

# Entropy deepens loading chemical potentials of small alcohols by narrow carbon nanotubes. Supplementary material

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## S1 Parameters

Table S1: Lennard Jones parameters and partial charges for all simulated species.

Molecule	Site	$\sigma$ (nm)	$\epsilon$ (kJ/mol)	q(e)
2*Water(SPC)	O	0.3165	0.6501	-0.82
	H	0	0	0.41
SWCNT	C	0.3361	0.4058	0
3*Methanol	CH <sub>3</sub>	0.3646	0.9444	0.176
	O	0.3954	0.8496	-0.574
	H	0	0	0.398
4*Methanol	CH <sub>3</sub>	0.3747	0.8671	0
	CH <sub>2</sub>	0.4070	0.4105	0.176
	O	0.2954	0.8496	-0.574
	H	0	0	0.398
Methane	CH <sub>4</sub>	0.37088	1.2659	0

## S2 Methane Simulations

Using the same methods presented in the main paper, periodic SWCNTs (along the z axis) of 3.19 nm in length and widths of 0.8, 0.9 -for the (6,6) and (7,7) tubes, respectively- were constructed. Methane loading was studied in (6,6) and (7,7) tubes - the CH<sub>4</sub>@(6,6) and CH<sub>4</sub>@(7,7) systems, respectively - and placed in boxes with dimensions  $3.6 \times 3.6 \times 3.19 \text{ nm}^3$  and  $3.7 \times 3.7 \times 3.19 \text{ nm}^3$ , respectively. A depiction of the simulated systems is shown in Fig. S1. To carry out the free-energy calculations, 9 (in the CH<sub>4</sub>@(6,6) system) or 11 (in the CH<sub>4</sub>@(7,7) system) molecules were placed within the pores to be sequentially decoupled via TI. The annihilation TI simulations, on average, encompassed 19 non-equidistant points and 11.2 ns of simulation time per point. Calculations were conducted using a non-bonded interactions soft-core potential with softness parameters  $\alpha_{LJ} = 0.5$  and  $\alpha_{CCRF} = 0.5 \text{ nm}^2$ . Each loading state, at  $\lambda = 0$ , (including an empty tube) was simulated for 100 ns, to obtain converged total potential energies to be used in Eq. (??). TI-MD for the decoupling of methane in water were performed as well.

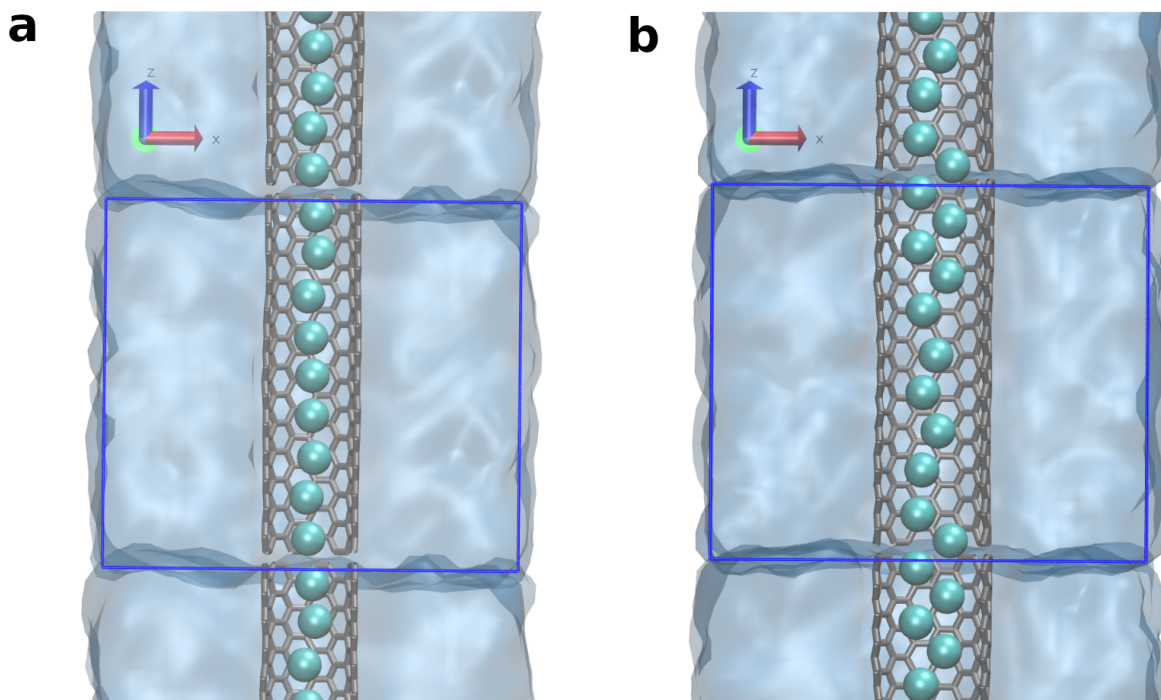


Figure S1: Methane systems. The periodic cell is depicted in blue. (a) methane in a (6,6) single-walled CNT system. (b) methane in a (7,7) single-walled CNT system.

Table S2:  $\Delta A_{(n+1,N-1)\rightarrow(n,N)}$ ,  $\Delta E_{(n+1,N-1)\rightarrow(n,N)}$ ,  $T\Delta S_{(n+1,N-1)\rightarrow(n,N)}$  in  $\text{kJ mol}^{-1}$  for the  $\text{CH}_4@(\text{6,6})$  and  $\text{CH}_4@(\text{7,7})$  systems.

# Pore loading transition	(6,6) SWCNT			(7,7) SWCNT		
	$\Delta A$	$\Delta E$	$T\Delta S$	$\Delta A$	$\Delta E$	$T\Delta S$
11 $\rightarrow$ 10	—	—	—	$-15.8 \pm 0.3$	$-3.5 \pm 1.1$	$12.2 \pm 1.2$
10 $\rightarrow$ 9	—	—	—	$-12.2 \pm 0.3$	$3.0 \pm 1.1$	$15.1 \pm 1.2$
9 $\rightarrow$ 8	$-18.0 \pm 0.5$	$2.0 \pm 1.1$	$19.9 \pm 1.2$	$-0.5 \pm 0.3$	$8.8 \pm 1.1$	$9.3 \pm 1.2$
8 $\rightarrow$ 7	$12.3 \pm 0.4$	$23.5 \pm 1.1$	$11.1 \pm 1.1$	$10.7 \pm 0.3$	$15.5 \pm 1.2$	$4.9 \pm 1.2$
7 $\rightarrow$ 6	$21.0 \pm 0.5$	$27.2 \pm 1.1$	$6.2 \pm 1.2$	$16.0 \pm 0.3$	$17.6 \pm 1.2$	$1.6 \pm 1.2$
6 $\rightarrow$ 5	$24.2 \pm 0.4$	$29.9 \pm 1.2$	$5.7 \pm 1.3$	$19.1 \pm 0.3$	$16.9 \pm 1.2$	$-2.1 \pm 1.2$
5 $\rightarrow$ 4	$26.6 \pm 0.4$	$28.0 \pm 1.2$	$1.4 \pm 1.2$	$21.4 \pm 0.3$	$17.2 \pm 1.2$	$-4.1 \pm 1.2$
4 $\rightarrow$ 3	$29.0 \pm 0.5$	$27.6 \pm 1.1$	$-1.4 \pm 1.2$	$23.5 \pm 0.3$	$17.8 \pm 1.2$	$-5.7 \pm 1.2$
3 $\rightarrow$ 2	$30.9 \pm 0.4$	$27.8 \pm 1.2$	$-3.1 \pm 1.3$	$26.0 \pm 0.3$	$16.6 \pm 1.1$	$-9.4 \pm 1.2$
2 $\rightarrow$ 1	$32.4 \pm 0.5$	$22.0 \pm 1.3$	$-10.4 \pm 1.4$	$27.3 \pm 0.3$	$16.5 \pm 1.1$	$-10.8 \pm 1.1$
1 $\rightarrow$ 0	$36.1 \pm 0.4$	$15.4 \pm 1.2$	$-20.7 \pm 1.3$	$31.2 \pm 0.3$	$4.4 \pm 1.2$	$-26.7 \pm 1.2$
$\text{CH}_4@\text{water}^2$	$-10.1 \pm 0.2$	$17.9 \pm 0.7$	$28.0 \pm 0.7$	—	—	—

