“Equilibrium and Transport Properties of Small Alkanes and Alkenes Confined in Single-Walled Carbon Nanotubes.”

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1.1 - Motivation

- Separation of close boiling point mixtures (olefin/paraffin) by distillation are energy intensive operations.

- Adsorption can play a role in improving this scenario (molecular-level knowledge of adsorption in confined nanospaces spaces is required).

- For small scale separations (pharmaceuticals, higher added value), nanotube-based membranes could be good future candidates.

- Extend our expertise from flat surfaces (carbon slitpores) to cilindrical geommetries.

1.2 – Adsorbents & Methodology

- Carbon nanotubes first identified in the early 90's [Iijima 1991]: possible applications range from storage nanomaterials (H_2,CH_4) and composites for electronics, to separating agents of organic vapors and chemical sensors.

- Study the adsorption and diffusion behaviour of fluids, when a bulk phase is exposed to direct contact with single-walled carbon nanotubes: Classical Molecular Dynamics (Newton's 3rd law) and Grand Canonical Monte Carlo simulations.

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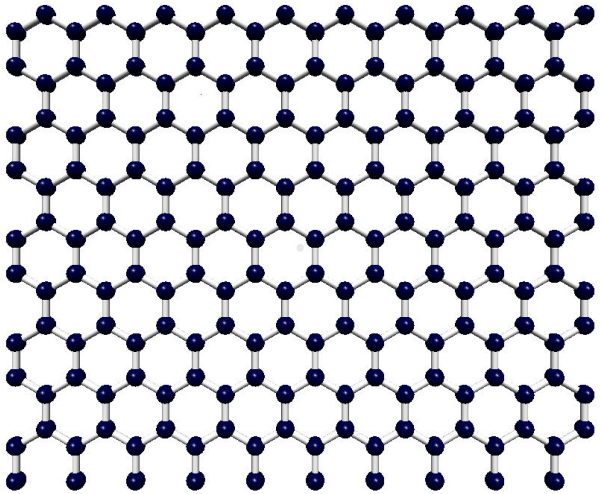
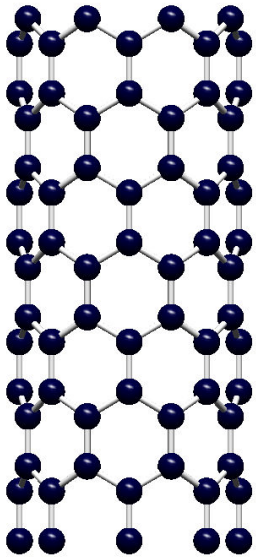
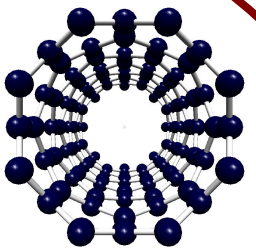


graphene sheet

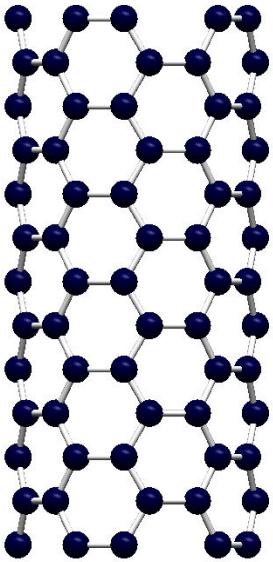
hexagonal simmetry

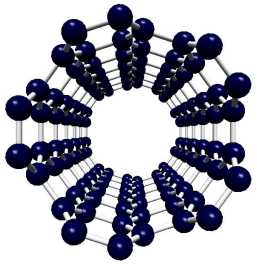
sp^2 carbons, 1.41 Å



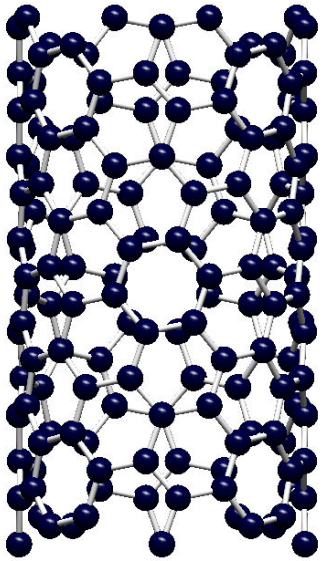


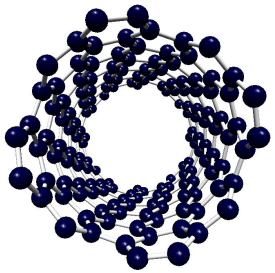
Zig-zag (8,0)





armchair (5,5)





chiral (8,4)

