

# **Clean, High Quality Low Emission Fuels with Fischer-Tropsch Synthesis: A Multiscale Study of Transport Properties in Confined Systems**

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## **Abstract**

The Fischer-Tropsch synthesis (FTS) is a polymerization reaction used extensively in the Gas-to-Liquids (GTL) process to transform synthesis gas into high quality low emission transportation fuels. The main FT reaction products, namely water, wax and small amounts of oxygenates (e.g. alcohols < 10 wt %), form a mixture through which the dissolved reactants diffuse, reach the catalytic nanoparticles and react. Key factors in ensuring FT reactor's activity and stability is the selection of the catalyst (e.g. Co) and the support material (e.g. TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, graphene). Unfortunately, FTS catalysts deactivate over time and the role of oxygenates and excess water in the loss of catalyst activity remain as open questions.

In order to gain a better understanding of the phase behavior of confined wax – water – alcohol mixtures in either hydrophilic or hydrophobic characteristics at reaction conditions, our efforts concentrated on the *n*-C<sub>28</sub> – H<sub>2</sub>O mixture at 473.15 K inside pristine graphene (G) and graphene oxide (GO) pores by means of Coarse Grained (CG) Molecular Dynamics (MD) simulations. Our simulations show that CG approaches capture the mixture's phase separation and component's diffusivity. The Co NP does not affect mixture phase separation but it is extensively covered by water. Our results showcase that CGMD can be employed to study FTS related processes at this scale and are expected to open new pathways in the investigation of

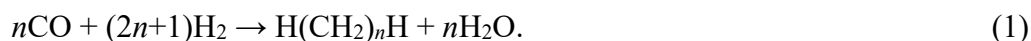
the effect of NPs on catalyst support interfaces in the presence of FTS relevant mixtures.

## Keywords

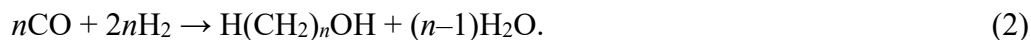
Molecular Dynamics Simulation, Coarse Graining, Fischer-Tropsch, Confined fluids

## 1. Introduction

The GTL process is an established, robust and economically viable technology in harnessing natural gas resources through the efficient conversion in the production of high quality and environmentally friendly transportation fuels. The initial stage of the GTL process involves manufacturing of syngas [1], which is converted into synthetic liquid hydrocarbons, primarily paraffins (from methane to waxes) and olefins using a catalyst via the FTS. The principal reaction describing the conversion to long-chain paraffins which are then converted into high-quality fuels such as diesel, kerosene, and lubricant oil products is [2]:



FTS products also include water and small amounts (< 10 wt%) of oxygenated compounds such as alcohols:



Commercially, FTS is catalyzed by a transition metal, with Co being established commercially as the best choice in terms of its performance in industrial low-temperature FTS applications, while materials often employed as catalyst carriers are SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> [1, 2]. Recently, graphene and its derivatives have been investigated as alternative supports due to their outstanding physical properties that allow for higher loadings of Co catalyst, with pristine G and GO most widely considered for FTS.

Ensuring the stable performance of the catalyst is vital to the GTL process, significant efforts on GTL research involve elucidation of catalyst deactivation. It is a fact that Co FTS catalysts deactivate over time. Among the numerous contributing factors reported in the literature, excess water reaction conditions are of special interest, since it is considered that when present they are responsible for sintering of catalytic NPs [3], leading to reduced lifetimes of the FT reactor and thus increasing operational costs. The degree of catalyst deactivation increases with increasing water partial pressure caused by high water loads [4]; however, the underlying mechanism remains largely unknown.

