Improved hydrogen adsorption capacity of doped carbon nanotube bundles

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Abstract

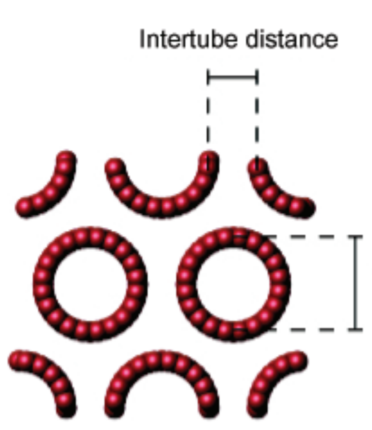
The ability of carbon nanostructures to store hydrogen still remains a controversial subject. For example, reported experimental values for hydrogen uptake in carbon nanotubes vary from 0,4% and 67% wt. In contrast, assuming a physisorption mechanism on graphite planes, most numerical studies agree to give a gravimetric volume of adsorbed hydrogen around 1% wt. at room temperature (293,0 K) and 10,0 MPa. Clearly, in order to explain the large hydrogen uptake obtained experimentally, one has to invoke a different adsorption mechanism than physisorption. The most trivial explanation of large hydrogen uptake in carbon nanotubes is to invoke the participation of residual metallic impurities (Fe, Co, Ni). Using various carbon nanostructures and with the help of Monte-Carlo simulation techniques, we have studied the effect of heteroatoms within carbon nanotube bundles.

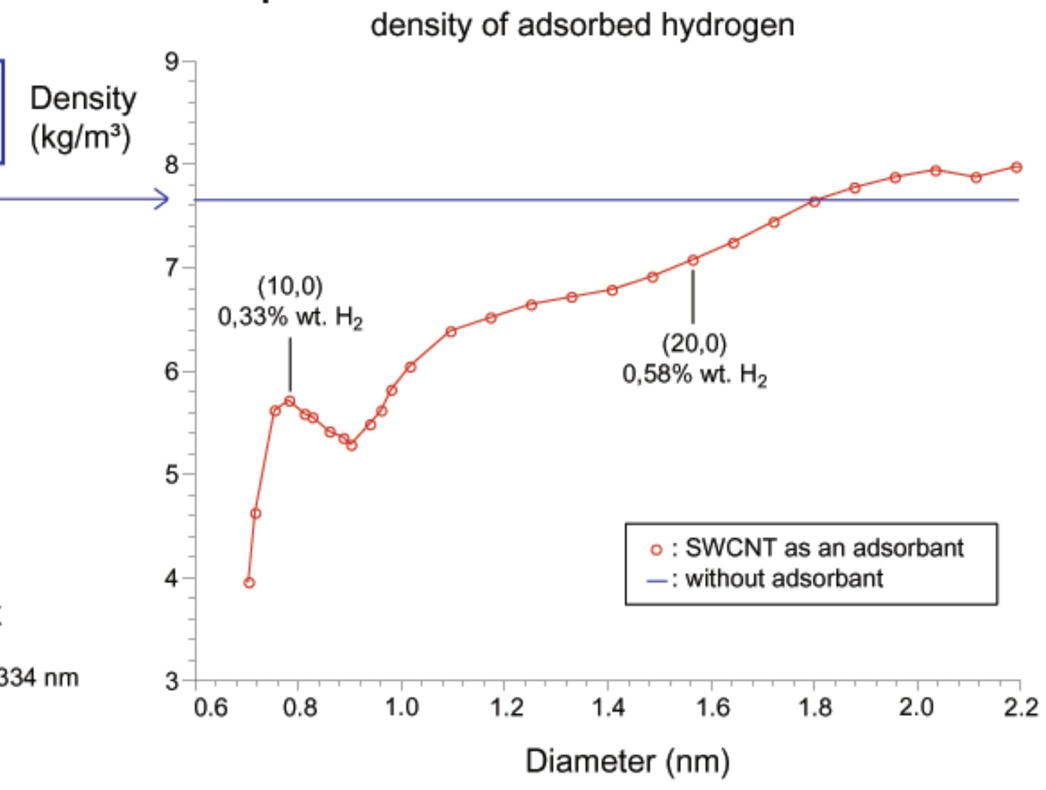
Hydrogen adsorption in carbon nanotubes

Hydrogen adsorption in single-walled carbon nanotubes (SWCNT) in an hexagonal structure depends on the tube diameter.