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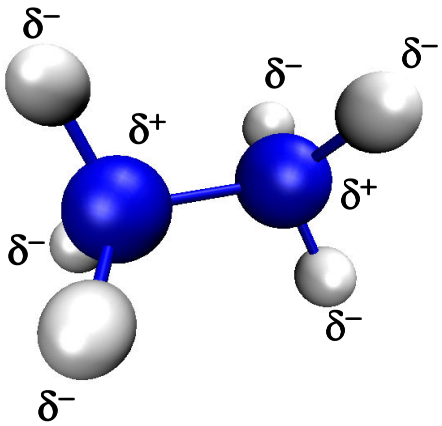
3.1 – All-atom potential (AA-OPLS)

- non bonded interactions : All-atom Lennard-Jones (12,6) with explicit Coulombic charges

$$U(r_{ij}) = \sum_i \sum_j \frac{q_i q_j e^2}{r_{ij}} + \left\{ 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] \right\} f_{ij}$$



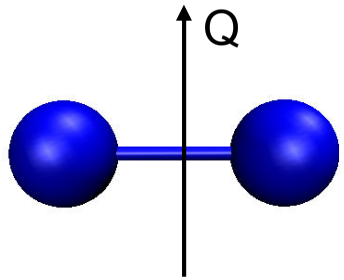
- bonds and angles : harmonic
- dihedrals : triple cosine

$$U(\phi_i) = \sum_i \frac{V_1^i}{2}[1+\cos(\phi_i)] + \frac{V_2^i}{2}[1-\cos(2\phi_i)] + \frac{V_3^i}{2}[1+\cos(3\phi_i)]$$

- nanotubes : All-atom graphitic carbons [Steele 1973]

3.2 – United-atom potential (2CLJQ)

- non bonded interactions : Lennard-Jones (12,6) beads (CH_2, CH_3) with a quadrupole moment at the center of mass



$$U(r_{ij}, r_{ab}) = \sum_i \sum_j 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{3}{4} \frac{Q^2}{(4\pi\varepsilon_0) r_{ab}^5} \left[1 - 5\left(c_i^2 + c_j^2\right) - 15 c_i^2 c_j^2 + 2\left(c - 5 c_i c_j\right)^2 \right]$$

3.3 – Single-walled carbon nanotubes

- frozen graphitic carbon atoms

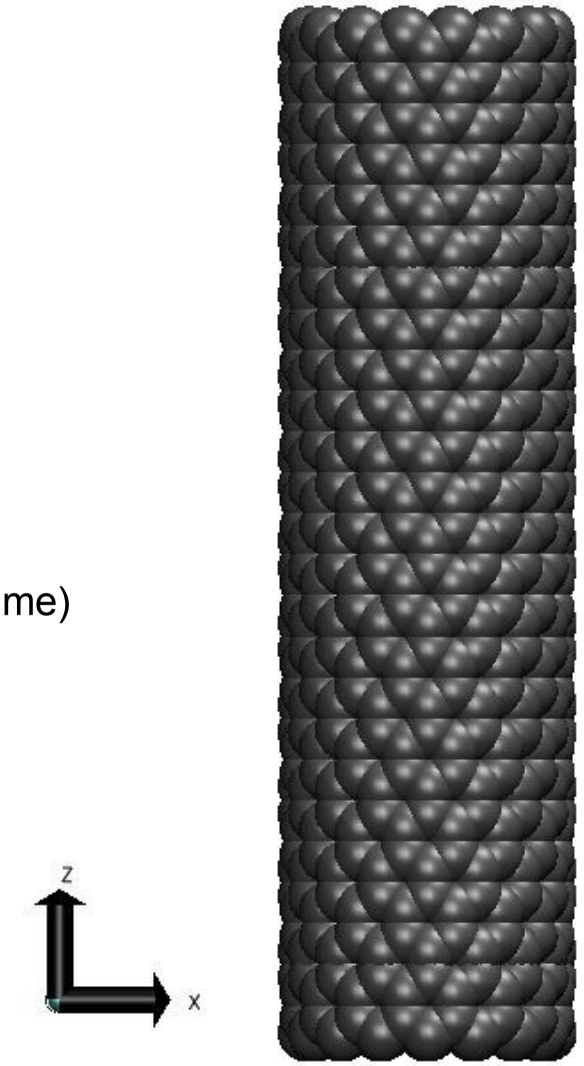
  d (C-C) = 1.42 Å

  squeezing out of the π orbitals

- explicit carbon atoms: corrugated nanotubes

- effective diameter: from surface to surface (accessible volume)

$$D_{eff} = D - \sigma_{CRT}$$



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4.1 – Classical Molecular Dynamics

- *NVT ensemble* (Nosé-Hoover thermostat)
- T = 300 K
- timestep = 1 fs (Verlet leapfrog algorithm)
- timescale 0.5 – 3ns
- Potential cutoff = 15 Å
- Ewald summation (fluids)