Molecular modeling techniques can be used to obtain the microscopic information that aids in understanding the fundamental mechanisms controlling individual steps of the FTS

process, which may otherwise be unattainable by current experimental methods. Ideally, all-atom (AA) MD simulations would be the tool of choice for the study of the Co NP inclusion as a surface phenomenon in the context of FTS. However, AA MD simulations still face inherent obstacles for studying complex mesoscale systems, particularly in the range of the aforementioned Co NP and pore sizes (pore sizes lie in the vicinity of 12 – 16 nm for the optimum Co crystallite size, just above 8 – 10 nm [2]), coupled with the unavailability of appropriate force field parameters. In the present work, we aimed at exploring by means of molecular modeling the phase behavior of the  $n$ -C<sub>28</sub> – H<sub>2</sub>O mixture at 473.15 K, inside G and GO catalyst support mesopores using the MARTINI [5] model. A thorough comparison to evaluate the performance of the MARTINI force field is made against AA simulations in both the bulk and confinement. Moreover, the effect of long chain alcohols on the phase behavior of wax – water mixture is also explored using dodecan-1-ol (C<sub>12</sub>H<sub>25</sub>OH, simply referred to as dodecanol) as a representative compound at 7% wt. composition, along with the transport properties of the individual components of the mixture. Our objective was to gain understanding of the phase behavior of wax – water – alcohol mixture at reaction conditions, by accounting for the effect of either hydrophilic or hydrophobic confinement and test the validity of using the MARTINI force field for studying systems of this class. Having validated the CG approach, we then proceed to investigate for the first time the behavior of our model wax – water mixture in the G and GO pores with the presence of a Co NP, for the purpose of which a new set of classical interaction potential parameters was developed. We anticipate that this study will pave the way for future simulation works regarding the FTS at a larger scale, combining hybrid-CG/AA modelling techniques for the examination of such complex processes.

## 2. Simulation Methods

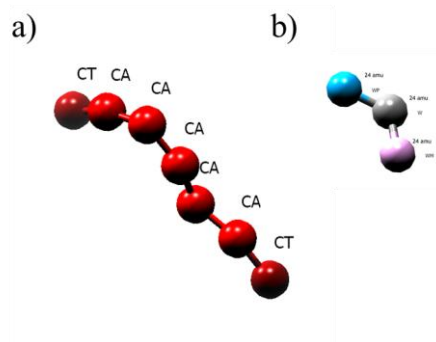
### 2.1. Force Fields

In line with our previous works and in order to model the wax – water mixture,  $n$ -C<sub>28</sub> was selected as a typical heavy  $n$ -alkane from the paraffin family [6, 7]. The composition of the  $n$ -C<sub>28</sub> – H<sub>2</sub>O mixture examined corresponds to the outlet of the FTS reactor and assumes a 1:1 H<sub>2</sub>O:CH<sub>x</sub> ( $x = 2$  or  $3$ ) ratio in the pore. Consequently, we set  $x_{H_2O} = 0.9655$  in all calculations presented. For the AA description of  $n$ -C<sub>28</sub> and dodecanol, the Transferable Potential for Phase Equilibria (TraPPE-UA) was employed, while water was represented by the TIP4P/2005. G and GO atoms were modelled as LJ spheres with  $\sigma$  and  $\varepsilon$  values taken from the OPLS-AA force field [8]. The MARTINI force field [5] was used for the CG description of all species involved.

### 2.2. Simulation Details

All simulations were set-up and executed by means of the Scienomics MAPS 4.2 software package [9]. The structure of our slit pore model consists of two blocks of five Bernal-stacked

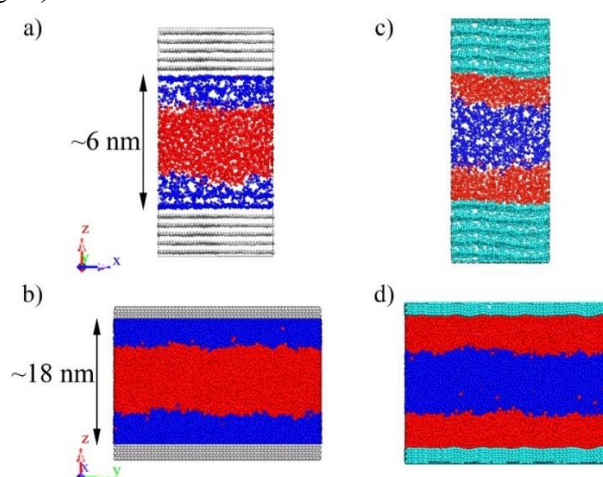
multilayer G (i.e. number of layers is equal to 10, with 5 G sheets in each block). Then, an extensive set of AA and CG MD simulations runs were performed in the canonical ( $NVT$ ) and isothermal-isobaric ( $NpT$ ) ensembles in GROMACS 2016.5. The integration time step used was 2 fs and 20 fs for the AA and CG simulations, respectively [8].