Graphic1 : Influence of carbon nanotube's diameter on the density of adsorbed hydrogen

The blue line represents the density of hydrogen at 10,0 MPa and 293,0 K.





Fixed parameters :
Temperature = 293,0 K
Pressure = 10,0 MPa
Intertube distance = 0,334 nm

Transition metal impurities

Hydrogen adsorption on nickel surfaces[1] and clusters[2] has been studied extensively. From these studies, we roughly approximated a Lennard-Jones potential between transition metal impurity and hydrogen (see **Figure1**). Lennard-Jones potential curves for carbon-hydrogen and hydrogen-hydrogen interactions are shown in **Figure2**.

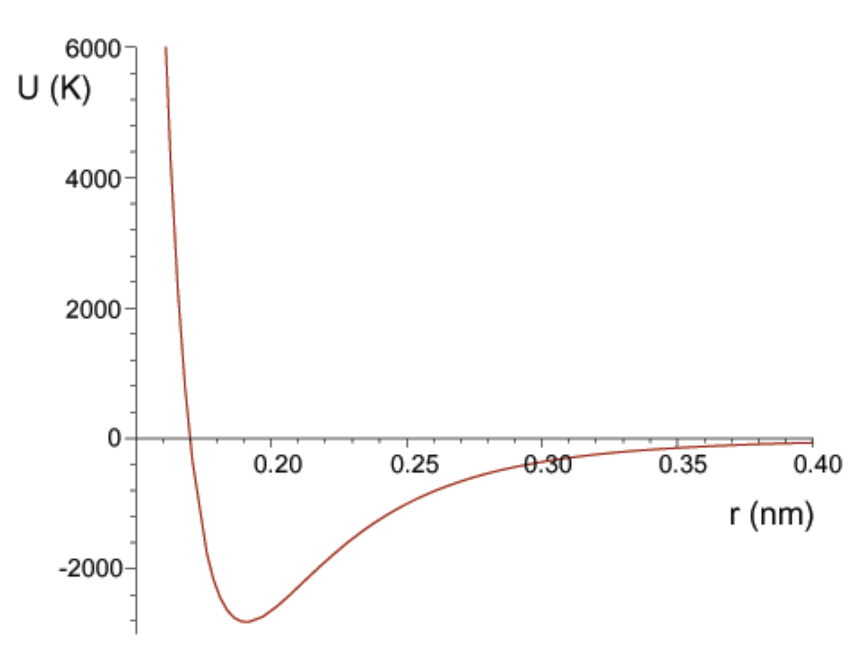


Figure1 : Modelised interaction potential between transition metal impurity and molecular hydrogen