MD box : $30 \times 30 \times 302$ Å (60 $\times$ 60 $\times$ 302 Å) ; SWCNT box : $30 \times 30 \times 52$ Å (60 $\times$ 60 $\times$ 52 Å)
N_{CRT} ≈ 800 atoms (L_z=52 Å), N_{fluid} = 150-1200 atoms (density)

4.2 – Grand Canonical Monte Carlo

- *μVT ensemble*
- T_{pure} = 300 K, 260 K ≤ T_{mix} ≤ 450 K
- $\text{cycles}_{\text{total}} = 30 \times 10^6$, $\text{cycles}_{\text{production}} = 5 \times 10^6$
- Potential cutoff = 20 Å
- GCMC box : 25 $\times$ 25 $\times$ 53 Å

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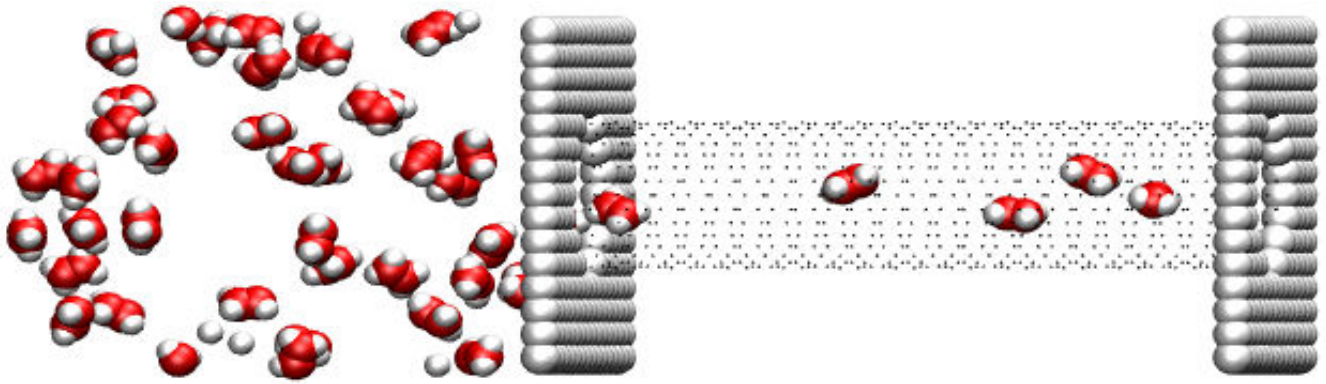
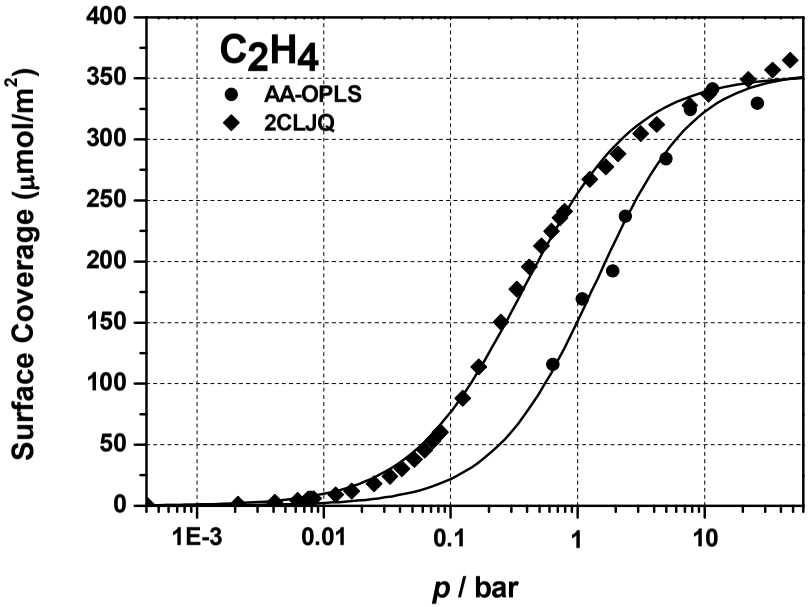
5.1 - Adsorption of pure fluids