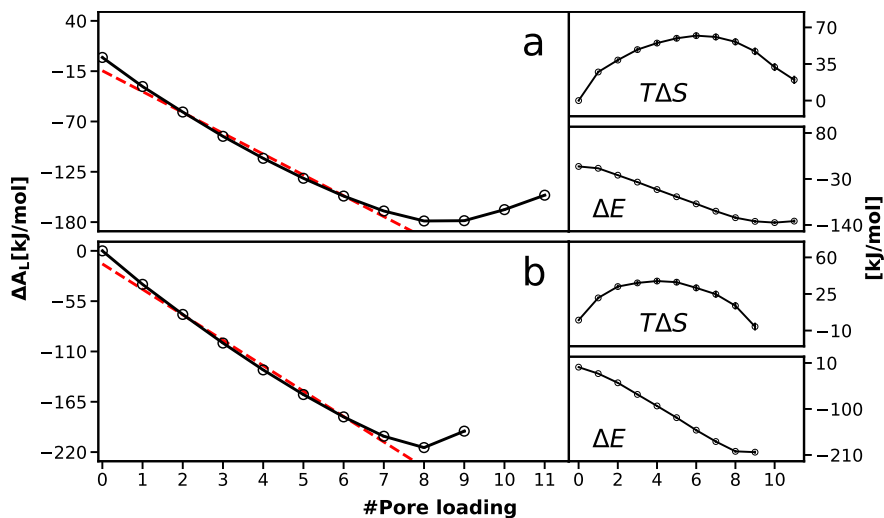


Figure S2: Cumulative transfer free energies from water ( $\Delta A_L$ ) of methane for the (7,7) system (a) and (6,6) system (b). A linear regression of the free energy, where the slope corresponds to the chemical potential of loading, is shown in red. Linear regressions used data from the first load up to the 7th and 9th loads for the (6,6) and the (7,7) systems, respectively. The panels on the right show the cumulative entropies and energies of transfer from water.

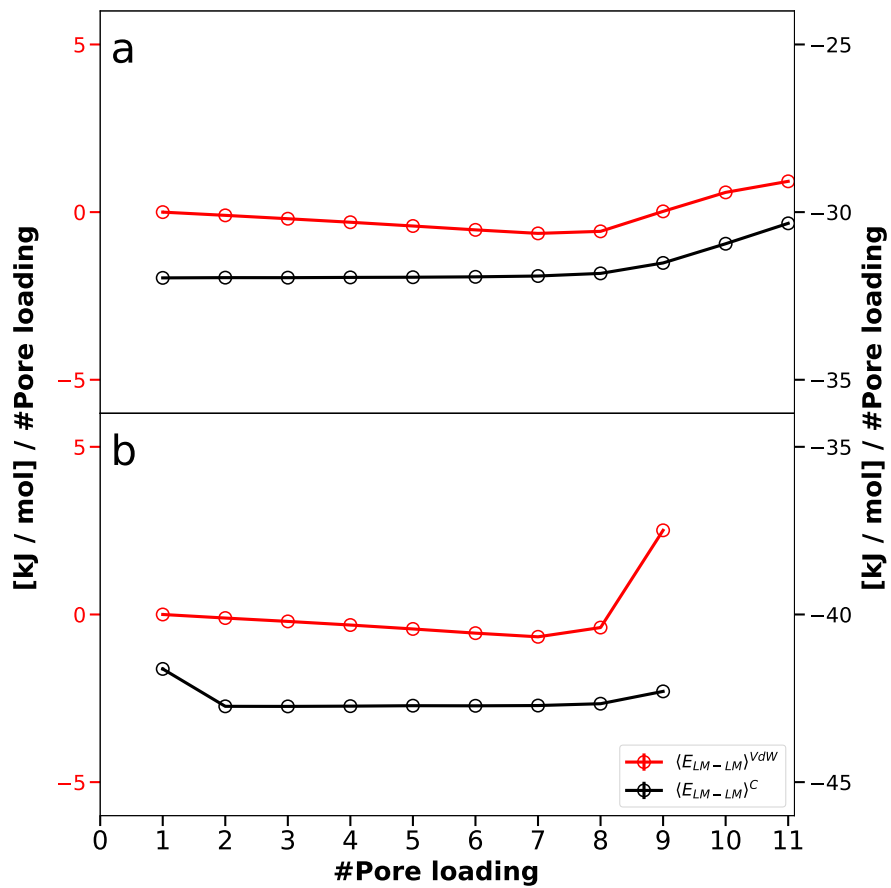


Figure S3: Normalised non-bonded interaction energies ( $E$ ) for the loaded molecule file components as a function of each loading state of methanol for the (6,6) system (a) and (7,7) system (b). Left y-axis: LM-LM interactions. Right y-axis: LM-T interactions. All energies are shown in the same scale. LM-T: loaded-molecules tube; LM-LM: loaded-molecules loaded-molecules. VdW: van der Waals.

