

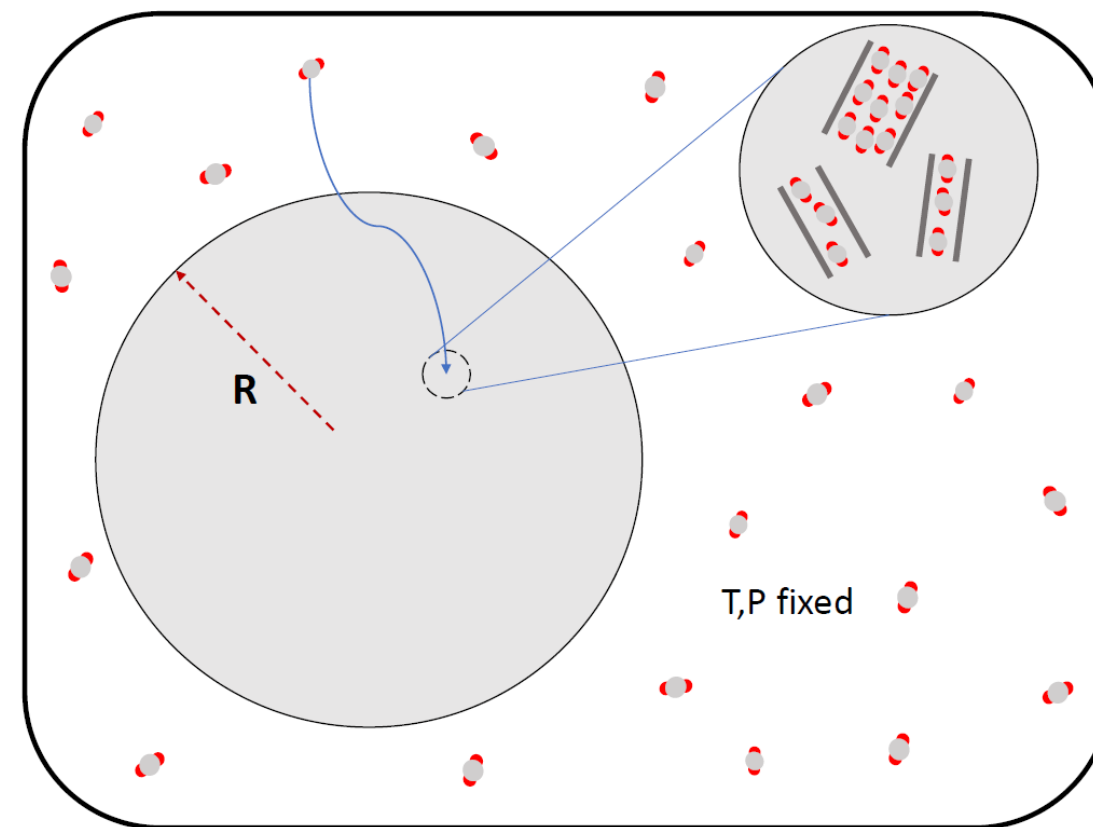


INTRODUCTION

Adsorption kinetics plays a key role in numerous industrial applications, and is accompanied by adsorption-induced deformation [1], in which molecules adsorbed onto the pore surfaces generate stress, resulting in dimensional changes in the material. Among other things, they control the permeability of coal, influence material degradation during TSA, and complicate the characterization of aerogels. In this work [2], we present a diffusion-based kinetic model that relies on classical density functional theory to calculate the required equilibrium properties and account for intraparticle diffusion, external surface barrier, and heat effects. We measured a series of CO₂ uptakes on a carbon molecular sieve (Shirasagi MSC CT-350) at 293 K to verify our model and assess its predictive capabilities. Additionally, data from the literature were used to test the precision of the description of adsorption-induced deformation.

Goal: to formulate the approach to study adsorption and deformation kinetics based on the combinations of cDFT and diffusion approximation

- What is the accuracy of the combined cDFT and diffusion-based description of adsorption and strain uptakes?
- How do different mass transfer resistances affect strain uptake?