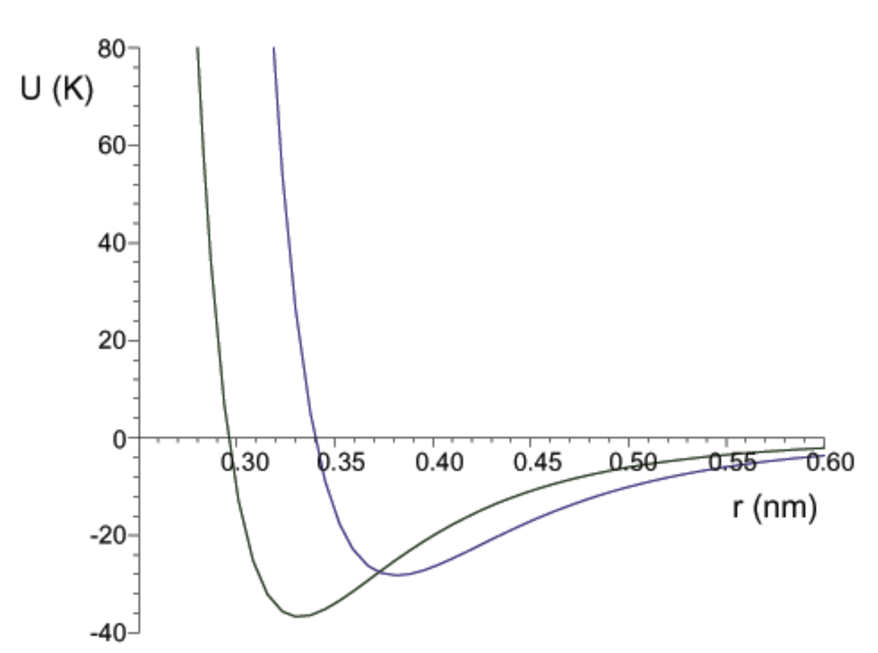


Figure2 : Carbon-hydrogen (blue) and hydrogen-hydrogen (green) interaction potential[3]

Doped carbon nanotube bundles configuration

We considered single-walled nanotubes placed in an hexagonal structure. Transition metal impurities were inserted using two schemes. In the first one, impurities are dispersed in various intertube channels of the bundle. In the other scheme, impurities are straightly aligned in a single intertube channel.