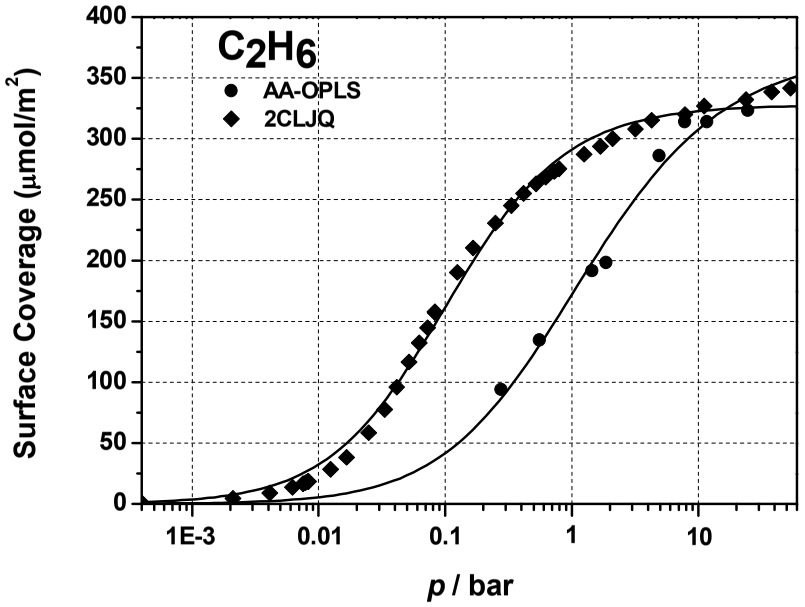
Bulk fluid equilibration @300K (t > 0.1ns)

- fluids: $4 \times 10^{-4} \leq p_{bulk} \leq 53.6$ bar



Bulk ethylene being adsorbed onto a zig-zag SWCNT (16,0)