- Homogeneous and isotropic medium
- Infinitely big adsorbate reservoir with fixed temperature and pressure
- No chemical adsorption
- Only small strains, typical for gas adsorption in solid microporous adsorbents
- Diffusion approximation of the fluid transport inside the porous body
- Possible existence of surface mass and heat transfer resistances

MAIN EQUATIONS

Mass balance [3,4]:

$$\frac{\partial q}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 D_0 \Gamma(q) \frac{\partial q}{\partial r} \right)$$

q – intraparticle concentration

D_0 – corrected diffusivity

$\Gamma(q)$ – thermodynamic factor

Heat balance [3,4]:

$$C_s \frac{dT}{dt} = (-\Delta H) \frac{dq}{dt} - ha(T - T_0)$$

ΔH – adsorption enthalpy

C_s – heat capacity

ha – heat transfer coefficient

I.C.: $q(r, 0) = q_0$ and $T(0) = T_0$

B.C.: $\frac{\partial q}{\partial r}(0, t) = 0$ and $D \frac{\partial q}{\partial r}(r, t) = k(q^* - q(R, t))$

$D = D_0 \Gamma(q)$

q^* – equilibrium surface concentration

k – external mass transfer coefficient

Equilibrium isotherm:

$$n(p) = \sum_j K(p, H_j) f_j(H_j)$$

$K(p, H)$ – kernel from cDFT:

- FMT model
- Mean-field approximation
- Effective quadrupolar interactions

Deformation isotherm:

$$\frac{\Delta V_p}{V_0} = \frac{1}{\phi M v_0} \sum_j f_j \bar{s}_j$$

M – effective bulk modulus

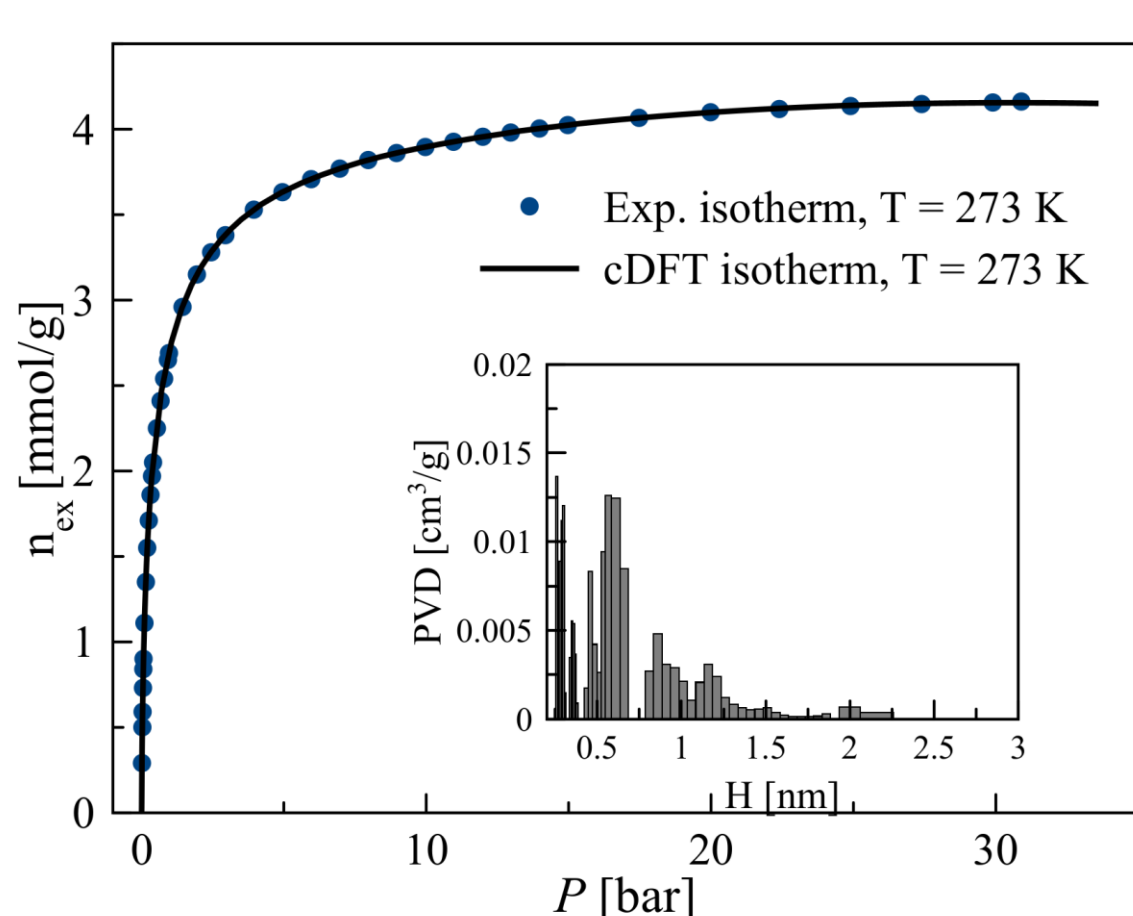
\bar{s} – average adsorption stress

ϕ – porosity

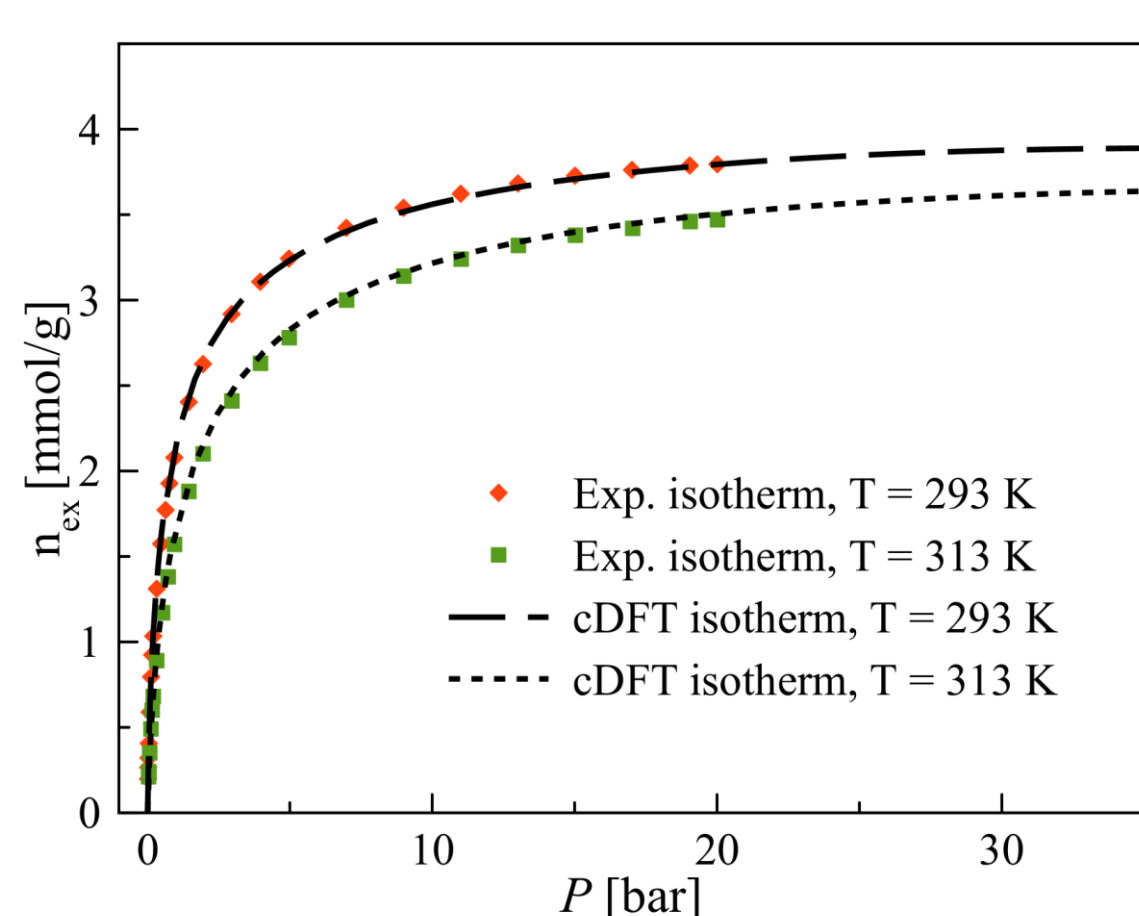
