Confined systems. New theory and applications

Fluids in mesopores: introduction to the phenomenon

Theoretical:
•shortcomings of standard thermodynamics for confined systems
•introducing the new concept of COS (=Curves of States)

Simulation of Pressure Jump Experiments:
•role of COS for dynamic behavior

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behavior of fluids in mesopores

natural phenomena

- hydrology of ground water
- natural purification and pollution

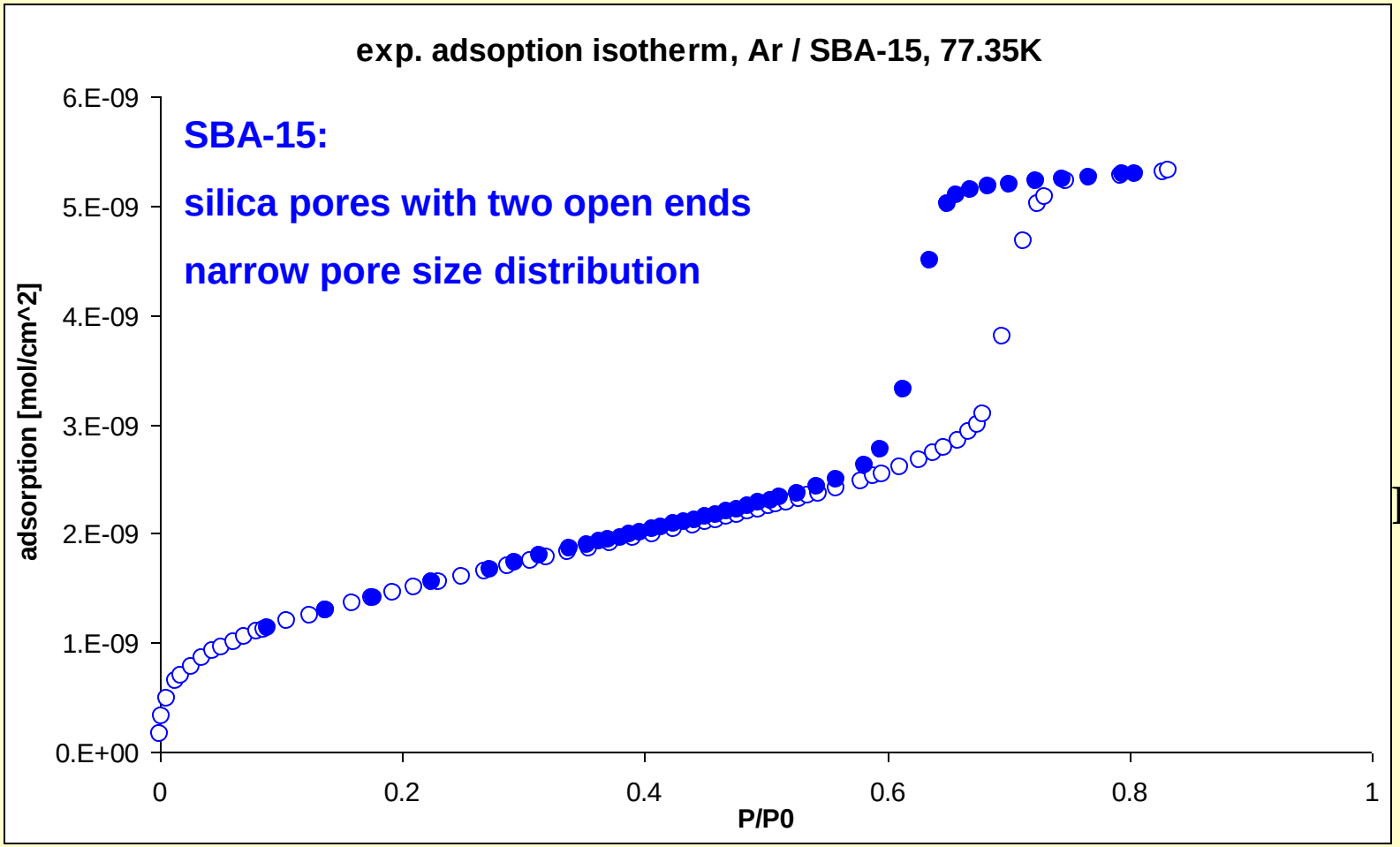
industrial activities

- oil extraction
- mixture separation, filtering
- catalysis
- sensor development