**Fig. 1.** Coarse-grained description of a)  $n$ -C<sub>28</sub> and b) water with the MARTINI force field. Different bead types are assigned to account for the different masses.

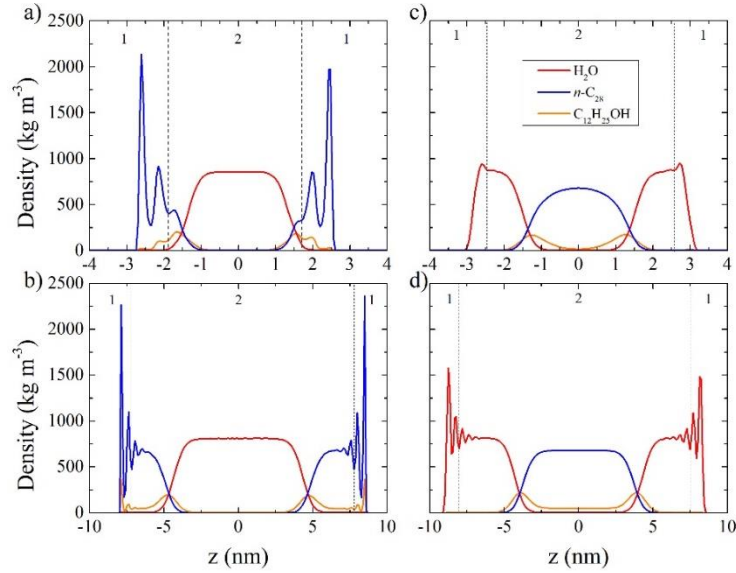
### 3. Results

Prior to studying these mixtures in confinement, the suitability of the MARTINI force field in the reproduction of several properties of  $n$ -alkanes ( $n$ -dodecane,  $n$ -octacosane) and complex wax mixtures ( $n$ -dodecane /  $n$ -octacosane binary mixture at a  $n$ -dodecane mole fraction of 0.3, and a model mixture of the commercially available hydrocarbon wax SX-70) was evaluated against several other well-established models [10]. Our results showed that using MARTINI for the description of such systems at elevated temperature and pressure conditions is a valid approach, which allowed for the investigation of these systems in graphene (G) / graphene oxide (GO) confinement (Fig. 2).



**Fig.2.** Equilibrated structures of the  $n$ -C<sub>28</sub>–H<sub>2</sub>O mixture in G (grey) and GO (cyan) pores, using AA (a and c) and CG (b and d) approaches, respectively.  $n$ -C<sub>28</sub> and H<sub>2</sub>O molecules are colored blue and red, respectively.

In both AA and CG simulations, phase separation of the mixture inside the G and GO pores was observed. Depending on the surface support chemical characteristics and developed interactions, different partitioning characteristics of either  $\text{H}_2\text{O}$  or  $n\text{-C}_{28}$  are observed. In the case of G, the oil-rich surface layer lies between the pore surface and a water-rich phase at the pore center, whereas in the case of GO confinement, this is completely reversed as now it is the water-rich surface layer that lies between the pore surface and an oil-rich phase occupies the center of the pore (Fig. 2). Then, dodecanol was introduced in order to explore the effects of long-chain alcohols on the phase behavior of wax – water inside mesopores and their impact on the two segregated phases. Partial density profiles are shown in Fig. 3. Addition of dodecanol brings no change in the positioning and the general characteristics of density profiles in either G or GO compared to the pure  $n\text{-C}_{28}$  –  $\text{H}_2\text{O}$  confined system. Inside the pores,  $n\text{-C}_{28}$  and water display a broad monolayer interfacing G and GO, respectively, with dodecanol being closer to the  $n\text{-C}_{28}$  –  $\text{H}_2\text{O}$  interface, acting as a surfactant. Dodecanol exhibits affinity only towards the G pore surface.