RESULTS

1st data set: six adsorption uptakes measured on Shirasagi MSC CT-350 at 293 K

PSD: 273 K CO₂ isotherm



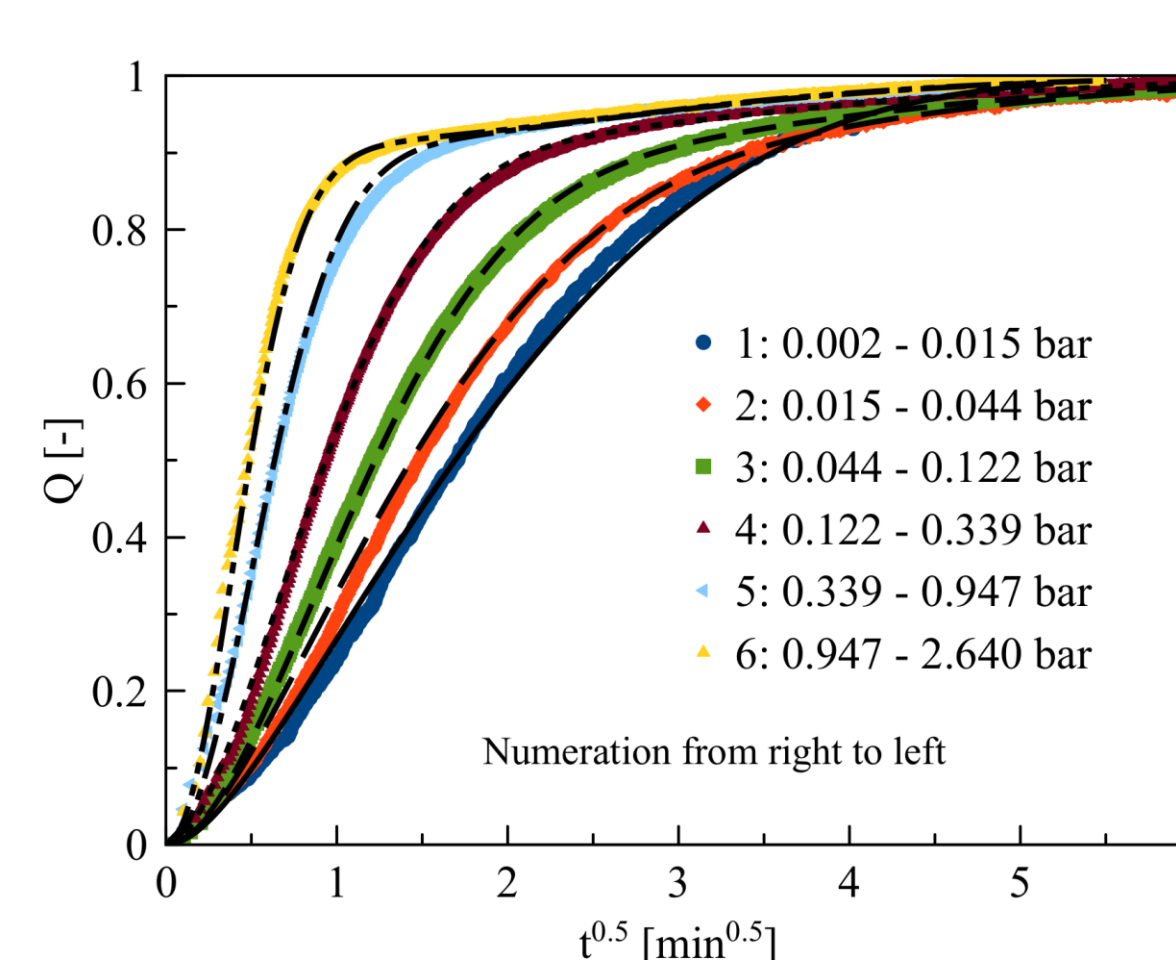
cDFT predicts T-dependent adsorption isotherms



