

## Supporting Information

### Deformation of microporous carbons during N<sub>2</sub>, Ar, and CO<sub>2</sub> adsorption: Insight from the density functional theory

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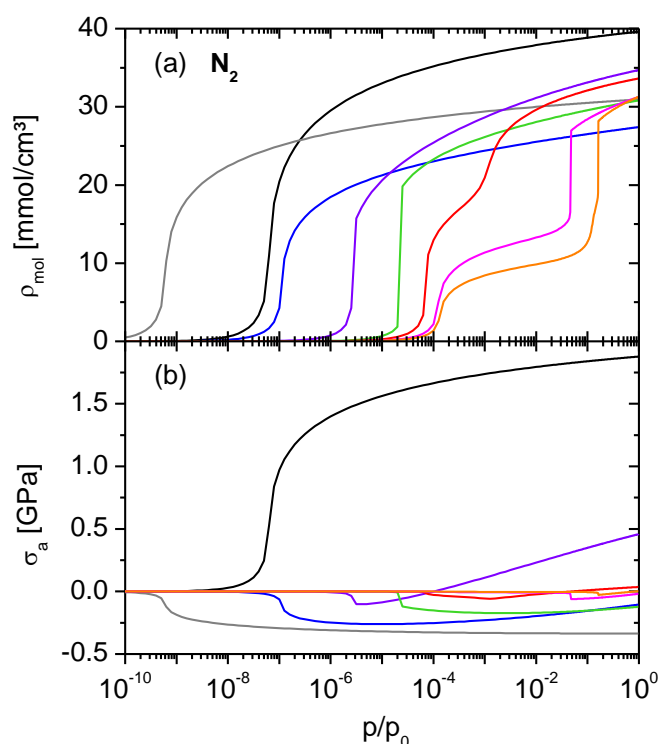


Figure S1: (a) Adsorption (given as average molar density  $\rho_{mol}$  of the adsorbate within the micropore) and (b) adsorption stress isotherms calculated by NLDFT for N<sub>2</sub> adsorption at 77 K. The respective pore widths are (from left to right) 4, 3, 5, 6, 8, 10, 15 and 20 Å.

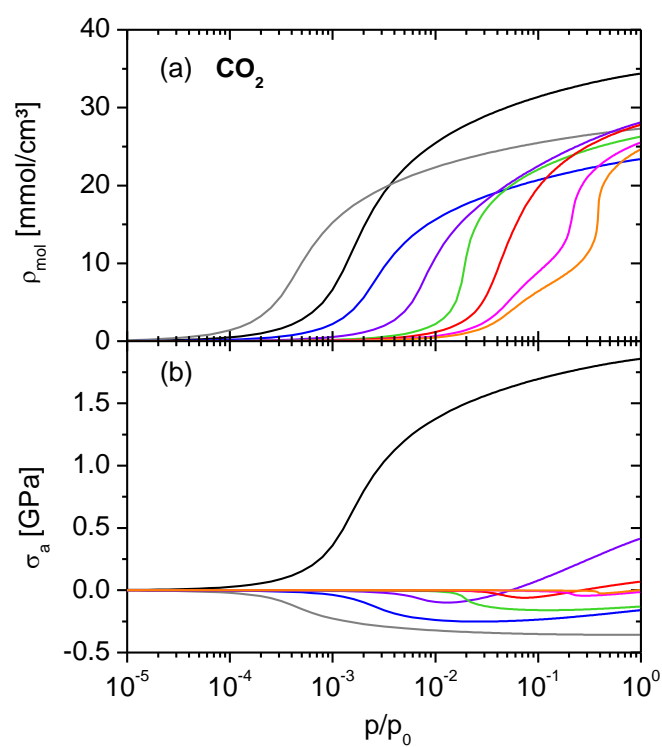


Figure S2: (a) Adsorption (given as average molar density  $\rho_{mol}$  of the adsorbate within the micropore) and (b) adsorption stress isotherms calculated by NLDFT for  $\text{CO}_2$  adsorption at 273 K. The respective pore widths are (from left to right) 4, 3, 5, 6, 8, 10, 15 and 20 Å.