## S3 Thermodynamic Integration

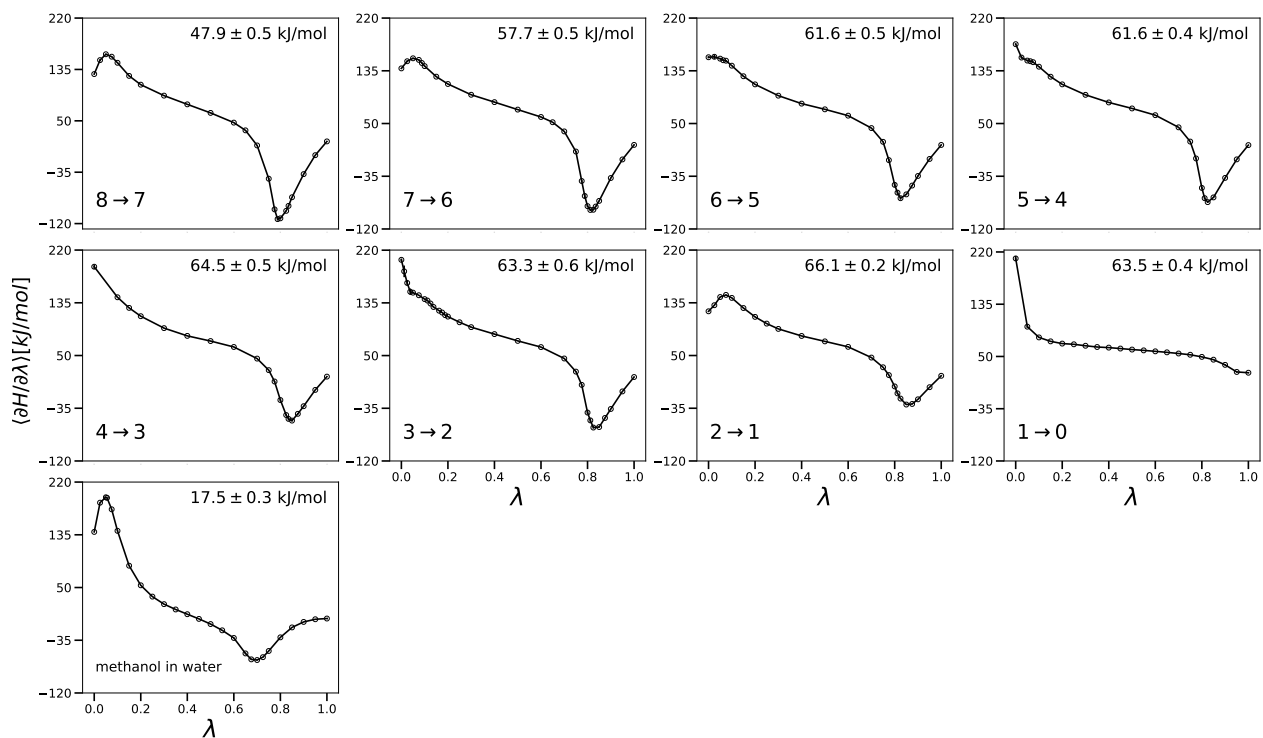


Figure S4: Thermodynamic integration perturbing a methanol molecule into dummy atoms at every loading state of the (6,6) carbon nanotube. The numerical value of the integral, employing the trapezoidal rule, is shown for each curve.

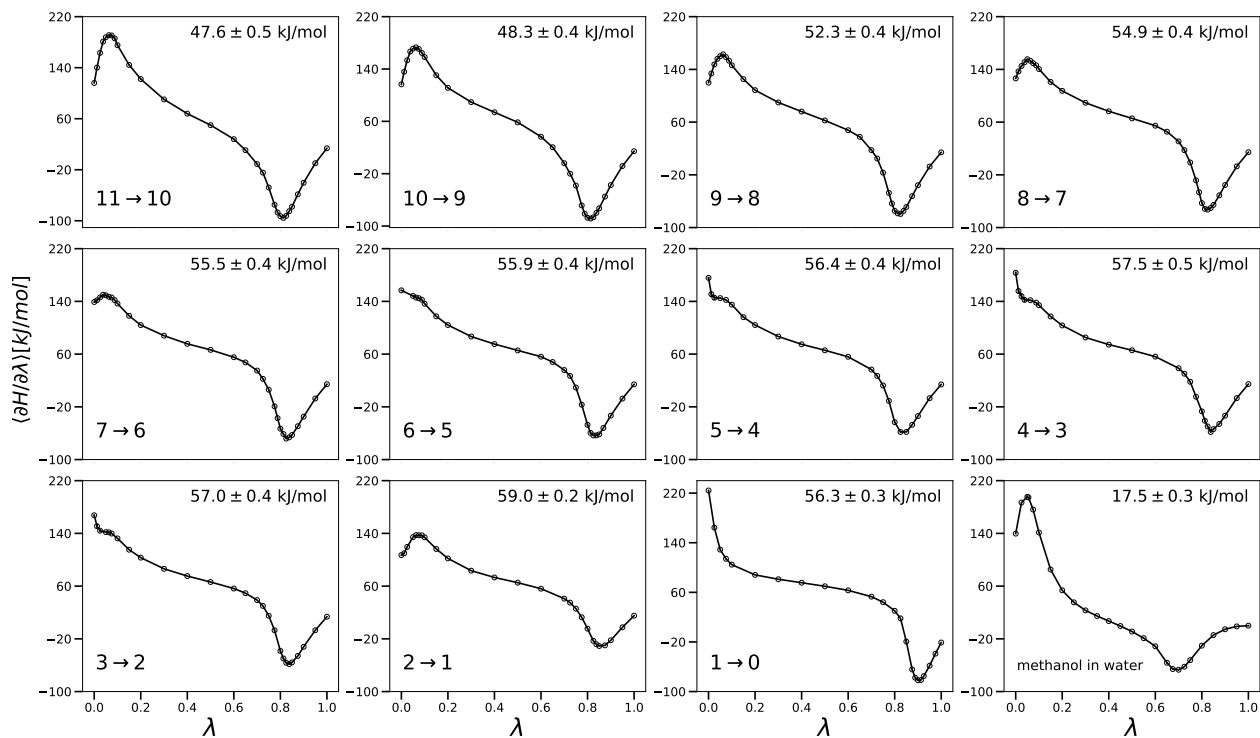


Figure S5: Thermodynamic integration perturbing a methanol molecule into dummy atoms at every loading state of the meth@(7,7) system. The numerical value of the integral, employing the trapezoidal rule, is shown for each curve.

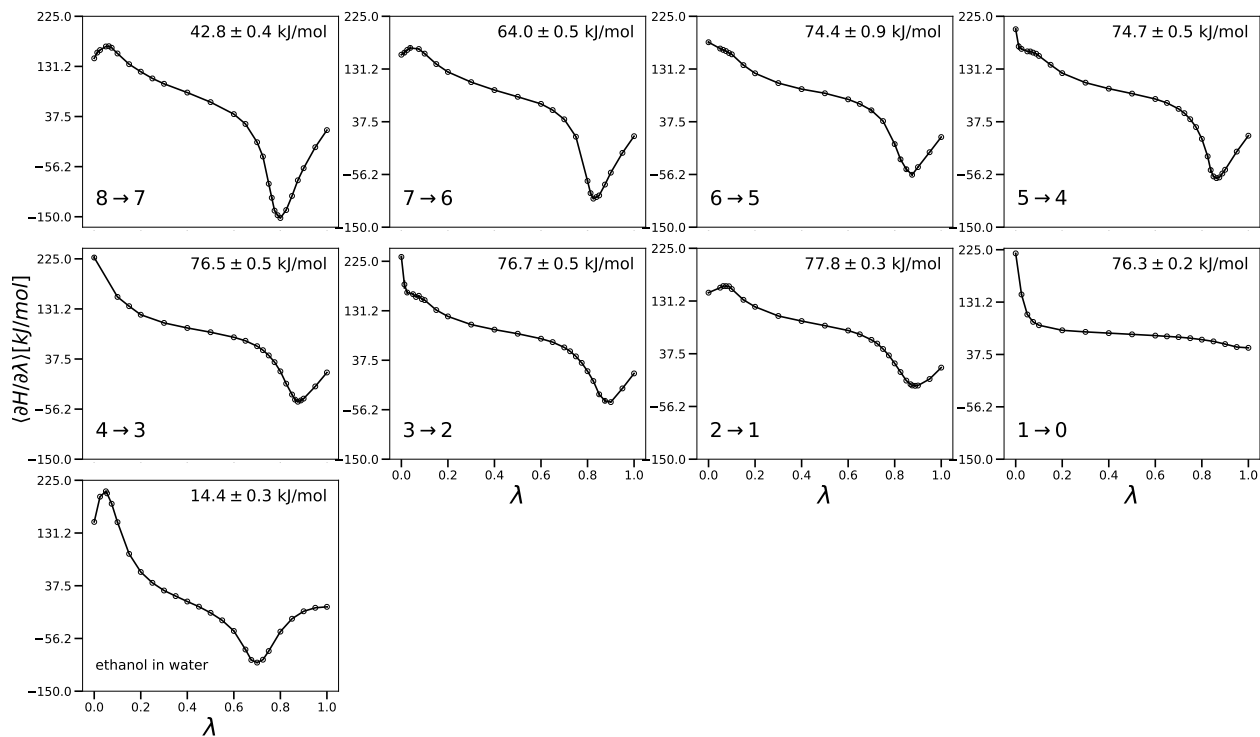


Figure S6: Thermodynamic integration perturbing an ethanol molecule into dummy atoms at every loading state of the eth@(7,7) system. The numerical value of the integral, employing the trapezoidal rule, is shown for each curve.

