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Adsorption under nanoconfinement: A theoretical-computational study revealing significant enhancement beyond the Langmuirian levels

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Supplementary Information (ESI)

Statistical-mechanical derivations

1. The case of n adsorbed molecules (one adsorbed molecule per surface site)

Considering equilibrium adsorption of an ideal gas in a closed "stoichiometric" nanosystem including overall n molecules capable to be adsorbed on a set of n sites, the canonical partition function is given by,

$$Q_n = \sum_{l=0}^{n} \frac{(nv^{pre}/\Lambda^3)^{n-l}}{(n-l)!} \frac{n!}{l!(n-l)!} z^l, \tag{S1}$$

where v^{pre} is the preadsorption volume per molecule, $\Lambda = \left(\frac{h^2}{2\pi mkT}\right)^{\frac{1}{2}}$ denotes the thermal de Broglie wavelength, and $z \equiv exp(-\beta E_{ads})$. The average coverage and pressure are given by,

$$\theta_n = \frac{1}{Q_n} \sum_{l=0}^{n} \frac{l}{n} \frac{(nv^{pre}/\Lambda^3)^{n-l}}{(n-l)!} \frac{n!}{l!(n-l)!} z^l, \tag{S2}$$

and

$$p_n = p^{pre}(1 - \theta_n), \tag{S3}$$

respectively, where $p^{pre} = kT/v^{pre}$.

2. Multiple adsorbed molecules per surface site

Considering a closed "stoichiometric" nanosystem that comprises k distinguishable adsorption sites capable of binding up to s molecules per site (maximum $n = ks$ molecules), the canonical partition function is given by,

$$Q_n^{(s)} = \sum_{l=0}^{n} \frac{(nv^{pre}/\Lambda^3)^{n-l}}{(n-l)!} g(l,k,s) z^l, \tag{S4}$$

where the number of distributions of l molecules on k sites is given by the sum[1],

$$g(l,k,s) = \sum_{j=0}^{k} (-1)^j \binom{k}{j} \binom{k+l-j(s+1)-1}{k-1}. \tag{S5}$$

The average coverage and pressure read,

$$\theta_n^{(s)} = \frac{1}{Q_n} \sum_{l=0}^{n} \frac{l}{k} \frac{(nv^{pre}/\Lambda^3)^{n-l}}{(n-l)!} g(l,k,s) z^l, \tag{S6}$$

and

$$p_n^{(s)} = \frac{1}{Q_n} \sum_{l=0}^{n} (n-l) \frac{kT}{nv^{pre}} \frac{(nv^{pre}/\Lambda^3)^{n-l}}{(n-l)!} g(l,k,s) z^l. \tag{S7}$$

In the thermodynamic limit, the grand canonical partition function for adsorption site in contact with a macroscopic reservoir of ideal gas having chemical potential $\mu = kT \, ln \frac{p\Lambda^3}{kT}$ (determined by pressure and temperature) is,

$$\Xi = \sum_{i=0}^{s} q^i = \frac{1-q^{s+1}}{1-q}, \tag{S8}$$

where

$$q \equiv exp[-\beta(E_{ads} - \mu)] = z\frac{p\Lambda^3}{kT} = pK_L. \tag{S9}$$

Correspondingly, the generalized adsorption isotherm is given by,

$$\theta = \frac{\partial \, ln \, \Xi}{\partial(\beta\mu)} = \frac{q+(sq-s-1)q^{s+1}}{(1-q)(1-q^{s+1})} = \frac{pK_L+(spK_L-s-1)(pK_L)^{s+1}}{(1-pK_L)[1-(pK_L)^{s+1}]}, \tag{S10}$$

For the case $s = 1$ it coincides with the Langmuir isotherm.