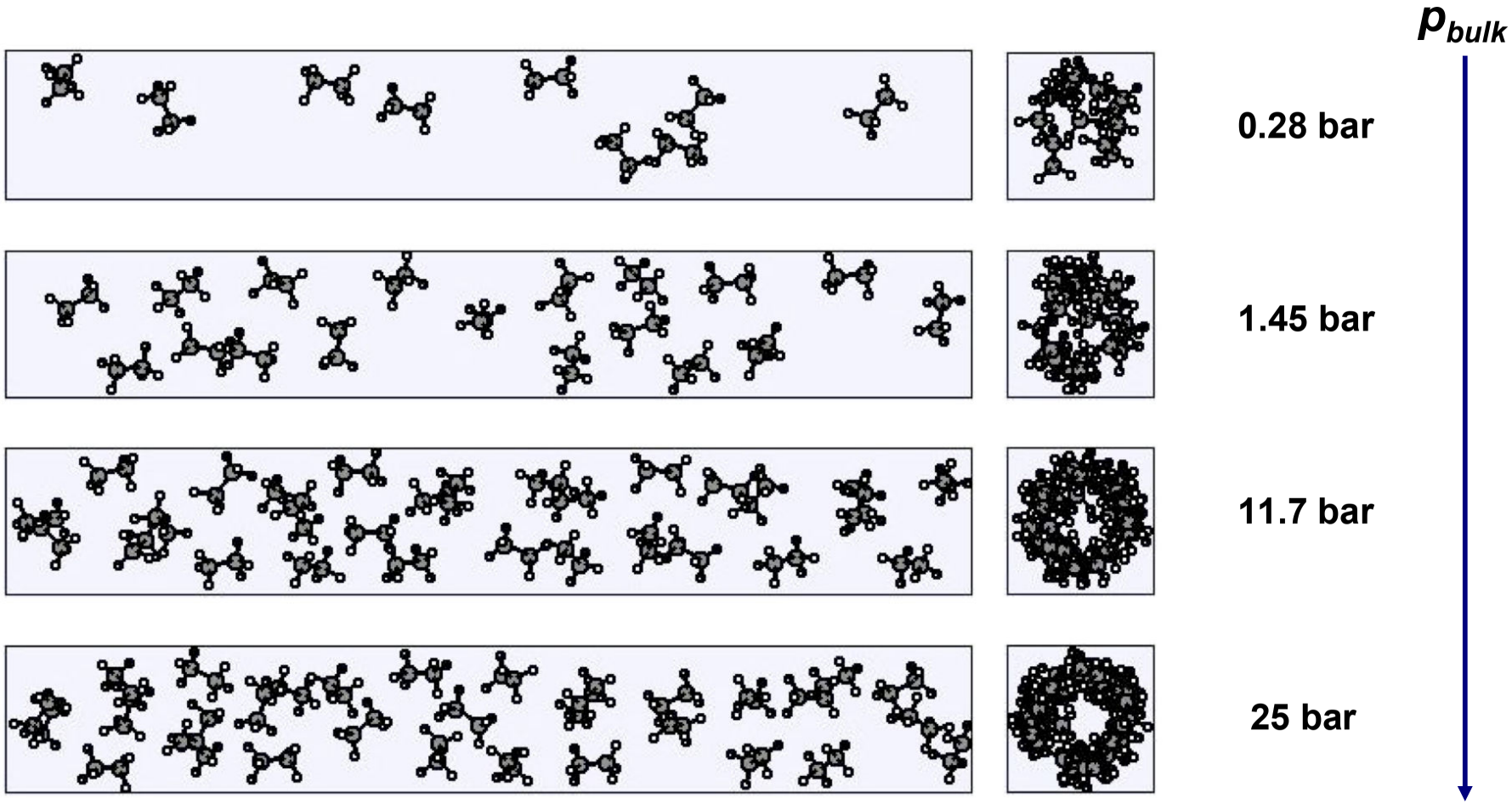




$$Toth: \quad C_{\mu} = C_{\mu s} \frac{bP}{\left[1+(bP)^{t}\right]^{1/t}}$$

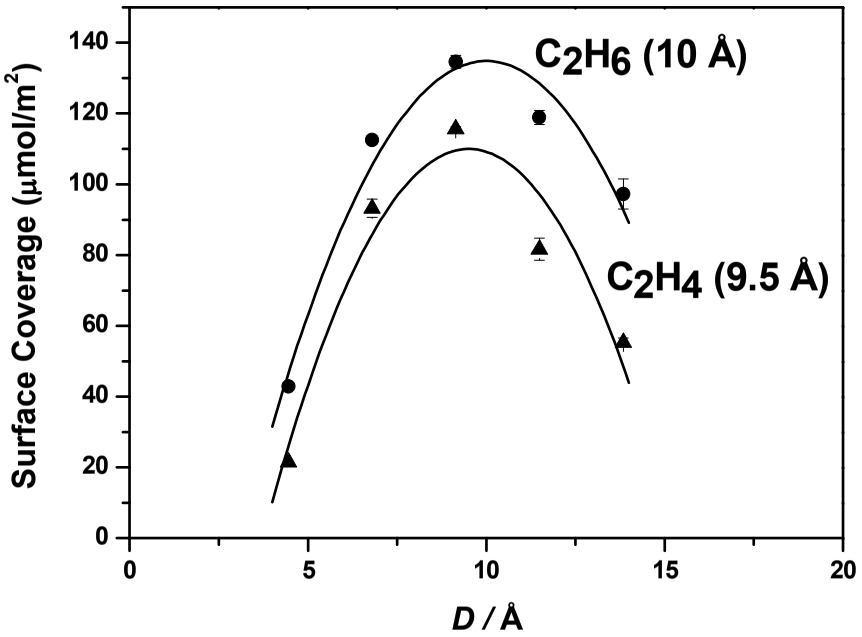
$$Sips: \quad C_{\mu} = C_{\mu s} \frac{(bP)^{1/n}}{1+(bP)^{1/n}}$$

- type I isotherms (IUPAC)
- similar behaviour with Sips and Toth isotherms
- overestimation with the 2CLJQ (inaccurate rigid behaviour and static charge distribution for flexible molecules like C_2H_6); convergence after p ≈ 10 bar [Cruz 2008]
- C_2H_6 is preferentiably adsorbed at low *p* (dispersive energy); cross-over around 3 – 6 bar (activated carbons, slitpores, higher *D* SWCNTs); at medium-high pressure C_2H_4 is the dominant species (entropic factor / packing efficiency) ; isosteric heats of adsorption (q_{iso} = – ΔH)


p_{bulk}
0.28 bar
1.45 bar
11.7 bar
25 bar

- armchair (9,9) and chiral (12,6) nanotubes present similar low pressure (p < 1 bar) adsorption capacities (– 3.4 % to 7 %)

- nanotubes loading capacity seems to be a quadratic function of the tubes' diameter (4.46 Å, 6.80 Å, 9.15 Å, 11.49 Å, 13.83 Å)

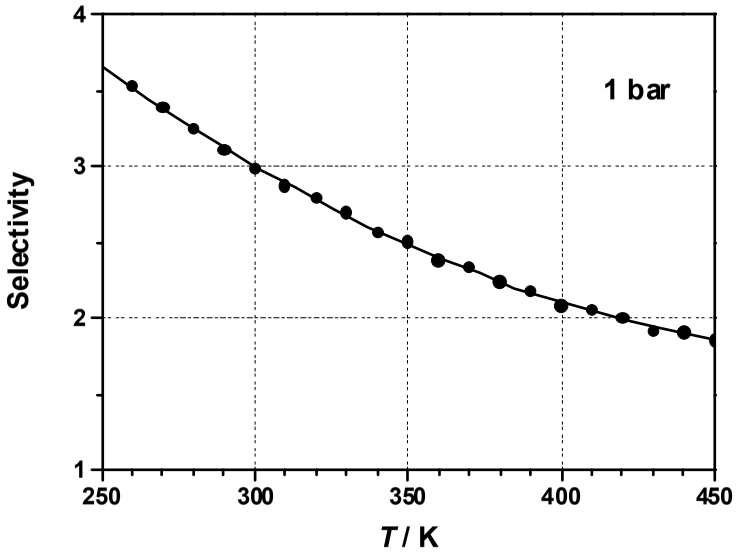


5.2 - Separation of binary mixtures (C_2H_4/C_2H_6)

$$S = \frac{(x_{ethane} / x_{ethylene})_{nanotube}}{(x_{ethane} / x_{ethylene})_{bulk}}$$