basic research

adsorption from vapor phase

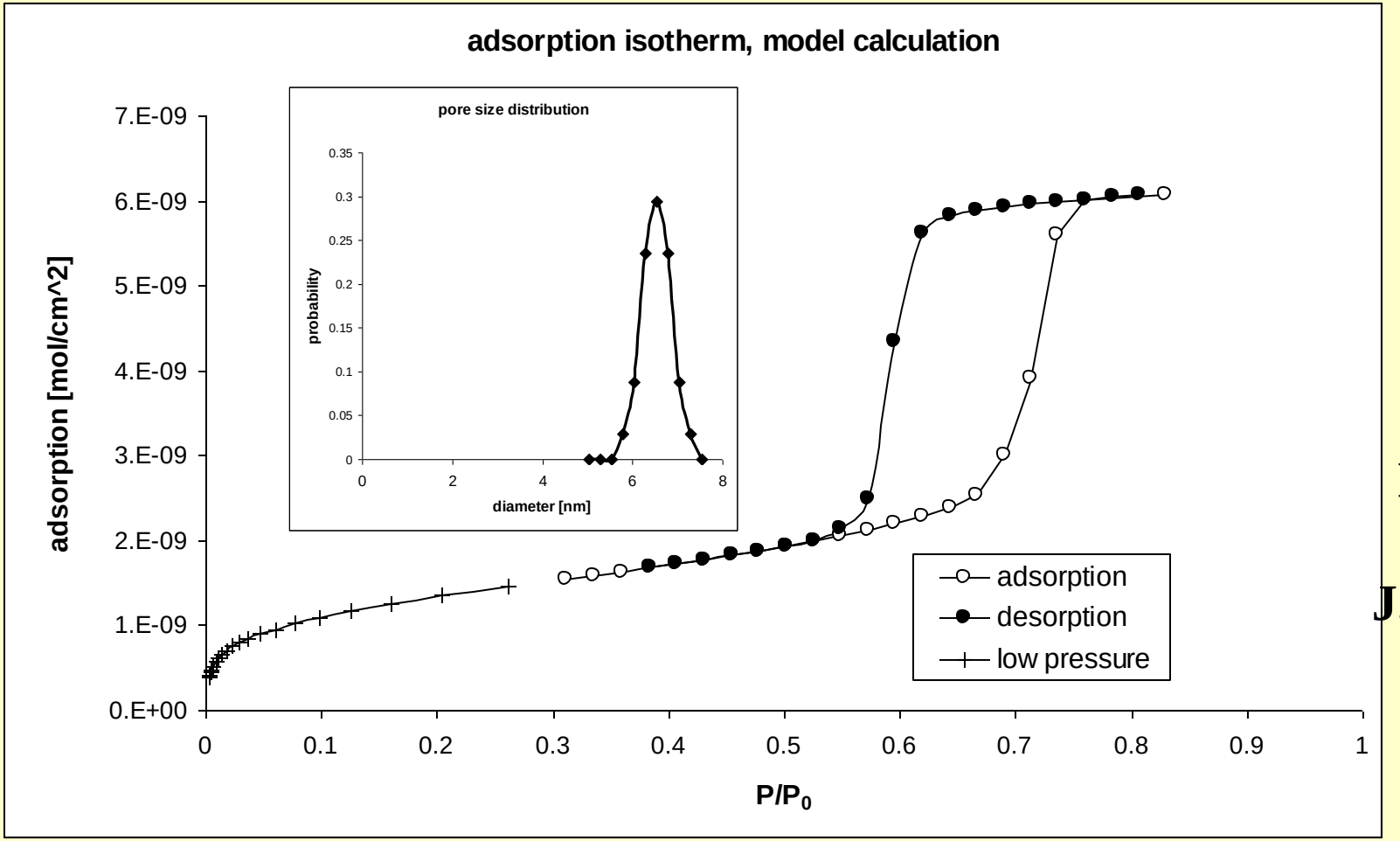
Adsorption Hysteresis in Porous Material