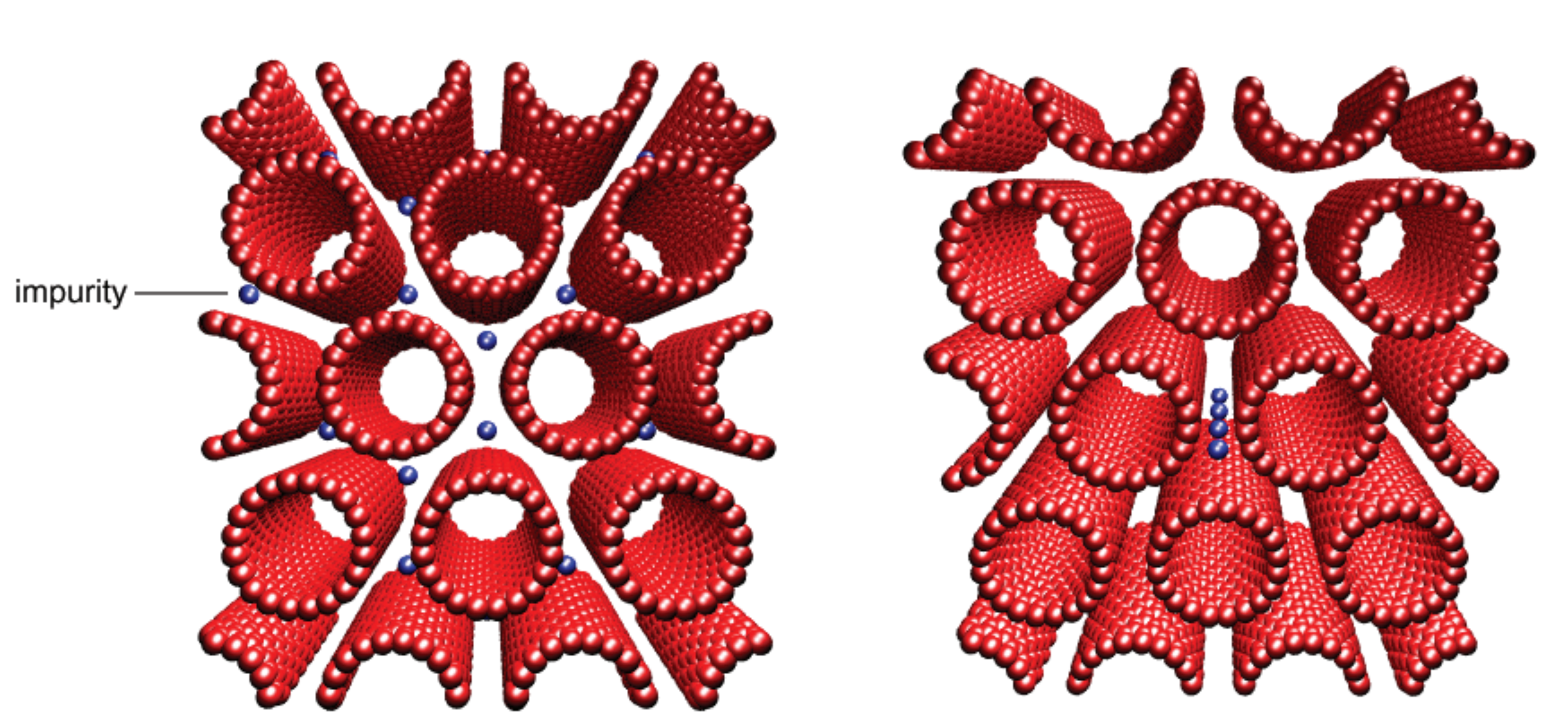
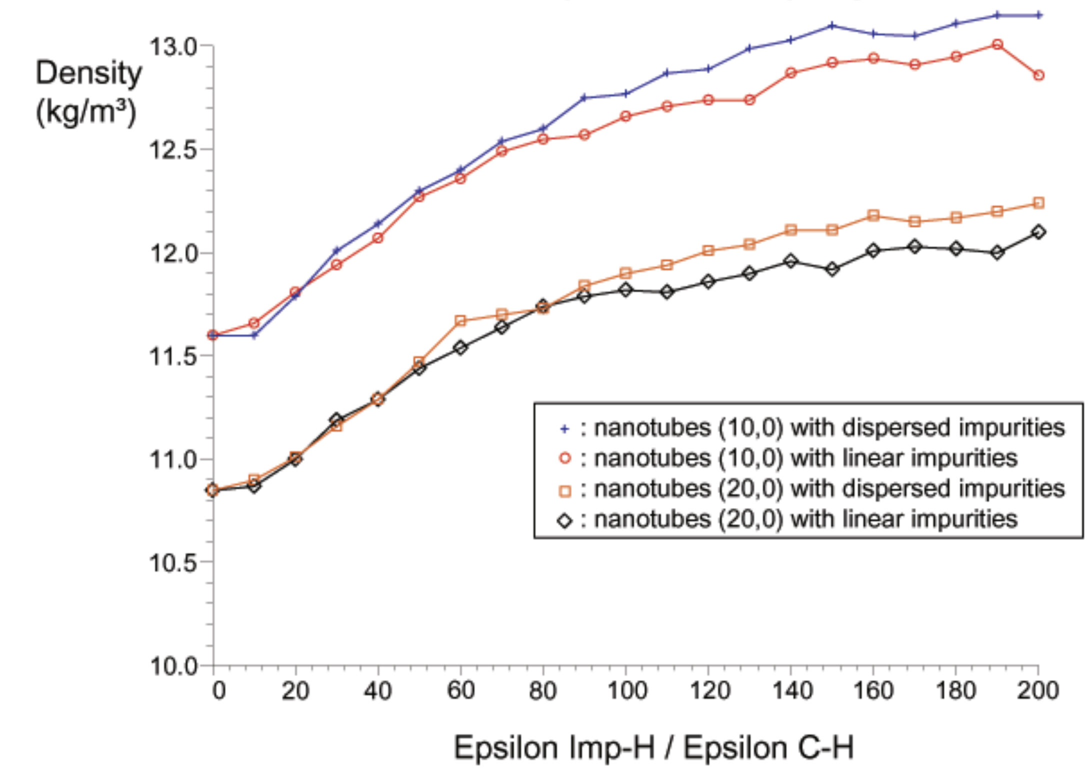