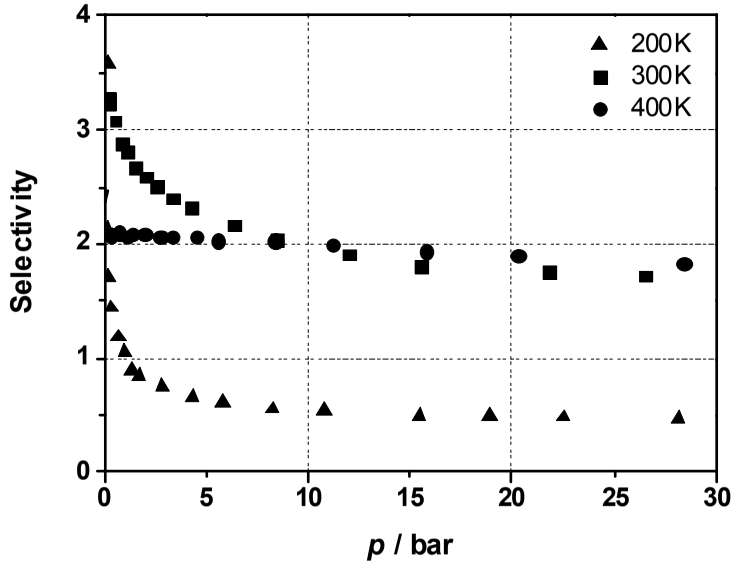
i) refinery mixture (90 mol % C_2H_4), p = 1 bar

- S decreases with T (high temperatures reduce the energetic differences between molecules); Selectivity's values are similar to larger nanotubes and other pore geommetries



ii) equimolar mixture, 0.1 ≤ p ≤ 30 bar

- S decreases rapidly up to p ≈ 10bar, and from then onwards gains a monotonical behaviour.
- the higher selectivity values coincide with the low pressure regions, where ethane is the preferentially adsorbed species



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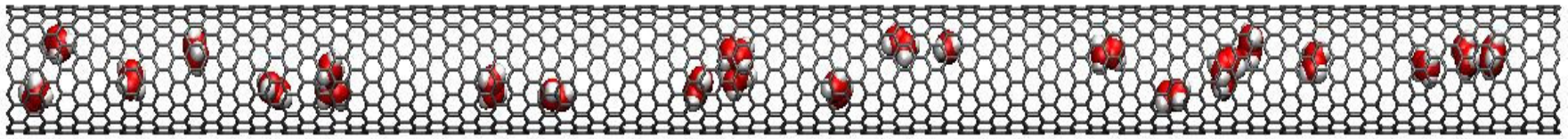
6.1 - Methodology

- Once the adsorption runs were finished, the upper volume of the simulation cell, containing the nanotube and the adsorbed molecules, was separated from the bulk fluid and replicated four times along the *z*-axis to produce a *30* × *30* × *206* Å supercell containing *ca.* 3000 graphitic carbon atoms.



- Molecular displacement has been monitored for 0.5 ns: bulk and confined fluids.

- $0.026 \leq \rho$ / mol·L^{-1} ≤ 15.751 (C_2H_4)
- $0.011 \leq \rho$ / mol·L^{-1} ≤ 14.055 (C_2H_6)

6.2 - Pore contact

- A previously reported helical diffusive path for pure C_2's in zig-zag SWCNT's [Mao 2000], has also been observed here for dense confined fluids and corresponding binary mixtures (wall simmetry and C – C bonds) .

ethaneSWCNT

- Not surprisingly, chiral tubes exhibit a more pronounced spiralling effect !

- No coherent displacement for armchair tubes.