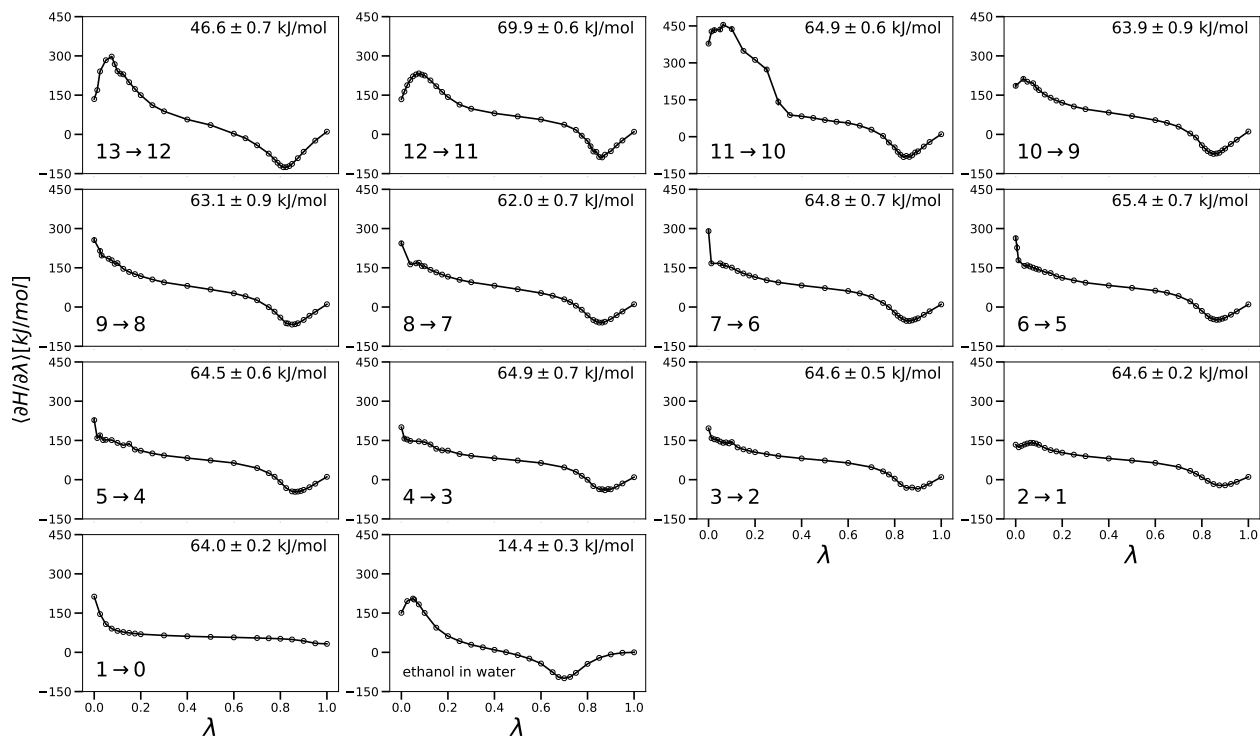


Figure S7: Thermodynamic integration perturbing an ethanol molecule into dummy atoms at every loading state of the eth@(8,8) system. The numerical value of the integral, employing the trapezoidal rule, is shown for each curve.

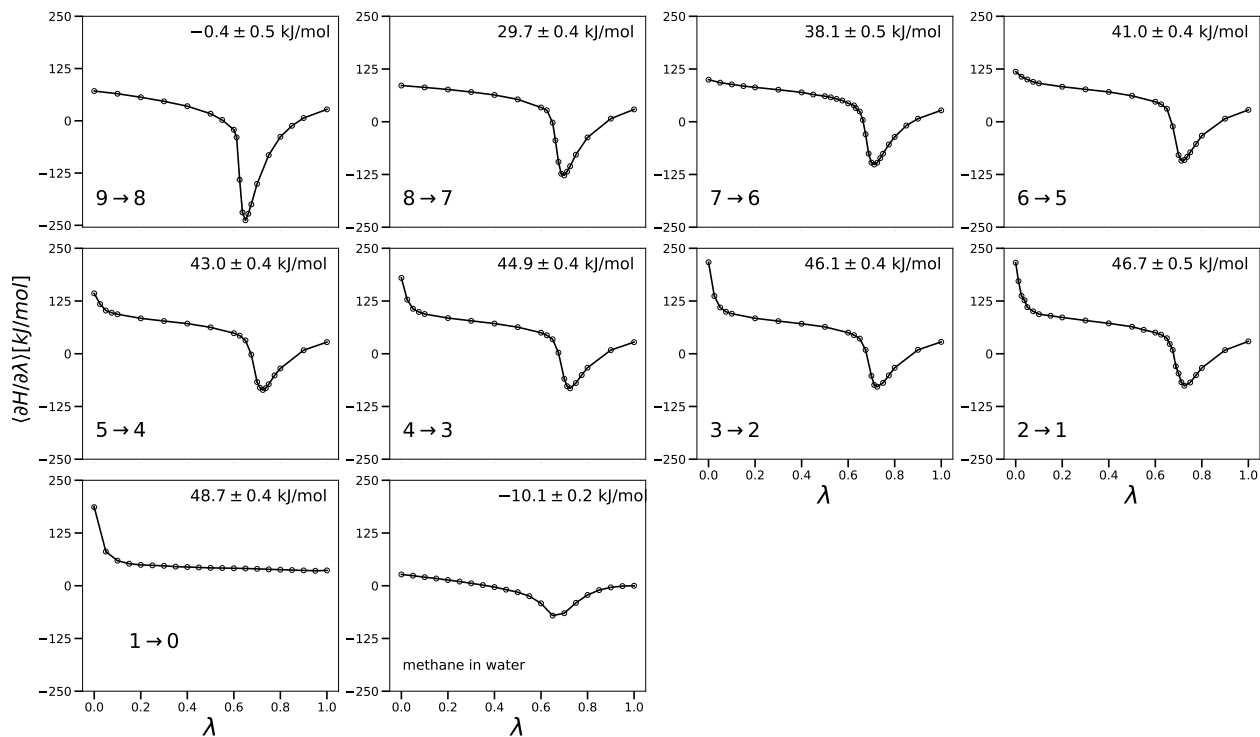


Figure S8: Thermodynamic integration perturbing a methane molecule into a dummy atom at every loading state of the (6,6) carbon nanotube. The numerical value of the integral, employing the trapezoidal rule, is shown for each curve.