Mass balance

Heat balance

Fit of the uptakes



- cDFT predicts correct temperature dependence of adsorption isotherms
- The model describes the uptakes measured on CMS influenced by intraparticle diffusion, external surface barrier, and heat effects
- Surface barrier is important for all uptakes, but it is a limiting factor only for uptakes 5 and 6
- Uptake 1 is isothermal

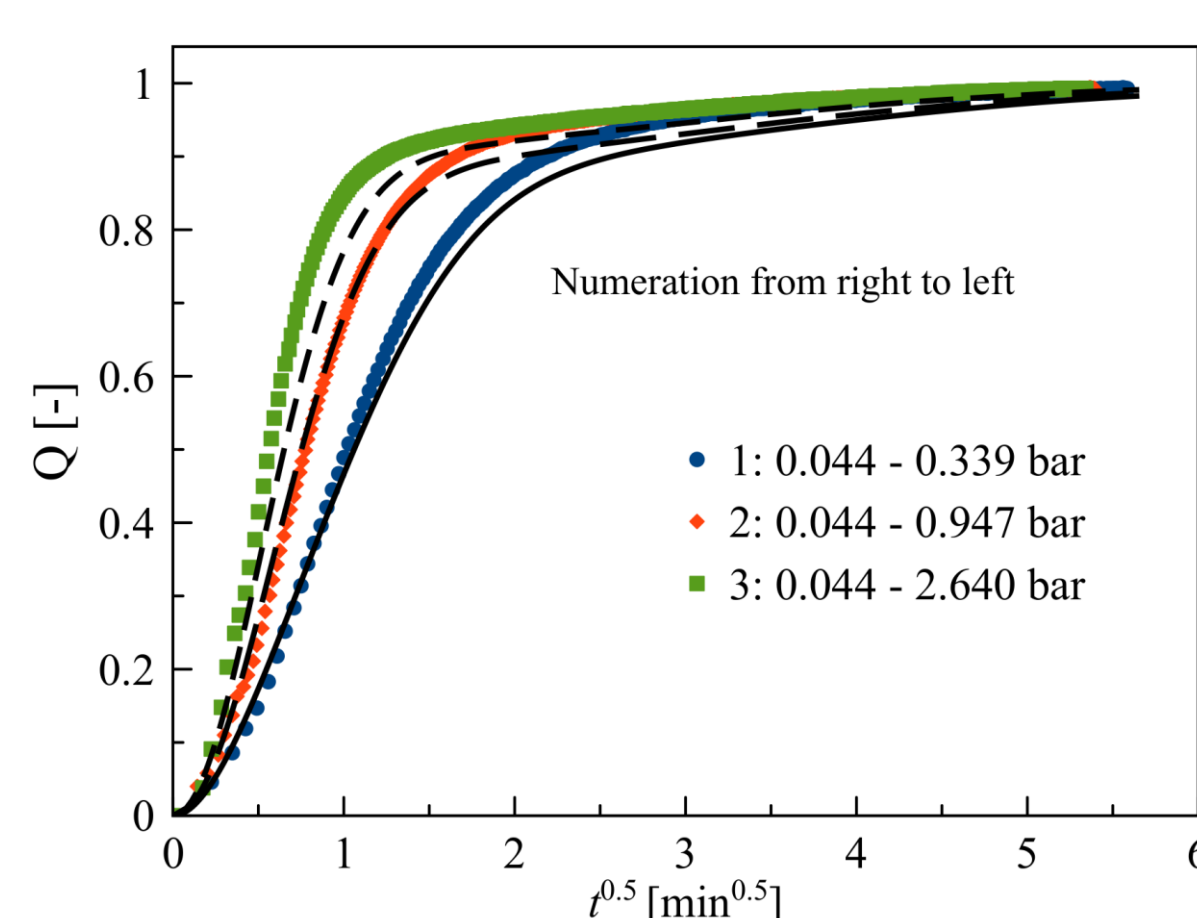
2nd data set: three adsorption uptakes measured on Shirasagi MSC CT-350 at 293 K