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The differential-equation method: Analytical solution and limiting cases

As derived elsewhere[2], the adsorption equilibrium is described by the differential equation,

$$\frac{1}{n}\frac{\partial \theta_n}{\partial ln K_L} = \frac{\theta_n}{p^{pre}K_L} - (1-\theta_n)^2. \tag{S11}$$

Its analytical solution gives the coverage,

$$\theta_n = 2 + \frac{1}{p^{pre}K_L} + \frac{1}{n}\left[1 - (n+1)\frac{L_{N+1}\left(-\frac{n}{p^{pre}K_L}\right)}{L_N\left(-\frac{n}{p^{pre}K_L}\right)}\right]. \tag{S12}$$

with $L_n(x)$ denoting the Laguerre polynomial[3]. An explicit expression of the power-series expansion for the Laguerre polynomials is given by[3],

$$L_n(x) = (-1)^{-n}\left[\frac{x^n}{n!} - \frac{nx^{n-1}}{1!(n-1)!} + \frac{n(n-1)x^{n-2}}{2!(n-2)!} - \cdots - (-1)^n nx + (-1)^n\right], \tag{S13}$$

where $x \equiv -\frac{n}{p^{pre}K_L}$ in the present case.

1) When v^{pre} is small, then $p^{pre}K_L$ is large, x is small and its higher powers can be neglected,

$$L_n(x) \approx (-1)^{-n}[-(-1)^n nx + (-1)^n]. \tag{S14}$$

Correspondingly,

$$\frac{L_{n+1}(x)}{L_n(x)} \approx \frac{(-1)^{-n-1}[-(-1)^{n+1}(n+1)x + (-1)^{n+1} + \cdots]}{(-1)^{-n}[-(-1)^n nx + (-1)^n + \cdots]} = 1 - x. \tag{S15}$$

Therefore,

$$\theta_n \approx 1 - \frac{n}{p^{pre}K_L}, \tag{S16}$$

for the present case of large $p^{pre}K_L$, namely, the adsorption is close to completion. Furthermore, since $p_n = p^{pre}(1-\theta_n)$ the pressure reaches a finite cut-off value $p_n^{max} = \frac{n}{K_L}$ (Fig. S1, see also Fig.1a).

2) When v^{pre} is large, then $p^{pre}K_L$ is small, x is largely negative, and its lower powers can be neglected, so

$$L_n(x) \approx (-1)^{-n}\frac{x^n}{n!}\left[1 - \frac{n^2}{x} + \frac{n^2(n-1)^2}{2x^2}\right]. \tag{S17}$$

Correspondingly,

$$\frac{L_{n+1}(x)}{L_n(x)} \approx \frac{(-1)^{-n-1}\frac{x^{n+1}}{(n+1)!}\left[1 - \frac{(n+1)^2}{x} + \frac{n^2(n+1)^2}{2x^2}\right]}{(-1)^{-n}\frac{x^n}{n!}\left[1 - \frac{n^2}{x} + \frac{n^2(n-1)^2}{2x^2}\right]} = -\frac{x}{n+1}\left(1 - (2n+1)\frac{1}{x} - n^2\frac{1}{x^2}\right), \tag{S18}$$

and

$$\theta_n \approx p^{pre}K_L, \tag{S19}$$

i.e., the coverage does not depend on the number of molecules and the NCEEA effect vanishes.

References

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2. L. Rubinovich and M. Polak, arXiv:2004.00651. 2020.
3. K. B. Oldham, J. C. Myland and J. Spanier, *An atlas of functions*, Springer Science+Business Media New York, 2009.
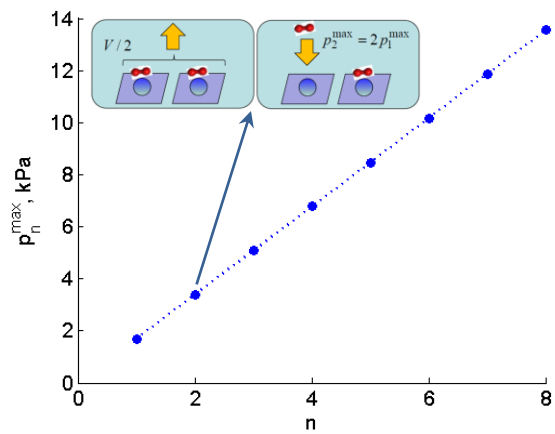
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Fig. S1 The cut-off (maximal) pressure increases linearly with system size. Insets: compared to the smallest 1-molecule system (Fig.1a), desorption from the twice larger number of sites in the 2-molecule system is counterbalanced by a twice higher pressure.