Figure3 : Different doped nanotube bundle configurations. Dispersed impurities (left) and linear impurities (right)

Results

Graphic2 : Influence of transition metal impurities potential on the density of adsorbed hydrogen

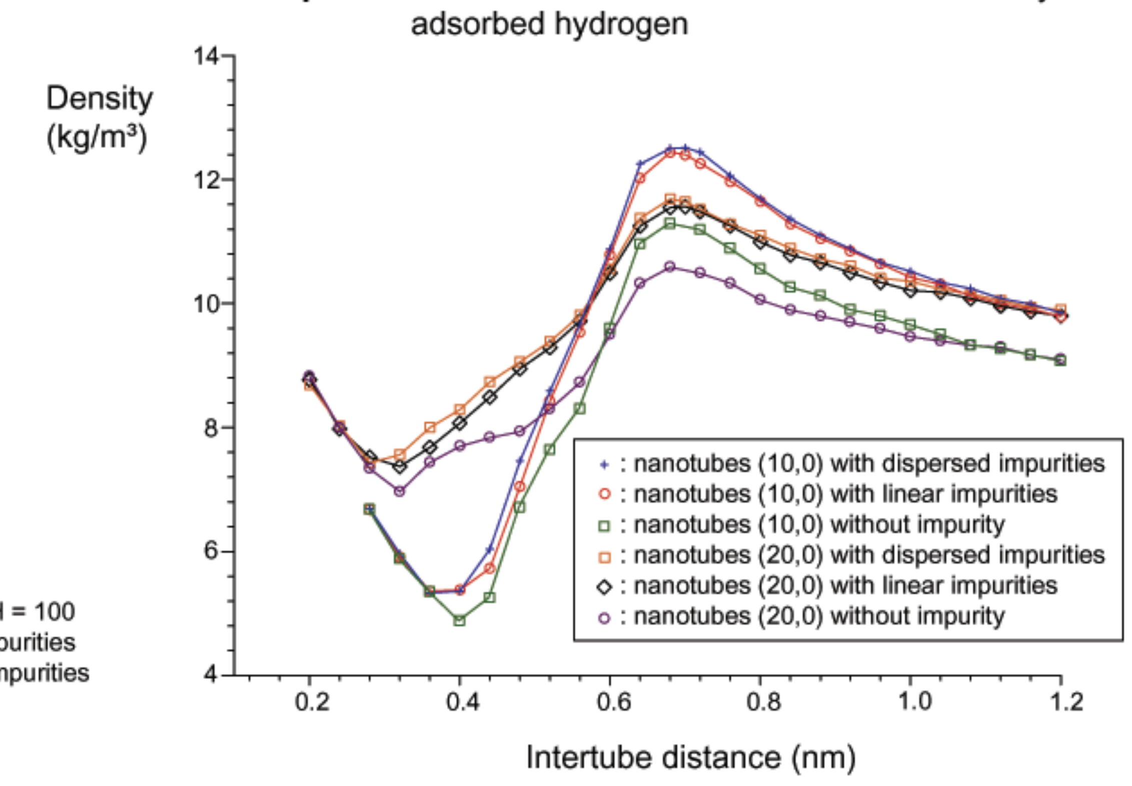


The sublinear behavior demonstrates that transition metal impurities are masked by adsorbed hydrogen on their surfaces.