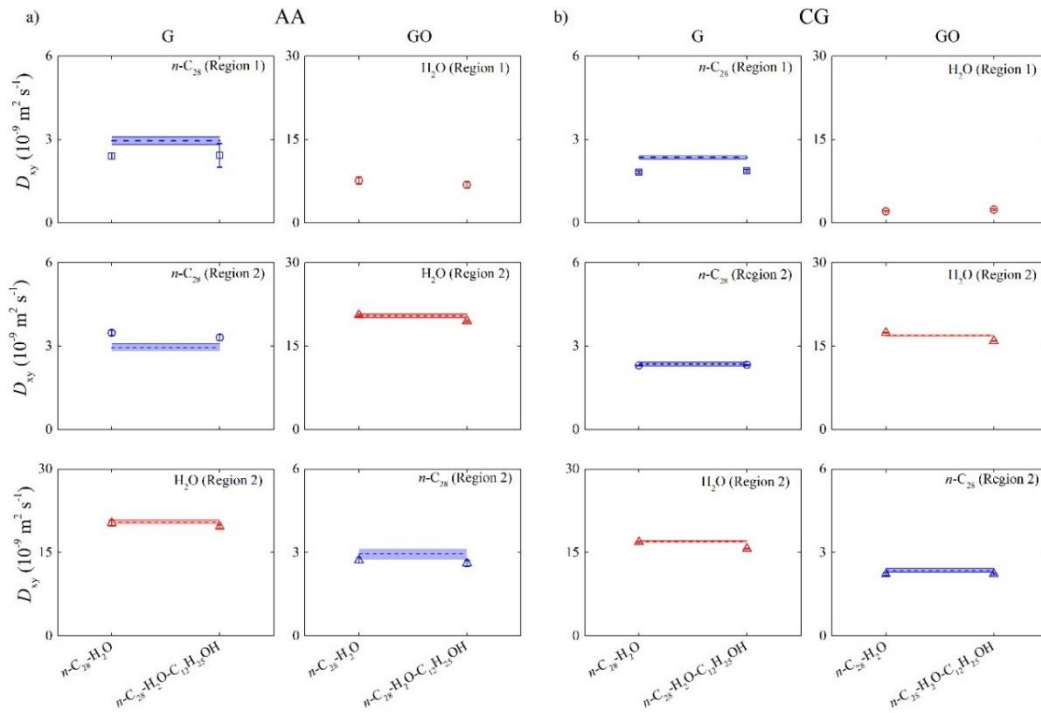


**Fig. 3.** Mass density profiles along the  $z$  direction of the  $n\text{-C}_{28}$  –  $\text{H}_2\text{O}$  –  $\text{C}_{12}\text{H}_{25}\text{OH}$  mixture in G and GO mesopore confinement at 473.15 K using AA (a and c) and CG (b and d) methods.

Subsequently, we performed an investigation on the  $n\text{-C}_{28}$  –  $\text{H}_2\text{O}$  mixture component dynamical properties, as the interactions arising with the surface affect the motion of each component as a function of the pore surface distance. The calculated lateral self-diffusion coefficients ( $D_{xy}$ ) for  $n\text{-C}_{28}$  and  $\text{H}_2\text{O}$  were obtained as a function of the pore surface distance, by calculating the 1/4 of the slope of the mean square displacement (MSD) of each component along the  $x$  and  $y$  directions at long simulation times according to the expression:

$$D_{xy} = \lim_{t \rightarrow \infty} \frac{1}{4} t \left\langle \left( x(t) - x(0) \right)^2 + \left( y(t) - y(0) \right)^2 \right\rangle \quad (3)$$

The diffusivity of  $n$ -C<sub>28</sub> and H<sub>2</sub>O in the G and GO pores is considered as the result of a two-dimensional move in the xy plane since the movement along the z direction is constrained by the confining pore surfaces; therefore, the z component of the diffusivity is ignored. As far as the AA systems are concerned, water's self-diffusion in the G pore is not influenced by confinement, while  $n$ -C<sub>28</sub> mobility is slightly below bulk-like levels at the graphene surface, displaying a minor increase closer to the pore center. It is evident that diffusivity bears a dependence on the distance from the nanopore center (Fig. 4).