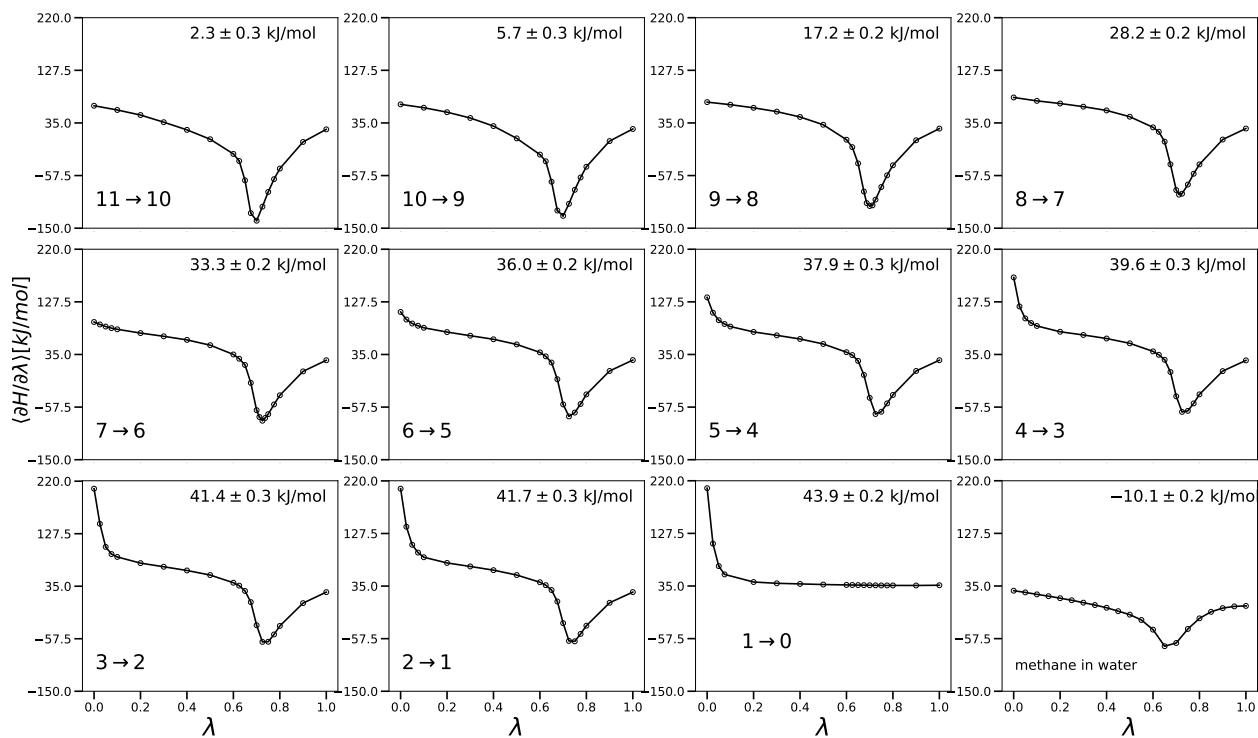


Figure S9: Thermodynamic integration perturbing a methane molecule into a dummy atom at every loading state of the (7,7) carbon nanotube. The numerical value of the integral, employing the trapezoidal rule, is shown for each curve.

## S4 Hydrogen Bonds

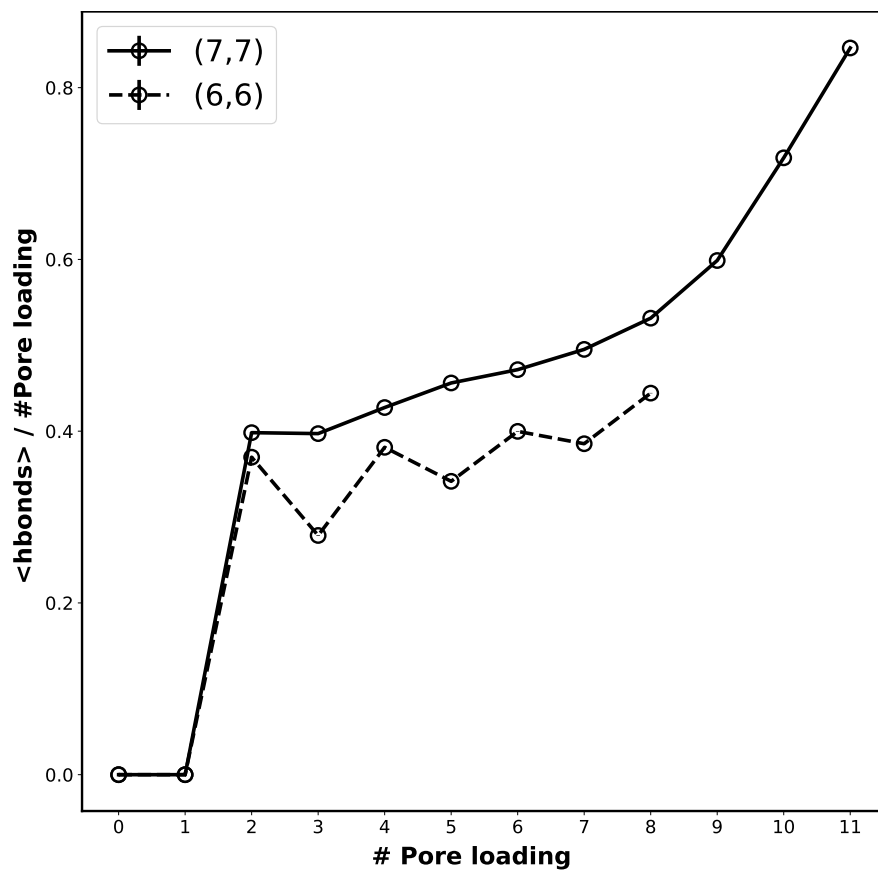


Figure S10: Average number of hydrogen bonds per methanol molecule as a function of the loading state for the (6,6) and (7,7) systems.

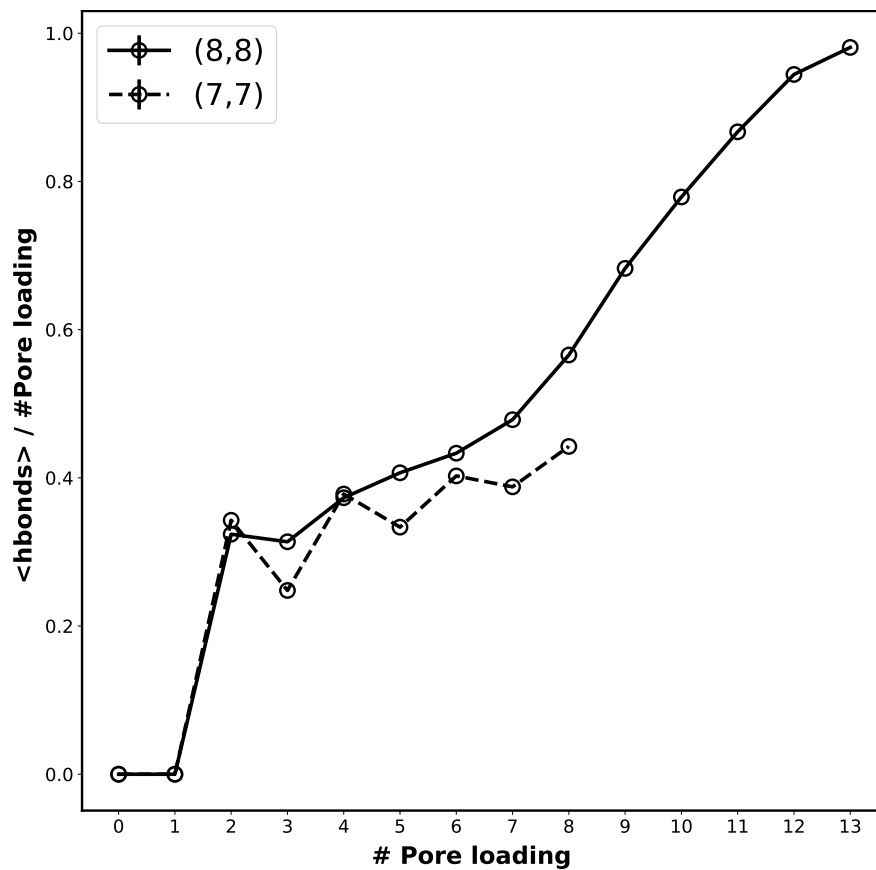


Figure S11: Average number of hydrogen bonds per ethanol molecule as a function of the loading state for the (7,7) and (8,8) systems.