Fixed parameters :
Temperature = 293,0 K
Pressure = 10,0 MPa
Intertube distance = 0,70 nm
(10,0) bundles contain 8 impurities
(20,0) bundles contain 16 impurities

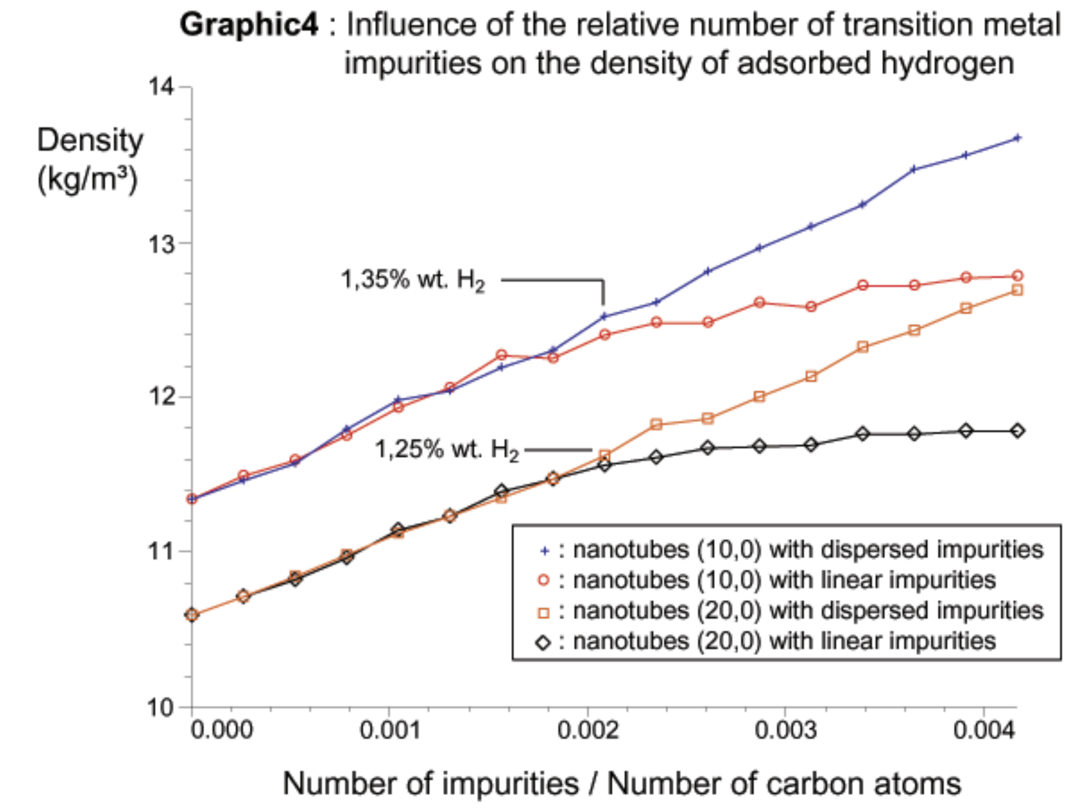
Graphic3 : Influence of intertube distance on the density of adsorbed hydrogen

Intertube pores become fully available to hydrogen for distances superior to 0,56 nm.



Fixed parameters :
Temperature = 293,0 K
Pressure = 10,0 MPa
Epsilon Imp-C / Epsilon C-H = 100
(10,0) bundles contain 8 impurities
(20,0) bundles contain 16 impurities

Graphic4 : Influence of the relative number of transition metal impurities on the density of adsorbed hydrogen



Fixed parameters :
Temperature = 293,0 K
Pressure = 10,0 MPa
Epsilon Imp-C / Epsilon C-H = 100
Intertube distance = 0,70 nm

Conclusions

- Undoped SWCNT in an hexagonal structure does not seem to be an interesting adsorbent for hydrogen : computed gas density is comparable to pressurized hydrogen.
- Impurities tend to adsorb a fixed number of hydrogen molecules on their surface. This number increases as the impurity potential in a sublinear fashion.
- If we consider our transition metal impurities were nickel atoms representing 1% wt. of the (10,0) bundle adsorbate, hydrogen adsorption can be increased from 5,7 kg/m³ (0,33% wt. H_2) to 12,5 kg/m³ (1,35% wt. H_2).

Acknowledgements

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