Prediction of uptakes

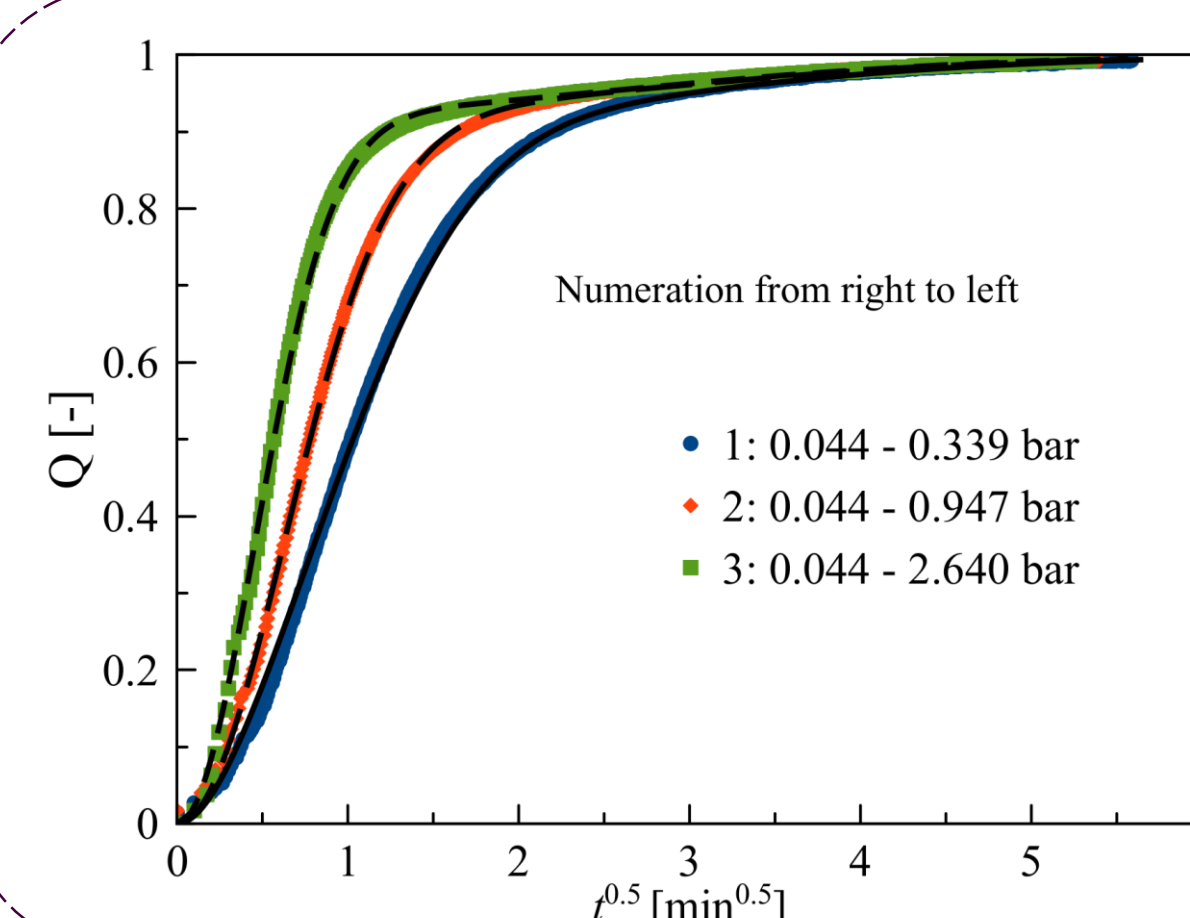
We used the obtained parameters from 1st data set (old) to predict D_0 and k :