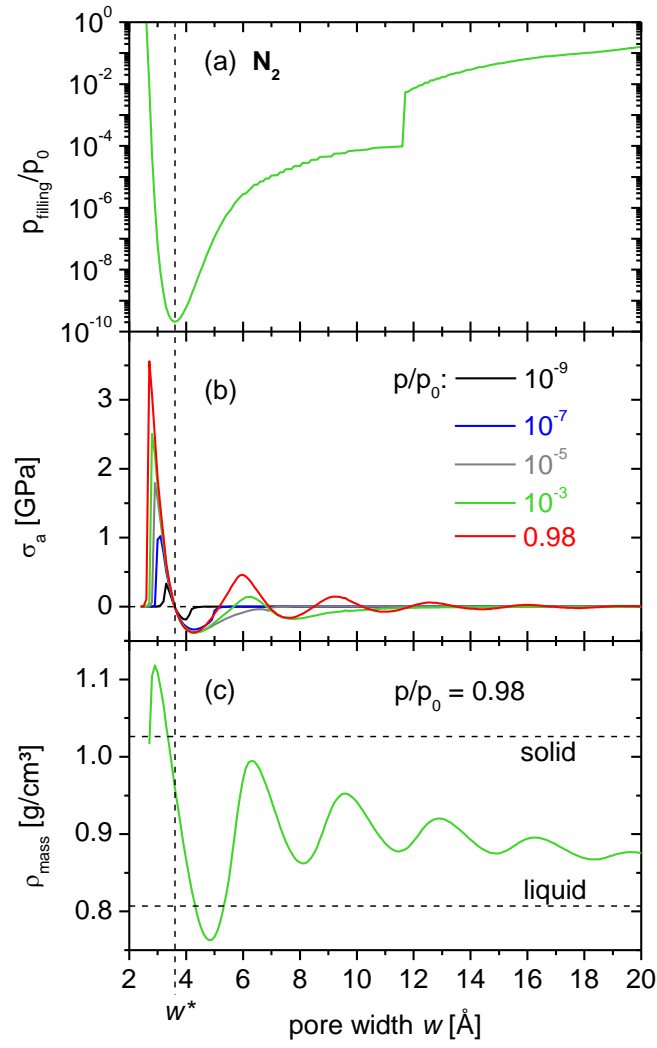


Figure S3: (a) Pore filling pressure  $p_{filling}/p_0$ , (b) adsorption stress  $\sigma_a$  and (c) adsorbate mass density  $\rho_{mass}$  calculated by NLDFT for  $N_2$  adsorption at 77 K as a function of the pore width  $w$ .  $w^*$  marks the minimum of  $p_{filling}/p_0$ . In (c) the dashed horizontal lines indicate the densities of liquid  $N_2$  at 77 K<sup>59</sup> and solid  $N_2$  at 21 K<sup>54</sup>.

