortuosity influence does not change significantly throughout the CVI process with its decreasing porosity.

With knowledge of the self diffusion coefficient  $D_{s,0}$  at an initial temperature  $T_0$  (1100 °C), an initial porosity  $\varepsilon_0$  (0.9) and an initial tortuosity  $\tau_0$  (1.0), the effective diffusion coefficient  $D_{s,eff}$  can be estimated according to any changes of the main process and geometry parameters. This correlation is given in equation 1.

$$D_{s,eff} = D_{s,0} * \frac{T^a}{T_0^a} * \frac{\varepsilon^b}{\varepsilon_0^b} * \frac{\tau_0^c}{\tau^c} \quad (1)$$



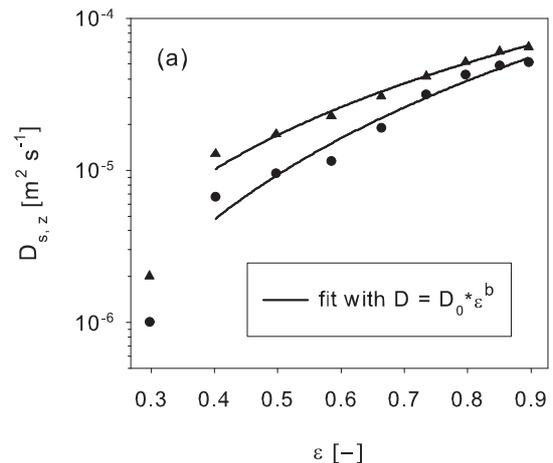
**Fig. 1** Snapshot indicating the increase of CNT tortuosity (a) and the decrease of porosity (b) due to growing of additional layers of MWNT during CVI of CNT forests.

## Conclusions

Molecular dynamics simulations have been performed to resolve the influence of key process parameters for the gas phase transport during CVI of VANTA for hydrogen and methane. The results were correlated for an estimation of the effective flux and effective diffusion coefficient.

For the self diffusion coefficient, the temperature dependency could be correlated with the Arrhenius method and with a power fit, which is close to the Chapman-Enskog relation, for temperatures above 800 °C. The porosity influence on diffusion inside VANTA is enhanced with an

exponent of 2.5 for axial and 5 for radial transport. The results indicate that radial transport of hydrogen and methane in VANTA is possible for porosities as small as 0.65, while axial transport is possible for porosities as low as 0.4. An important parameter on transport is also CNT tortuosity, which is found to decrease the self diffusion with exponents up to 63. With the simulation results, both the self diffusion and the fluid flux can be estimated for changing key parameters, which can be used in the next step for modeling gas and surface reactions as well as deposition kinetics.



**Fig. 2** Axial self-diffusion coefficient of hydrogen (triangles) and methane (circles) versus the VANTA porosity at a temperature of 1100 °C.

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