EQUILIBRIUM AND TRANSPORT PROPERTIES OF SMALL ALKANES AND ALKENES CONFINED IN SINGLE-WALLED CARBON NANOTUBES.

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In recent years it has been suggested that carbon nanotubes (CNTs) could be used as active separating agents both in carbon adsorbents and in membranes [1-3]. To efficiently use CNTs in such separation devices, it becomes essential not only to study their selectivity/equilibrium properties but also to understand the confined fluid dynamics. This work presents molecular simulation results of both the adsorption and diffusion of low molecular weight saturated (alkanes) and unsaturated (alkenes) hydrocarbons inside single-walled carbon nanotubes (SWCNTs) of different topologies.

Classical Molecular Dynamics simulations were employed to study both the adsorption and the flow dynamics. Large-scale simulations were set up where several open-ended SWCNTs were exposed to a bulk fluid in an overall canonical ensemble. The endohedral physical adsorption and non-equilibrium diffusion into the pore was monitored until steady state conditions were attained [4]. We present adsorption isotherms for both components at 300K for pressures up to 30 bar. We have seen that the adsorption is insensitive to the chirality of the nanotubes. Additionally, our results show that for the binary mixtures there is only a modest selectivity of the adsorption towards ethane. During the transient period of filling up the nanotubes we have observed a spiralling diffusion path for the molecules at low loading. This unique observation has been previously reported for water [5] and similar systems [6]. We have determined it is a property of the nanotube symmetry, as it is not seen in armchair type nanotubes.

The corresponding confined phase from the previously described simulations, containing the nanotube and the adsorbed molecules, was separated from the bulk fluid phase and replicated four times along the *z*–axis to produce a 3.0 × 3.0 × 20.6 nm supercell containing *ca.* 3000 graphitic carbon atoms ($D_{eff} \approx 0.9$ nm, $L_{eff} \approx 20.6$ nm) and the mean-squared displacement evaluated for different loadings and tube topologies, using a chiral (12,6) tube and an armchair (9,9) tube. Dynamical properties of C_2H_4 and C_2H_6, both in the bulk fluid phase and confined inside SWCNTs of different symmetries, have been investigated in the regions 0.026 $\text{mol·L}^{-1} < \rho < 15.751\ \text{mol·L}^{-1}$ and 0.011 $\text{mol·L}^{-1} < \rho < 14.055\ \text{mol·L}^{-1}$, respectively.

From the mean square displacement curves, $<r^2>$ of confined fluids (Figure 2) [7,8], as expected, we observed a monotonical decrease of the self-diffusion coefficient with increasing density. As for the bulk fluids, an empirical correlation has been established that enabled direct comparison with experimental data; in the case of ethylene, discrepancies were found to be less than 5 %, up to $\rho \approx 10\ \text{mol·L}^{-1}$ [9]. Upon confinement inside a SWCNT, nanotube topology seems to be a relatively unimportant factor influencing the molecules dynamics, according to what has been suggested by previous studies for zig-zag and armchair symmetries [5,6]. The high-density systems confined onto a zig-zag lattice, usually exhibited a dominant Fickian-type mode of transport, although a transition seemed to occur for molecular densities $\rho < 5.5\ \text{mol·L}^{-1}$. Below this threshold, molecules moved with a mixed mode transport, combining components from Fickian and ballistic diffusion.

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Figures:

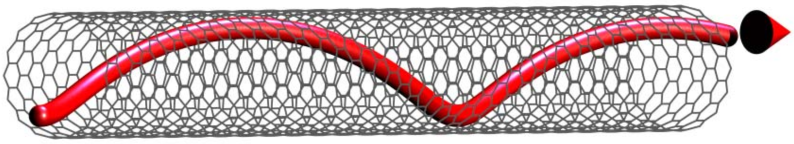

Figure 1. Unique spiral diffusion path inside a zig-zag (16,0) topology.

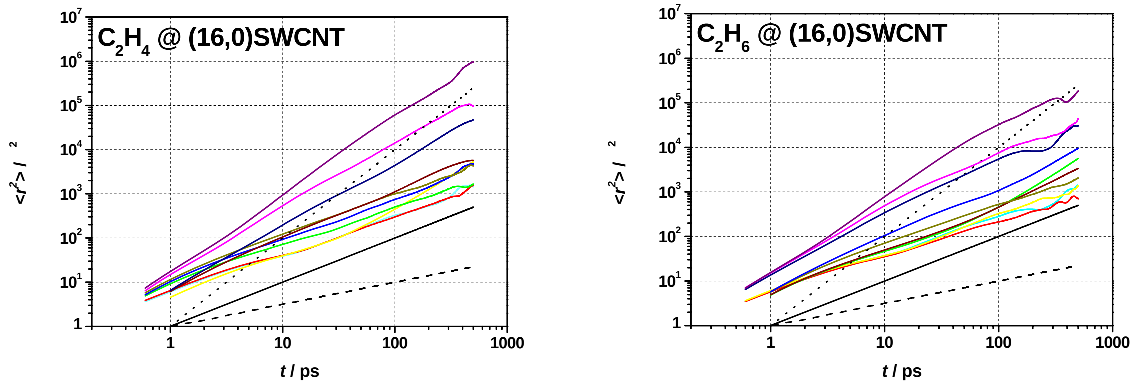

Figure 2. Mean squared displacement $<r^2>$ for fluids confined in a (16,0) zig-zag SWCNT (T = 300 K). Density increases from top to bottom, respectively, from 0.242 mol·L^{-1} to 15.751 mol·L^{-1} (C2H4) and from 0.242 mol·L^{-1} to 14.055 mol·L^{-1} (C_2H_6). The different diffusion mechanisms are indicated for comparison purposes: ballistic (dotted), Fickian (straight line) and single-filed (dashed).