## S5 Dipolar orientation

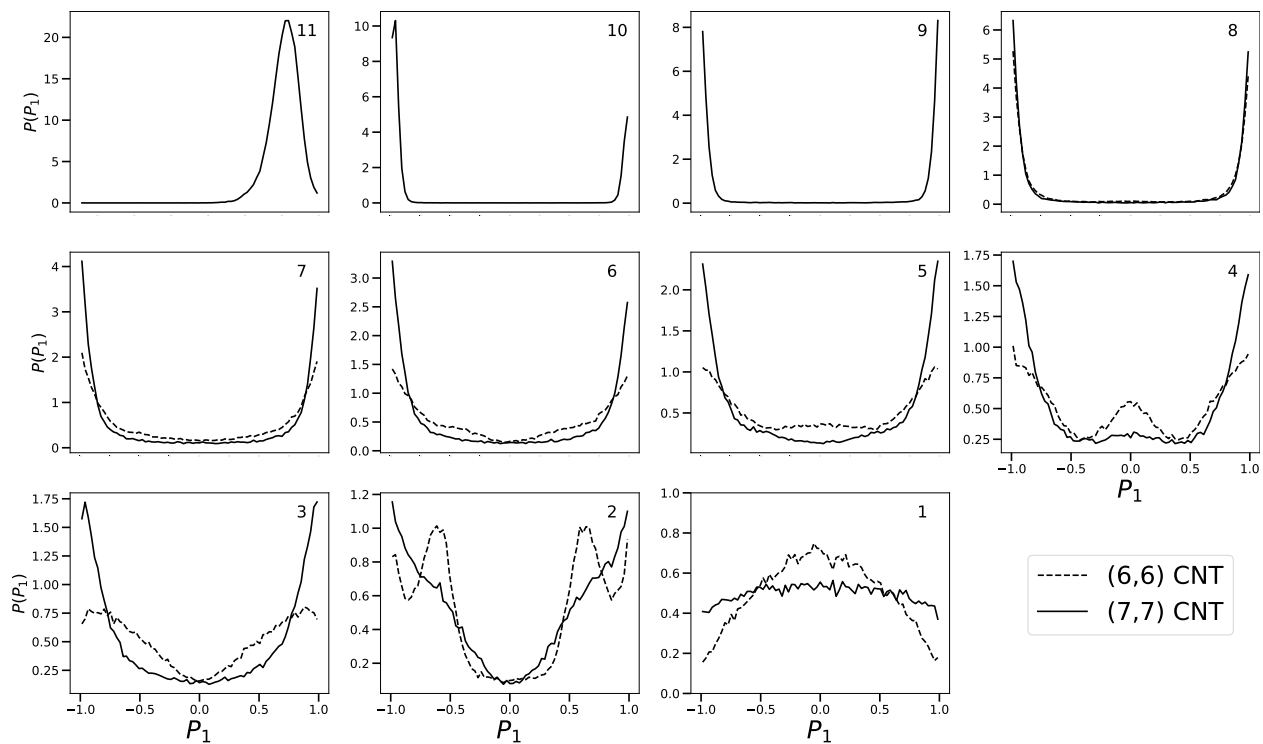


Figure S12: Distribution of  $P_1$  of methanol at each loading state for the (6,6) and (7,7) system.  $P_1$  is the cosine of the angle between the alcohol dipole and the  $z$ -axis

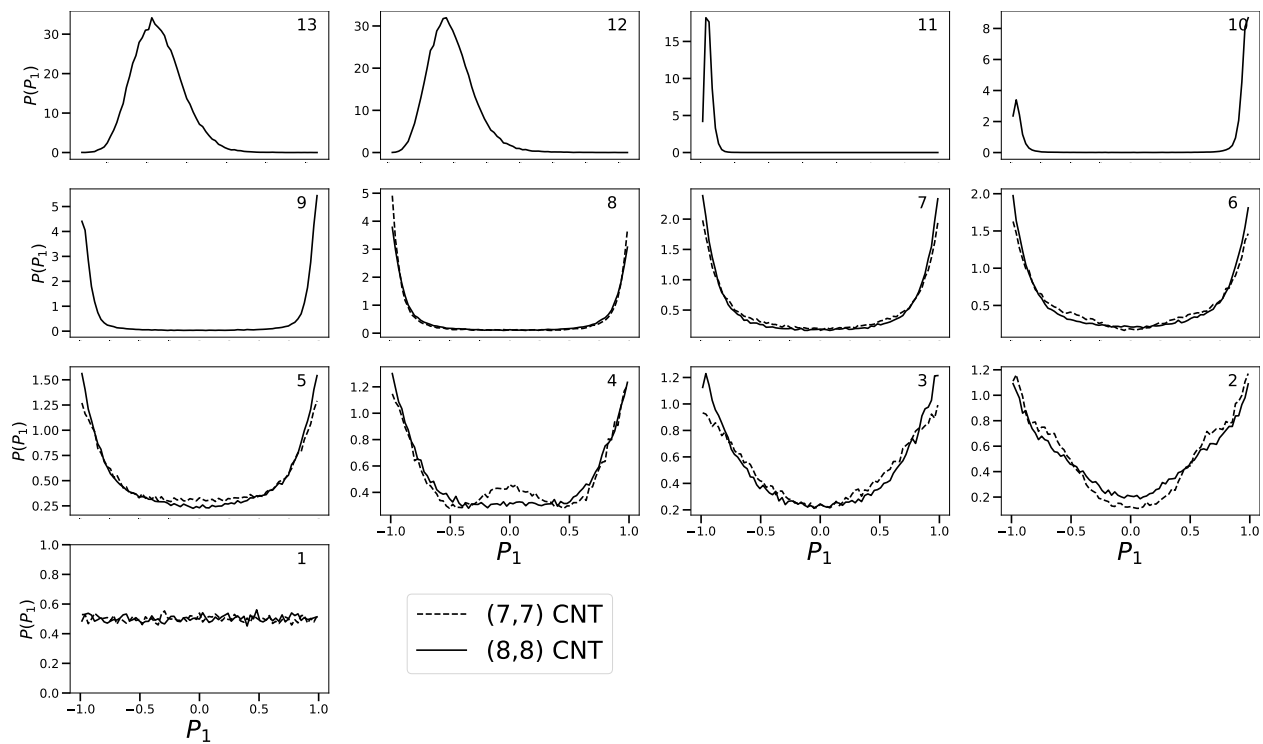


Figure S13: Distribution of  $P_1$  of ethanol at each loading state for the (7,7) and (8,8) system.  $P_1$  is the cosine of the angle between the alcohol dipole and the  $z$ -axis

## S6 Adsorption onto graphene

MD simulations of a single methanol, ethanol or methane molecule over a graphene monolayer solvated in water were run for 83 ns each. Graphene was modelled with the same parameters as the SWCNT (i.e.  $sp^2$  carbon atoms). Values for water were also obtained from the trajectories of 100 molecules of water in the methanol simulation.