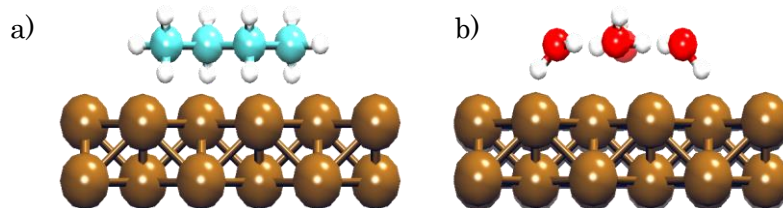


**Fig. 4.** Self-diffusion coefficients,  $D_{xy}$ , of H<sub>2</sub>O and  $n$ -C<sub>28</sub> in the wax – water and wax – water – alcohol mixtures confined in G and GO at 473.15 K using a) AA and b) CG descriptions. Bulk  $D_{xy}$  values are shown with dashed lines along with their block average uncertainties (shaded regions) for comparison.

In the GO pore, this situation is reversed with water's self-diffusion influenced by confinement and  $n$ -C<sub>28</sub> diffusivity being restored to bulk-like levels (Fig. 4). Dodecanol addition in the G confined  $n$ -C<sub>28</sub> – H<sub>2</sub>O mixture results to a slight water self-diffusion reduction in Region 2, while  $n$ -C<sub>28</sub> diffusivities do not change. As far as the CG systems are concerned, similar findings are observed.

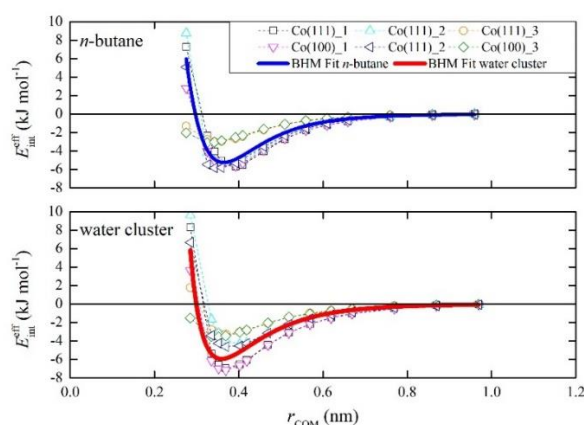
The examination of the confined  $n$ -C<sub>28</sub> – H<sub>2</sub>O mixtures with or without the presence of oxygenates inside G and GO pore, using both AA and CG approaches shows that the CG model

manages to capture the essential features of these systems in confinement in terms of the component distribution inside the pore and their mobility characteristics. This allowed for the introduction of Co nanoparticles inside the CG pores. Since there are no available classical parameters for Co, an interaction potential was developed [8], by employing density functional theory (DFT) methods at the PBE96/cc-pVTZ level of theory to determine the interactions between *n*-butane ( $C_4H_{10}$ ) and a four-water molecule cluster with a 24 atom cluster of Co (111) and (100) surfaces (Fig. 5).