R.Rockmann
PhD Thesis
2007
U Leipzig

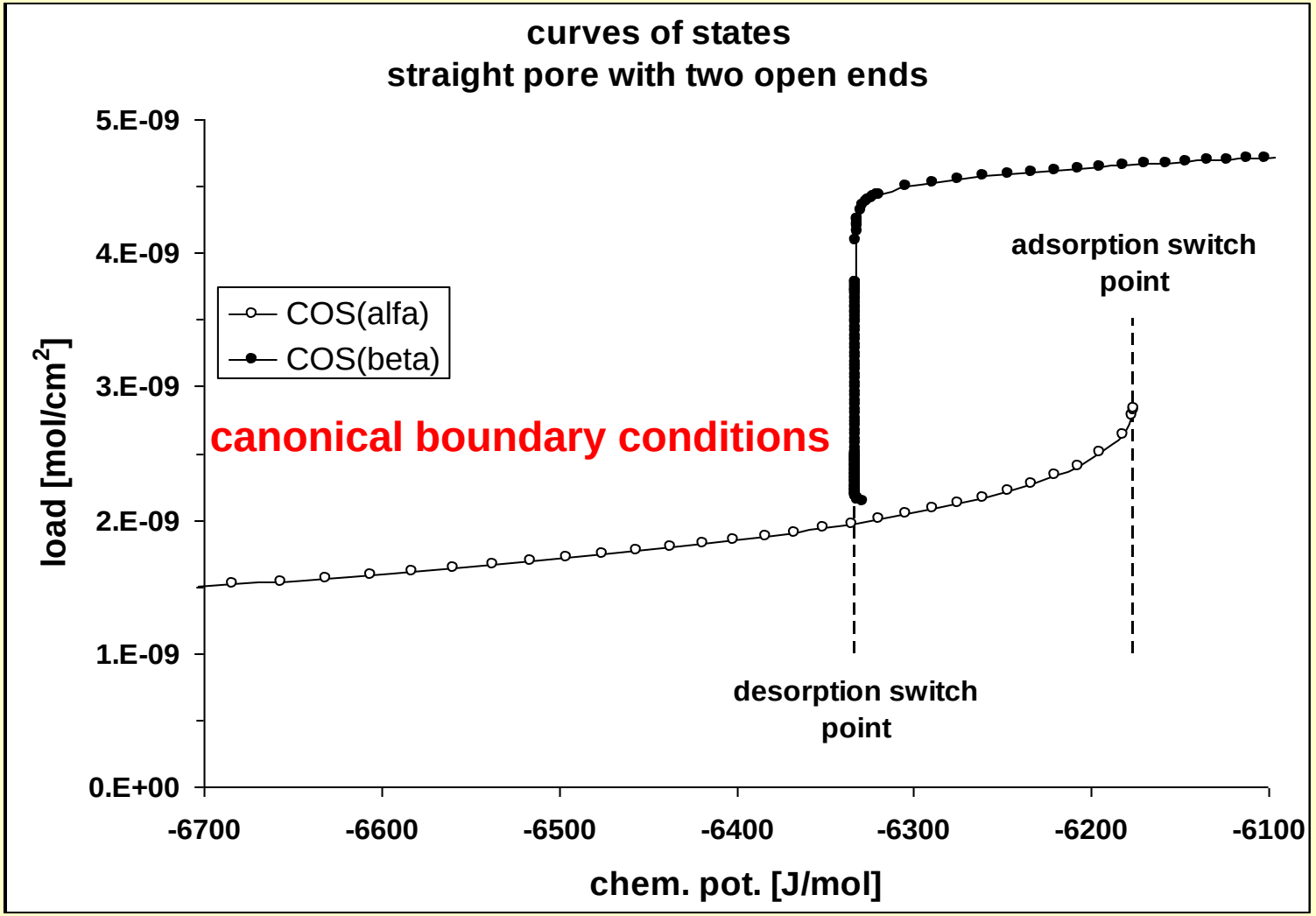
adsorption from vapor phase

Adsorption Hysteresis in Porous Material



H.Morgner (2010) J.Phys.Chem. C 114 8877-83

Curves of States (introduction)