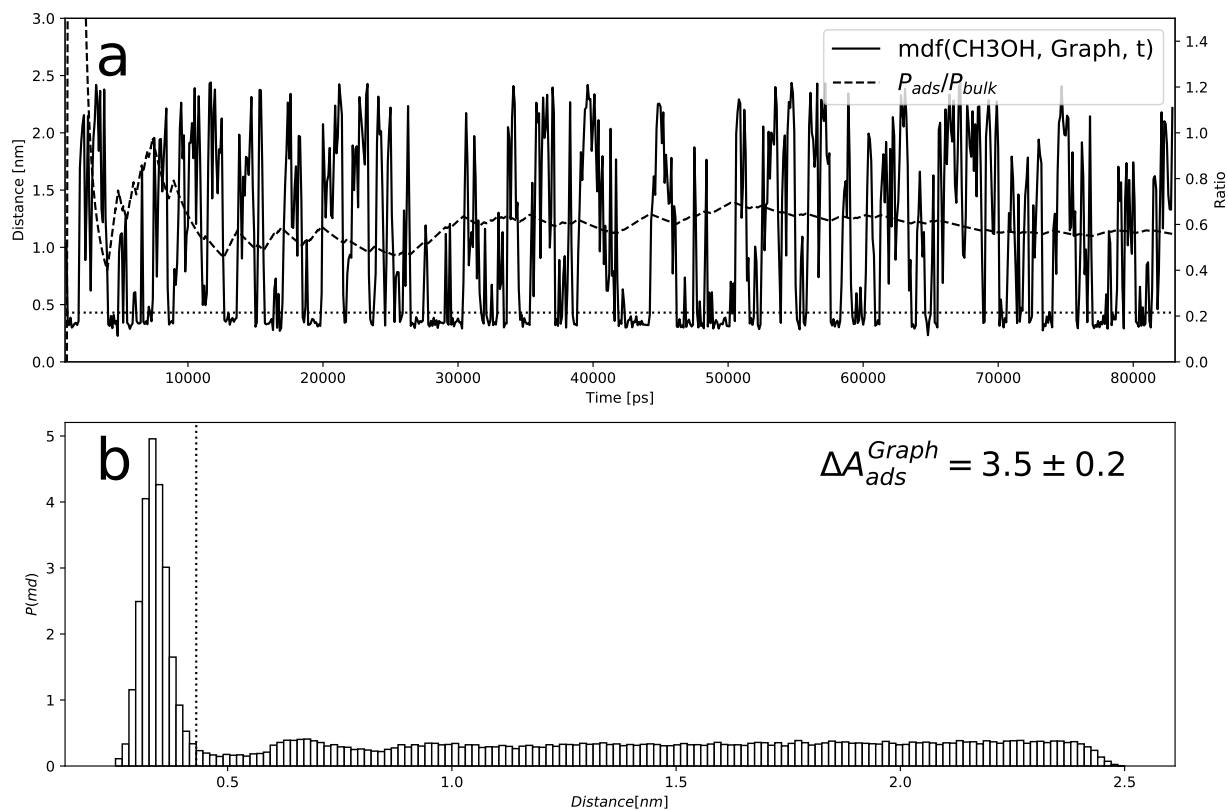


Figure S14: Minimum distance function (mdf) between a single methanol molecule in solution and a graphene monolayer. The mdf() is defined as returning the shortest distance among any pair of atoms of both molecules. a) The time evolution of the mdf and of the ratio between the adsorbed and free (in the bulk) states. b) Distribution of the mdf. In both plots the threshold used to differentiate the adsorbed and free states (0.43 nm) is delimited with a dotted line.

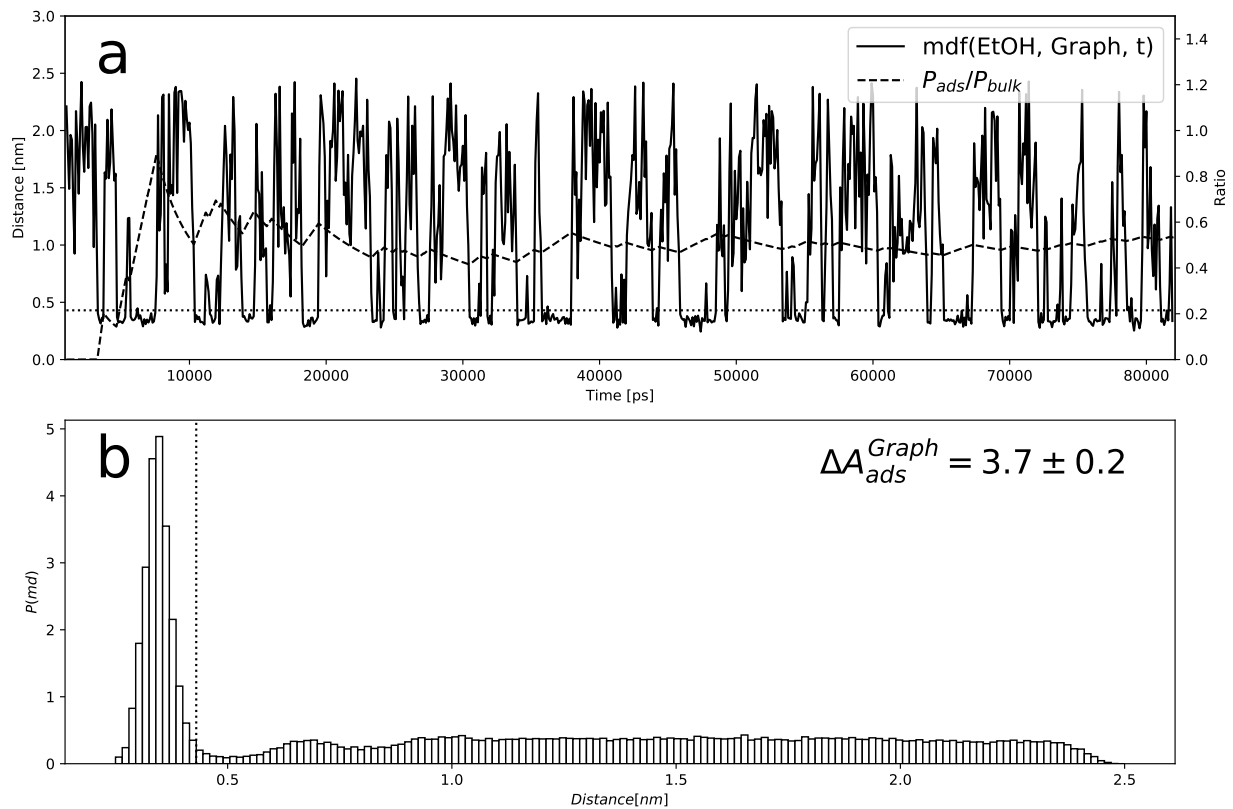


Figure S15: Minimum distance function (mdf) between a single ethanol molecule in solution and a graphene monolayer. The mdf() is defined as returning the shortest distance among any pair of atoms of both molecules. a) The time evolution of the mdf and of the ratio between the adsorbed and free (in the bulk) states. b) Distribution of the mdf. In both plots the threshold used to differentiate the adsorbed and free states (0.43 nm) is delimited with a dotted line.