**Fig. 5.** A cluster of 24 Co (100) atoms with a) *n*-butane ( $C_4H_{10}$ ) and b) a four-water molecule cluster.

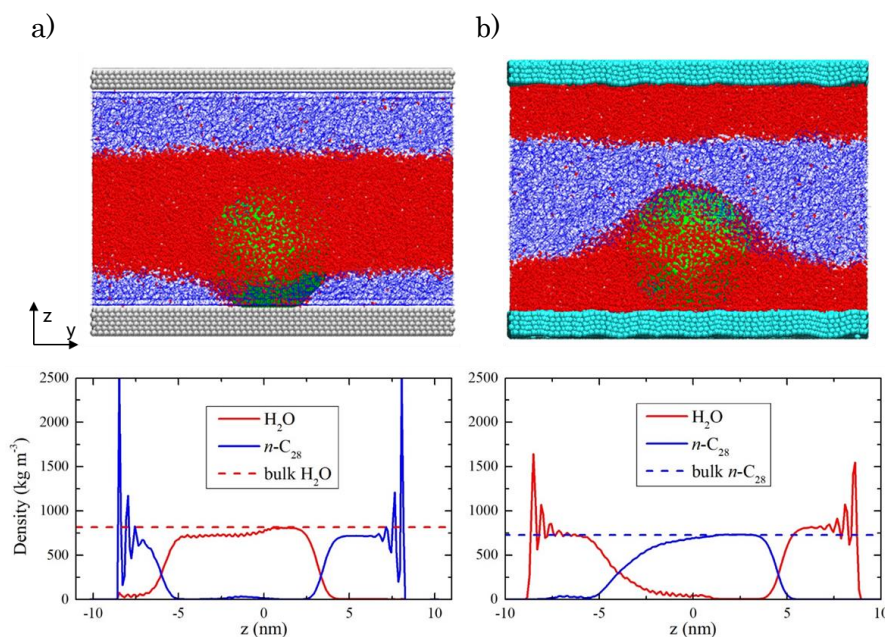
This selection was based on the AA to CG mapping used by MARTINI (i.e. 4 heavy atoms to 1 bead) [8]. The interaction energy was calculated at a given distance  $r$  of the closest atom of the molecular fragment from the Co cluster which, for each orientation, is the difference between the energy of the pair minus that of the isolated fragment and metal cluster. The discrete points of interaction energy were then divided by the number of Co atoms and rescaled with respect to the center-of-mass of the molecular fragments and fitted to a Born–Huggins–Meyer (BHM) classical intermolecular potential to yield the effective interaction between Co and water and wax CG beads (Fig. 6).



**Fig. 6.** Effective interaction energies,  $E_{\text{int}}^{\text{eff}}$ , of Co with *n*-butane (top) and the four-molecule water cluster (bottom) as a function of their COM distance,  $r_{\text{COM}}$ . Blue and red lines represent the fit to a classical Born–Huggins–Meyer potential between each metallic Co bead and the CG *n*-butane (C1) and water (W) beads, respectively.



Subsequently, we performed CG simulations of the  $n\text{-C}_{28} - \text{H}_2\text{O}$  mixture inside the Co nanoparticle containing pore. Our results show that even though the presence of the Co nanoparticle does not significantly perturb the phase separation of the mixture inside the G and GO pores, there is a somewhat increased affinity of water towards the Co nanoparticle (Fig. 7). Sadeqzadeh et al. [11], proposed a water-assisted sintering mechanism for Co supported NPs, where water facilitates sintering by reducing the particle surface energy via oxidation, which results in thermodynamically stable particles with increased mobility. Our simulations hint at water's possible role in promoting sintering by such a manner.



**Fig. 7.** Equilibrated (top) conformations of the confined  $n\text{-C}_{28} - \text{H}_2\text{O}$  mixture at 473.15K and 3.4 MPa pressure in a) G (gray) and b) GO (cyan). The fcc Co NP is shown in green. Mass density profiles along the  $z$  direction of the  $n\text{-C}_{28} - \text{H}_2\text{O}$  mixture are also illustrated (bottom).

## 6. Conclusions

AA and CG MD simulations for  $n\text{-C}_{28} - \text{H}_2\text{O}$  mixtures with dodecanol in the bulk and confined in both G and GO slit mesopores were performed. From the comparison with AA simulations and experimental data it can be safely concluded that the utilization of CG models offers a quantitative prediction that properly reproduces the trends of several structural, thermodynamic, and dynamic properties with lower computational effort. Our preliminary simulations with the inclusion of a Co NP, for which novel parameters for use with CGMD simulations were developed from DFT calculations, show that water in high concentrations does exhibit extended coverage of the Co NP in either hydrophobic or hydrophilic confinement, but phase separation inside the pore is preserved. More importantly, the present study shows that MARTINI can be potentially used to study systems relevant to the FTS process.



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