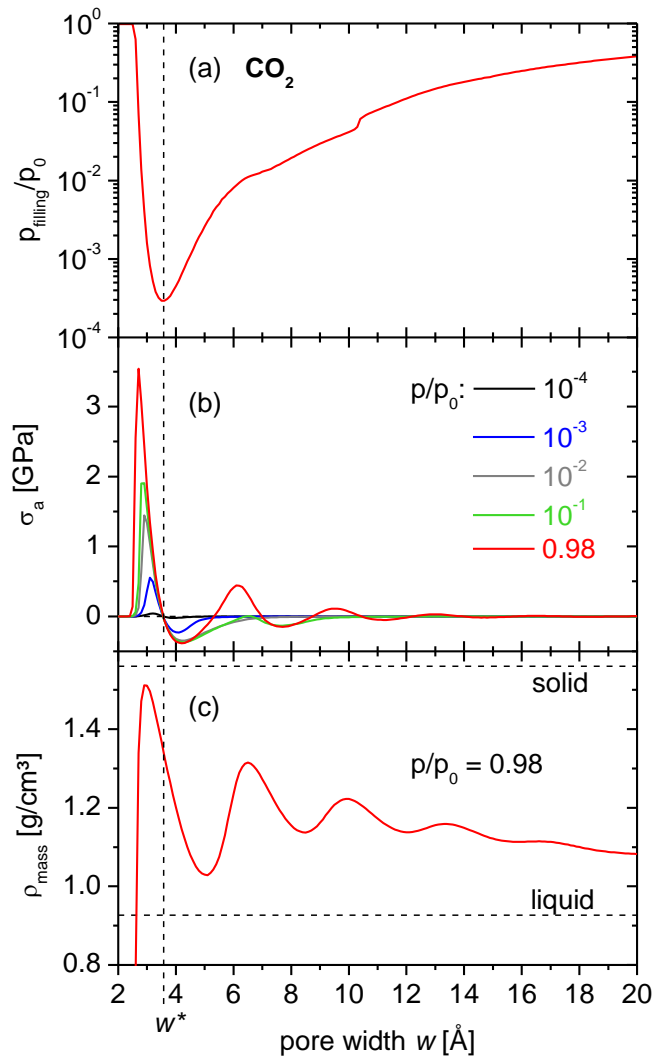


Figure S4: (a) Pore filling pressure  $p_{\text{filling}}/p_0$ , (b) adsorption stress  $\sigma_a$  and (c) adsorbate mass density  $\rho_{\text{mass}}$  calculated by NLDFT for CO<sub>2</sub> adsorption at 273 K as a function of the pore width  $w$ .  $w^*$  marks the minimum of  $p_{\text{filling}}/p_0$ . In (c) the dashed horizontal lines indicate the densities of liquid CO<sub>2</sub> at 273 K<sup>59</sup> and solid CO<sub>2</sub> at 194 K<sup>54</sup>.

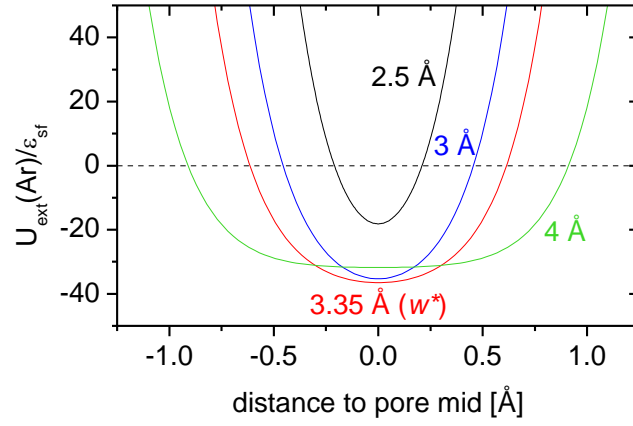


Figure S5: The external potential  $U_{ext}$  (Equation 10) for Ar adsorption in pores of width  $w$  equal to 2.5, 3, 3.35 and 4 Å.  $w = w^* = 3.35$  Å corresponds to the minimum of the relative filling pressure.

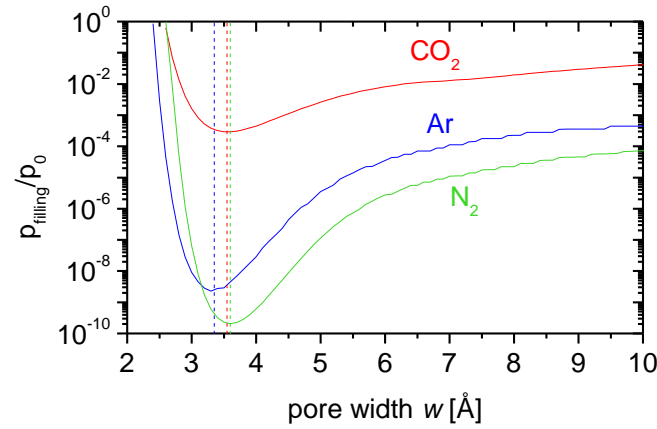


Figure S6: Relative pore filling pressure  $p_{filling}/p_0$  as a function of the pore width  $w$  for the adsorbates Ar (77 K),  $N_2$  (77 K) and  $CO_2$  (273 K). The dotted lines mark the minima  $w^*(Ar) \approx 3.35$  Å,  $w^*(CO_2) \approx 3.55$  Å and  $w^*(N_2) \approx 3.6$  Å.