$$p_{new} = \sum_i w_i p_i$$

p_i – old parameter
 w_i – weight of the old uptake



Best fit of uptakes

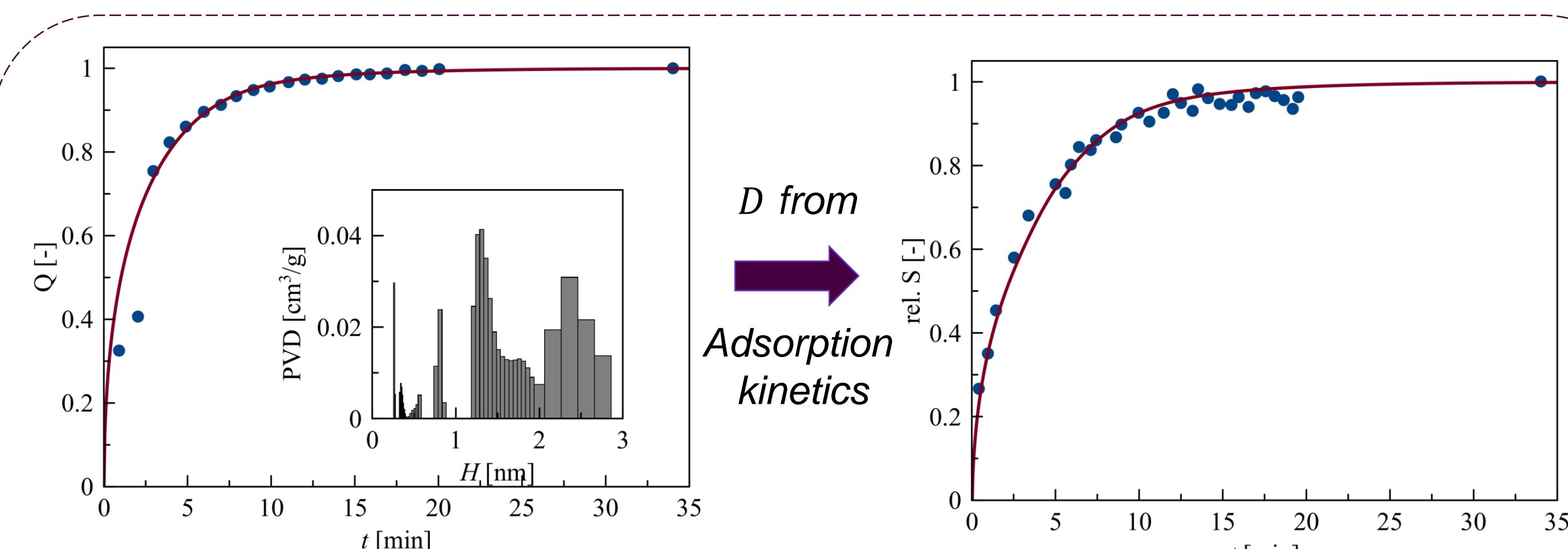


Predicted parameters based on the values obtained from 1st and the parameters from the direct fit of the experimental data given in brackets.

