

## Quantification of the confinement effect in microporous materials

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### Supporting Info

#### Principal curvatures of a surface in 3D-space

In the case of three-dimensional surfaces the concept of curvature can be used as follows: for any point P on a surface (Fig. S1), we can find a unique tangent plane (T) and its corresponding normal vector N. The intersection of a plane containing the normal vector N with the surface defines a two-dimensional curve (c). If the plane containing the normal vector is fully rotated about the normal vector by increasing the angle  $\theta$ , we obtain an infinite set of curves  $c(\omega)$ , each having a curvature  $\kappa(\omega)$ . The mean curvature (KH) at the point P is obtained by averaging  $\kappa$  over all angles  $\omega$ .

$$KH = \frac{1}{2\pi} \int_0^{2\pi} \kappa(\omega) d\omega = \frac{1}{2\pi} \int_0^{2\pi} [\kappa_1 \cos^2 \omega + \kappa_2 \sin^2 \omega] d\omega = \frac{1}{2} (\kappa_1 + \kappa_2) \quad (1)$$

where  $\kappa_1$  and  $\kappa_2$ , are the minimum and maximum values of  $\kappa$ . These values are known as the principal curvatures. Therefore KH is the arithmetic mean of the principal curvatures.

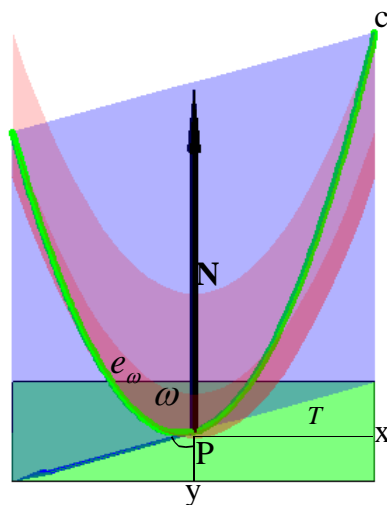


Fig. S1. Illustration of the determination of the curvature in 3D-space.

### Experimental Heats of Adsorption of CH<sub>4</sub> and CO<sub>2</sub>:

**Table 1.** Experimental zero coverage heats of adsorption of CO<sub>2</sub> and CH<sub>4</sub>

Framework	$\Delta H$ , CH <sub>4</sub> , kJ/mol	Ref.	$\Delta H$ , CO <sub>2</sub> , kJ/mol	Ref.
<b>MFI</b>	21	1	27	1
<b>FAU</b>	14	2	17	3
ZIF-8	12	4	16 <sup>a</sup>	5
IRMOF-1	9.3	6	15	6
<b>BEA</b>	19	3	21	3
<b>AFI</b>	14	This work	--	--

<sup>a</sup> Calculated in reference <sup>5</sup> using molecular simulations by the fluctuation method.

### Determination of the heat of adsorption of CH<sub>4</sub> in zeolite AFI:

GCMC (Grand Canonical Monte Carlo) simulations combined with a bias scheme for the insertion of the center of mass of the guest molecules were performed to calculate the heats of adsorption of CH<sub>4</sub> with the GIBBS code v.9.2. Due to the spherical model consisting in a single LJ centre used to describe the CH<sub>4</sub> molecule (the force field parameters are those shown in Table 2 of the main text), only insertions and deletions were used to sample the configurational space. Systems were allowed to equilibrate for at least one million MC steps followed by production runs of at least 10 million MC steps. The atomic positions of the solid were frozen during the simulations and taken from [www.iza-structure.org](http://www.iza-structure.org).

Isosteric heats of adsorption  $q_{st}$  were calculated according to:

$$q_{st} = H_b - \left[ \frac{\partial(U_a)}{\partial N} \right]_{T,V}$$

where  $H_b$  is the enthalpy of the bulk phase and  $U_a$  is the energy of the adsorbed phase. Using a fluctuations method with ideal gas assumptions under Henry's regime, the isosteric heats can be readily calculated from GCMC simulation according to:

$$q_{st} = RT - \frac{\langle U_{ext}^s N \rangle - \langle U_{ext}^s \rangle \langle N \rangle}{\langle N^2 \rangle - \langle N \rangle^2}$$

where  $U_{ext}^s$  is the intermolecular energy of the adsorbed phase and  $N$  is the number of adsorbed molecules. The angle brackets denote averages in the grand canonical ensemble.

## References

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