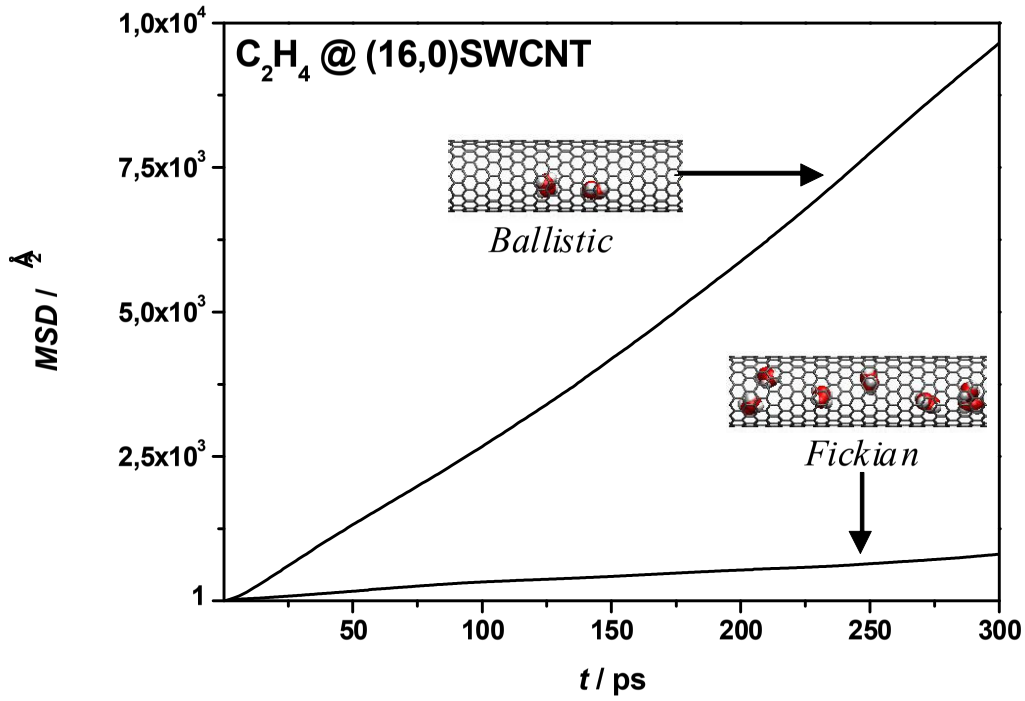
6.3 - Effective diffusion

$$MSD = r^2 = \left\langle [r(t) - r(0)]^2 \right\rangle$$

$$Fickian: dr^2 \propto Ddt$$

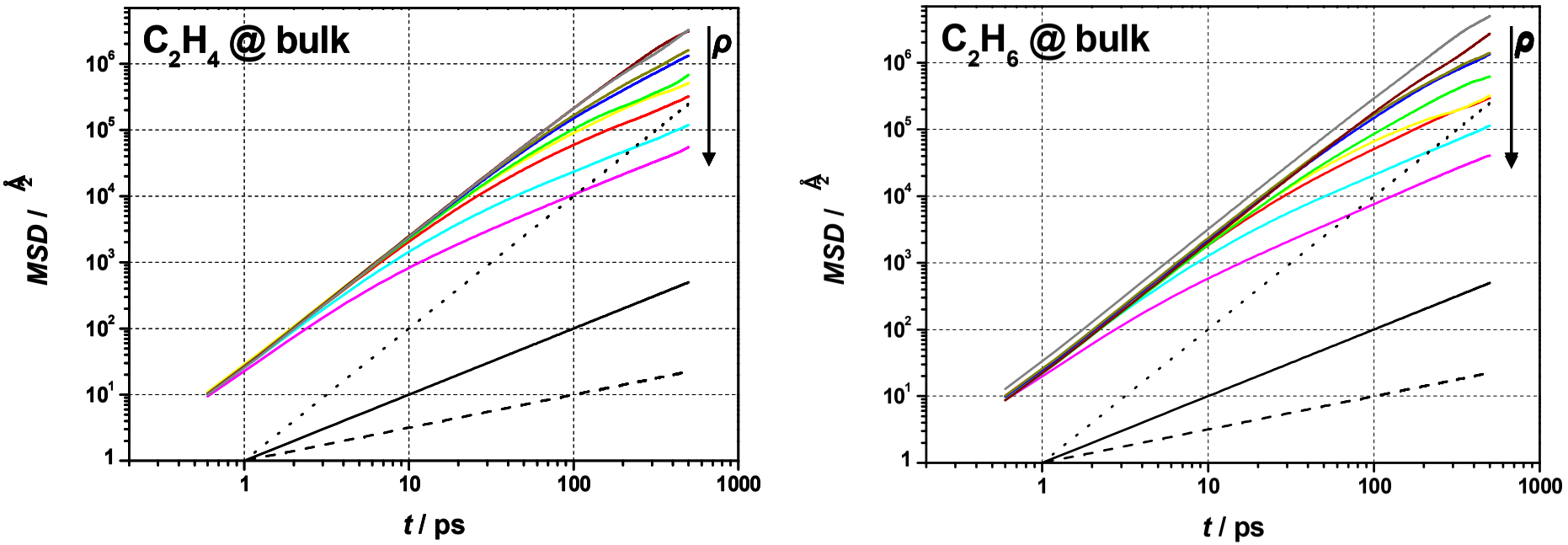
$$Ballistic: dr^2 \propto Bdt^2$$

$$D = \frac{1}{6}\frac{d}{dt}\left\langle [r(t) - r(0)]^2 \right\rangle$$



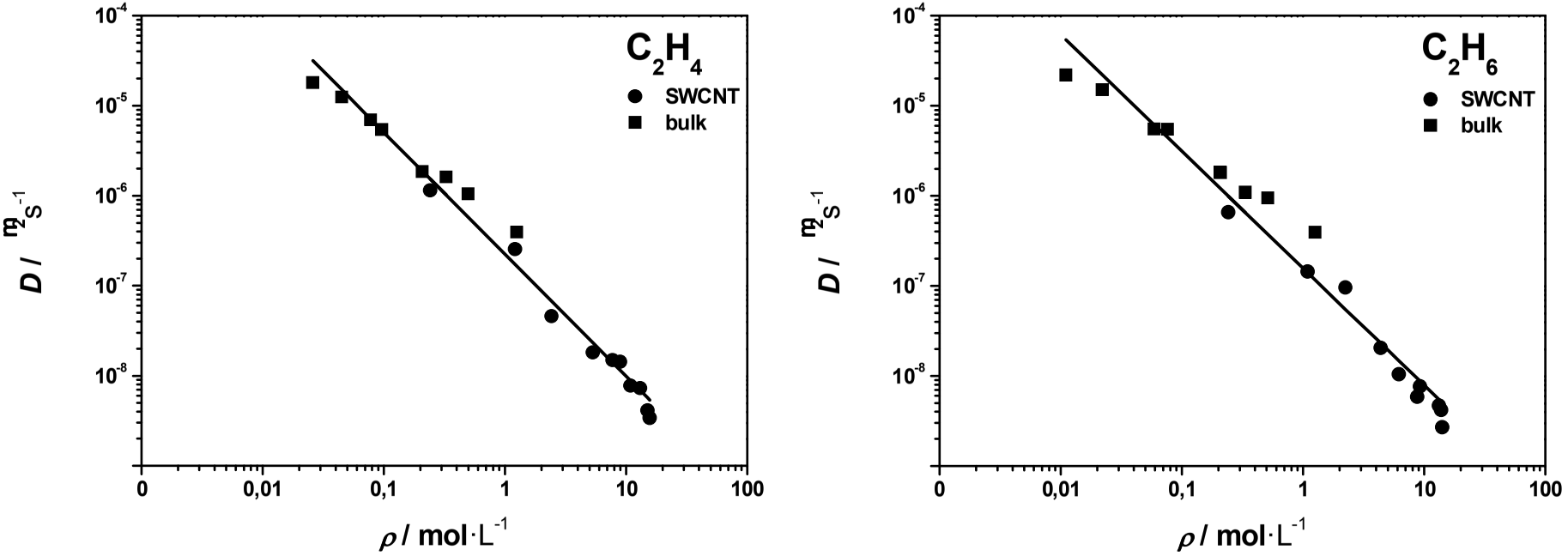
- Linear behaviour => Fickian-type diffusion => self-diffusion (effective), D (10^{-8} m^2/s,)

6.3 - Effective diffusion



- increase of *D*, with decrease of molecules inside the tube, untill transition to outside the Fickian regime: $\rho < 5.5$ mol·L^{-1} (@SWCNT) [Cruz 2008]
- low density systems : ballistic and mixed type regimes (free space available for molecular jumps)
- no significative influence of the SWCNT's simmetry on the Fickian diffusivities (Zig-zag, armchair and chiral nanotubes)

6.3 - Scaling laws



- confined phase diffusion data can be estimated by the knowledge of the corresponding bulk fluid structural properties, and this idea can become immediately appealing when one keeps in mind practical and industrial applications (*e.g.* nanofluidics).

- $D_{bulk} = A \cdot \rho^{-B}$: empirical correlation verified for ethylene, against experimental data up to $\rho \approx 9.9$ mol·L^{-1} (discrepancies less than 5 %).

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7.1 - Conclusions

- Results seem to show that the adsorption and transport behaviour of the pure fluids is relatively independent of host simmetry.

- Relatively small changes in the nanotube diameter can have a marked effect on the transport and adsorption properties. Further work would be required to confirm the present findings in a larger pore with/temperature range.

- Ethane is the preferred adsorbed species (low p), ethylene diffusivities are larger than those of ethane, although the difference is relatively minor.

- Confined fluids' diffusion data can be estimated from the corresponding bulk phases (scaling law).

7.2 - Perspectives

- C_3 fluids and their binary mixtures (D - ρ scaling law).

Acknowledgements

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