Step #	D_0/R^2 [s ⁻¹]	k/R [s ⁻¹]
1: 0.044 - 0.339 bar	1.05e-3	6.2e-3
2: 0.044 - 0.947 bar	-	7.8e-3 (6.6e-3)
3: 0.044 - 2.640 bar	-	1.05e-2 (1.25e-2)

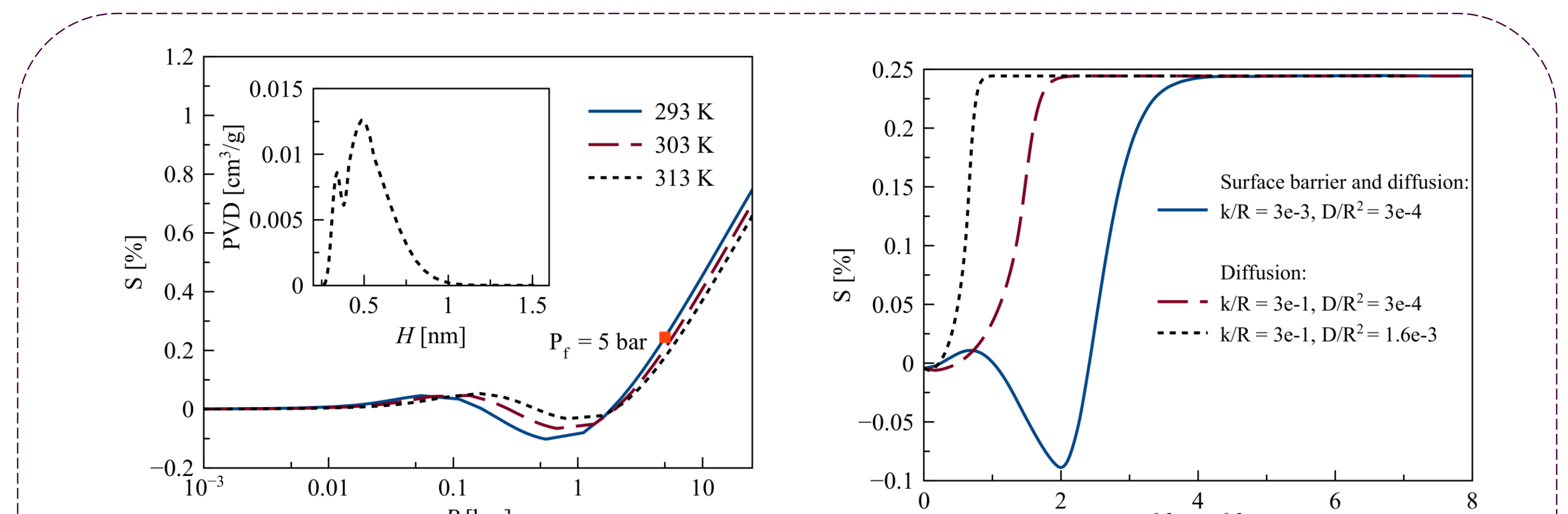
Kinetics of adsorption-induced deformation

Literature data from Ref.[5]: AC Chemviron at 303 K



PSD: adsorption and strain isotherms at 318 K

Hypothetical microporous material



"Speed" of adsorption changes the deformation curves

CONCLUSIONS

- We formulated the combined cDFT and diffusion approach to study adsorption and deformation kinetics
- The model can quantitatively describe the adsorption kinetic defined by intraparticle diffusion, external surface barrier, and heat effects
- The model can quantitatively describe existing experimental adsorption and deformation uptakes of carbon dioxide on AC Chemviron
- We made predictions regarding the shapes of kinetic strain uptakes depending on the "speed" of the adsorption process

REFERENCES

1. A. Kolesnikov et al. Journal of Physics: Condensed Matter, 34 (2021)
2. A. Kolesnikov et al. submitted to journal
3. J. Kärger et al. Diffusion in nanoporous materials, Wiley (2012)
4. J. Crank, The mathematics of diffusion, Oxford university press (1979)
5. L. Perrier et al. Review of Scientific Instruments, 88 (2017)