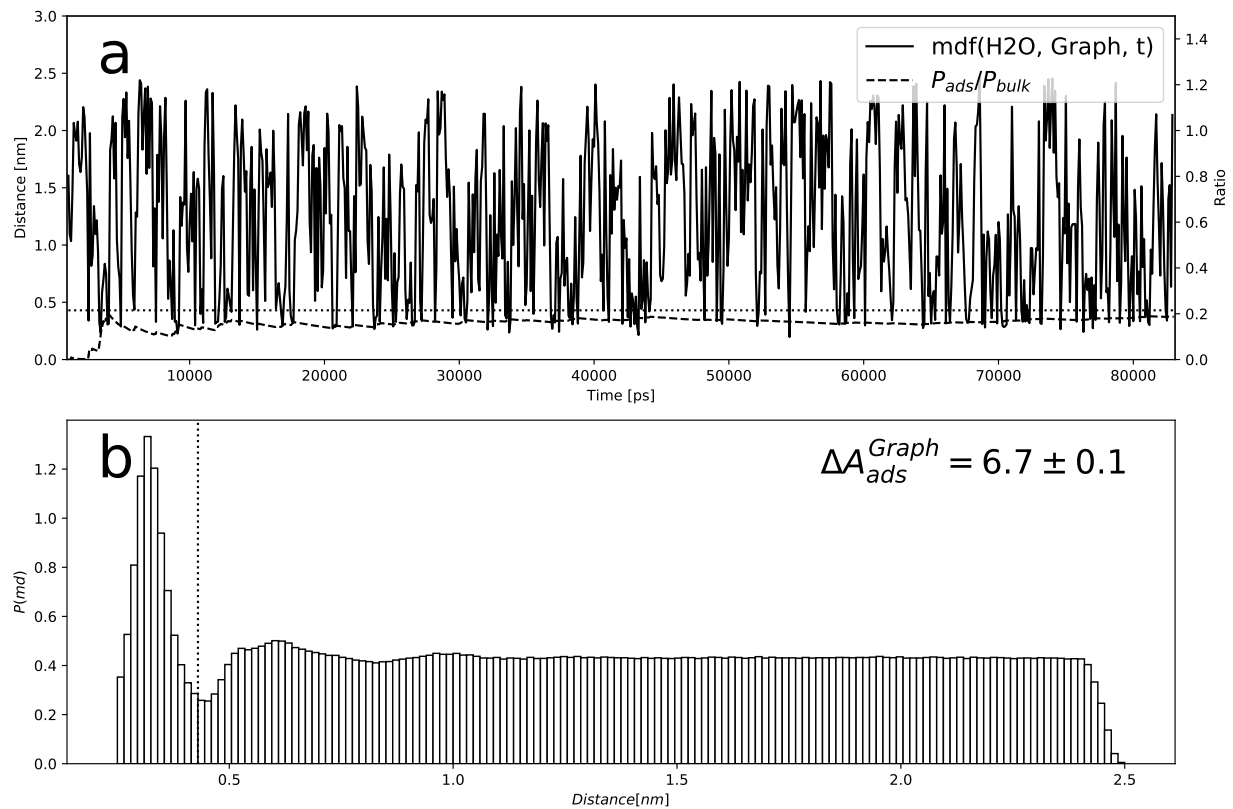


Figure S16: Minimum distance function (mdf) between molecules of water and a graphene monolayer. The mdf() is defined as returning the shortest distance among any pair of atoms of both molecules. a) The time evolution of the mdf and of the ratio between the adsorbed and free (in the bulk) states of a single water molecule. b) Distribution of the mdf for 100 water molecules. In both plots the threshold used to differentiate the adsorbed and free states (0.43 nm) is delimited with a dotted line.



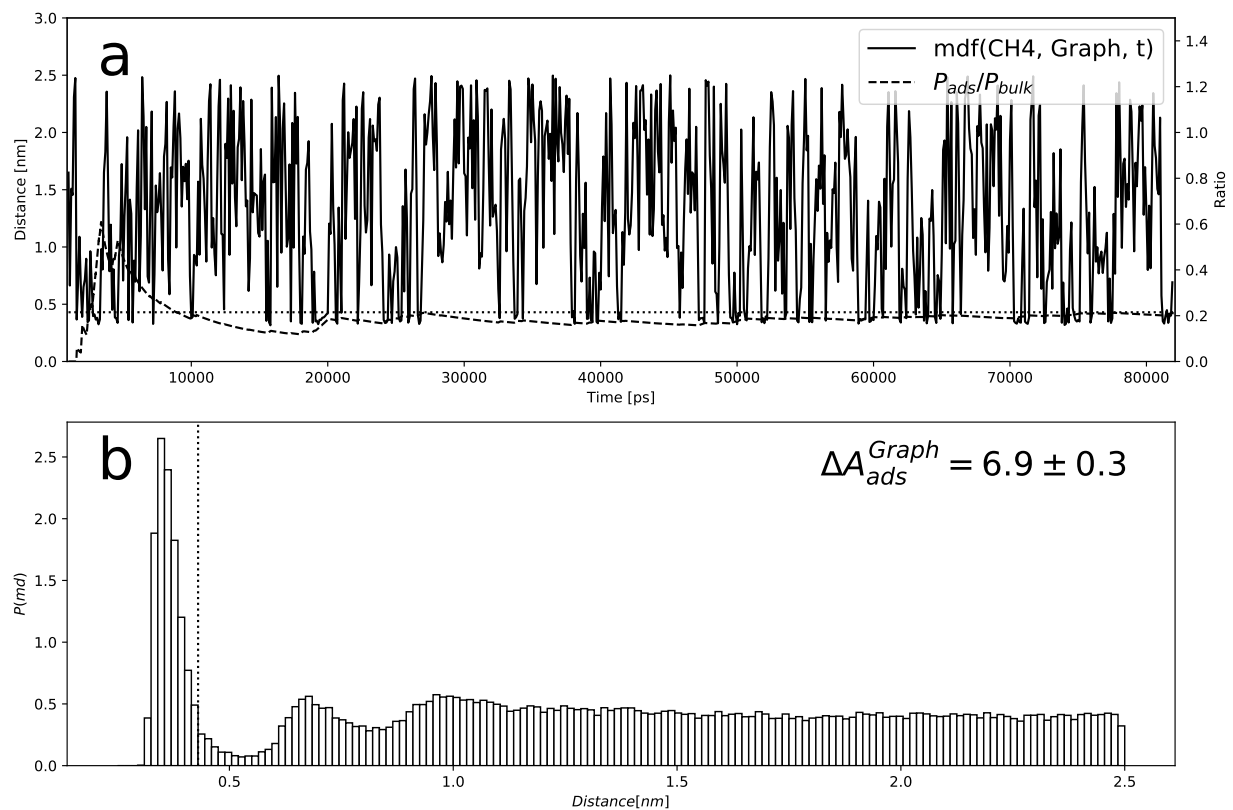


Figure S17: Minimum distance function (mdf) between methanol and graphene. The  $mdf()$  is defined as returning the shortest distance among any pair of atoms of both molecules. a) The time evolution of the mdf and of the ratio between the adsorbed and free (in the bulk) states. b) Distribution of the mdf. In both plots the limit used to differentiate the adsorbed and free states (0.43 nm) is delimited with as dotted line.