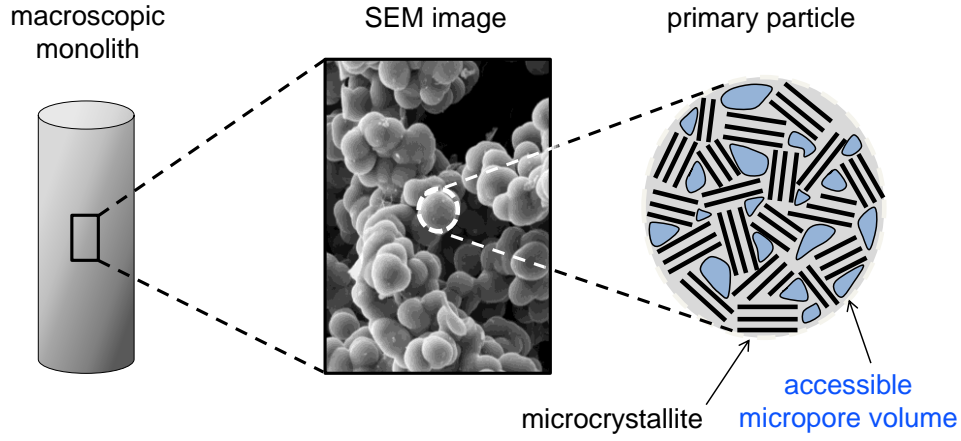


Figure S7: Schematic of the structure of the sample investigated in ref 31. The internal structure of the monolithic sample rod is a disordered 3-dimensional network of approximately spherical primary particles. The primary particles in turn consist of randomly orientated microcrystallites, whose interspaces form accessible micropore volume. See also ref 31 and references therein.

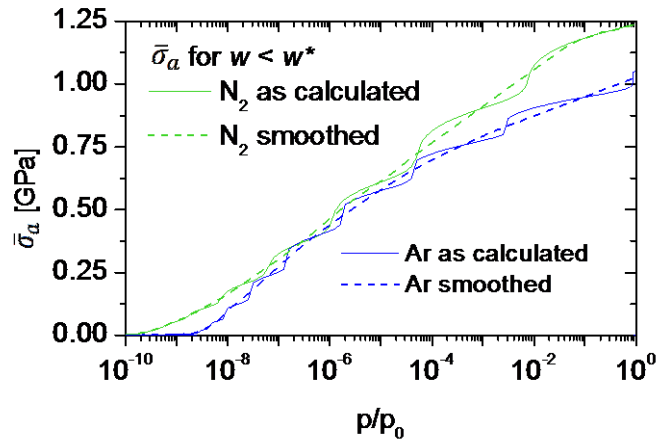


Figure S8: As discussed in the main part of this work the assumption of homogenous pore walls leads to a step like pore filling in the computational adsorption isotherms at cryogenic temperatures (compare Figures 1a and S2a). These filling steps are also found in the corresponding computational strain isotherms (compare Figures 1b and S2b). Since the number of our computational isotherms is finite (10 pores per Angstrom), the calculated average adsorption stress  $\bar{\sigma}_a$  (Eq. 17) for the rather small interval of expansive pores  $2 \text{ \AA} < w < w^*$  also exhibits an unphysical stepwise behavior. Solutions to this problem would be either a drastically increased number of computational isotherms for pore widths  $w < w^*$  or a smoothing of  $\bar{\sigma}_a$  in the respective regime. Here we chose the latter. Figure S6 shows the average adsorption stress  $\bar{\sigma}_a$  calculated according to Equation 17 for  $w < w^*$  both for Ar and  $\text{N}_2$  adsorption (solid lines) and respective smoothed data (dotted lines).