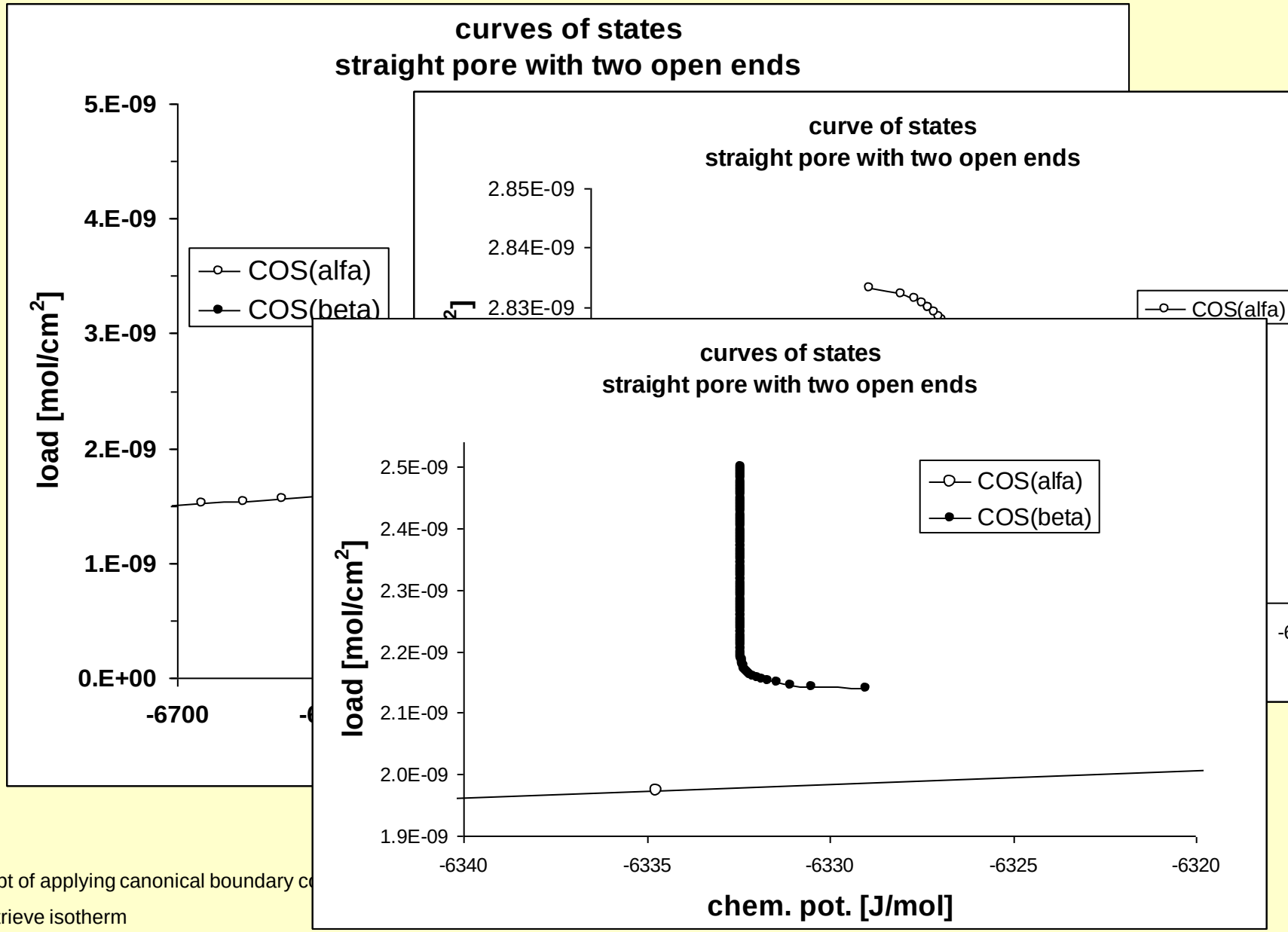
H. Morgner

J. Chem. Chem. Eng. 5 (2011) 456 - 472

COS and concept of applying canonical boundary conditions

COS allow to retrieve isotherm

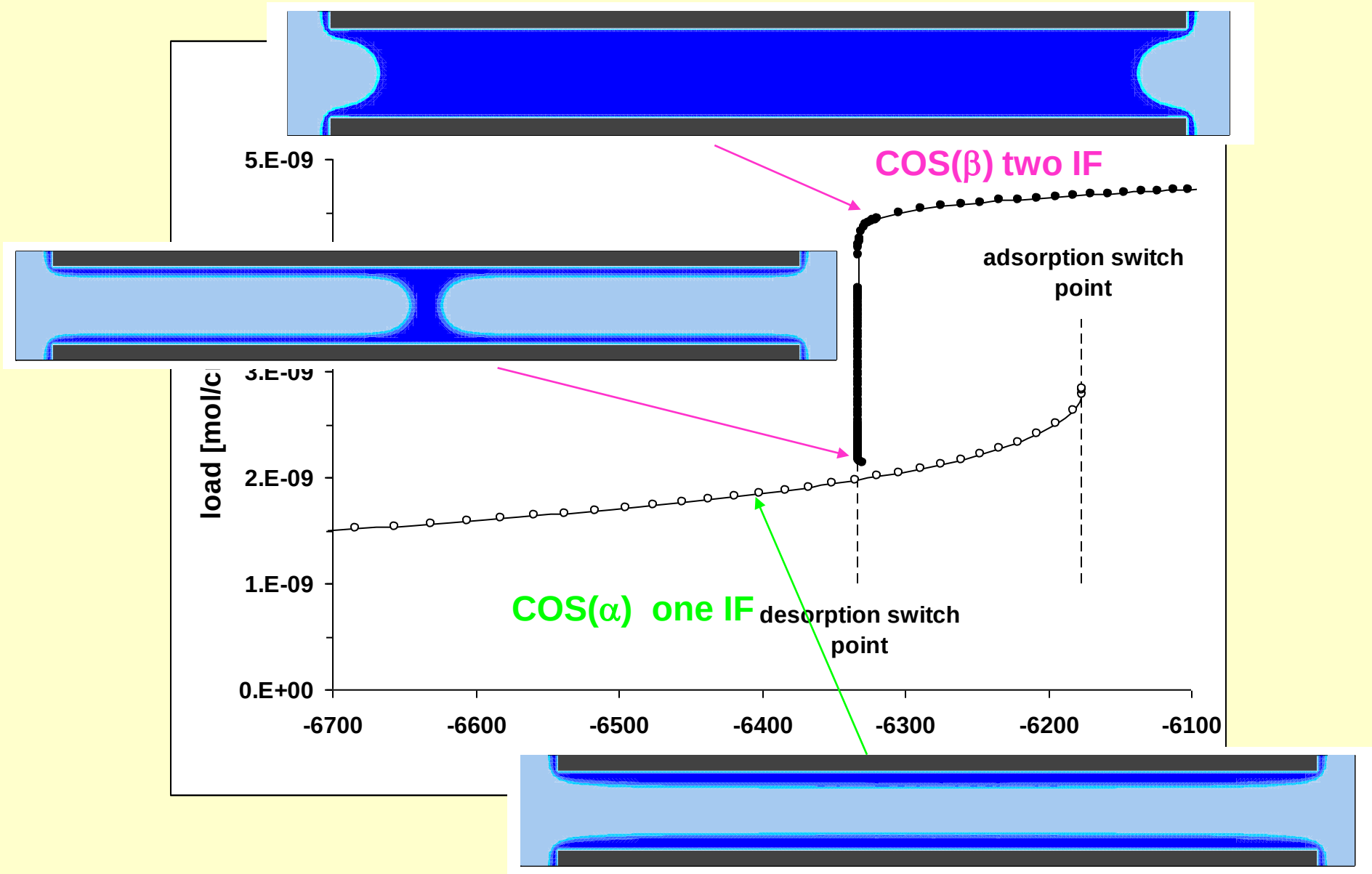
Curves of States (shape)



COS and concept of applying canonical boundary c

COS allow to retrieve isotherm

Curves of States (filling pattern)



COS and concept of applying canonical boundary conditions

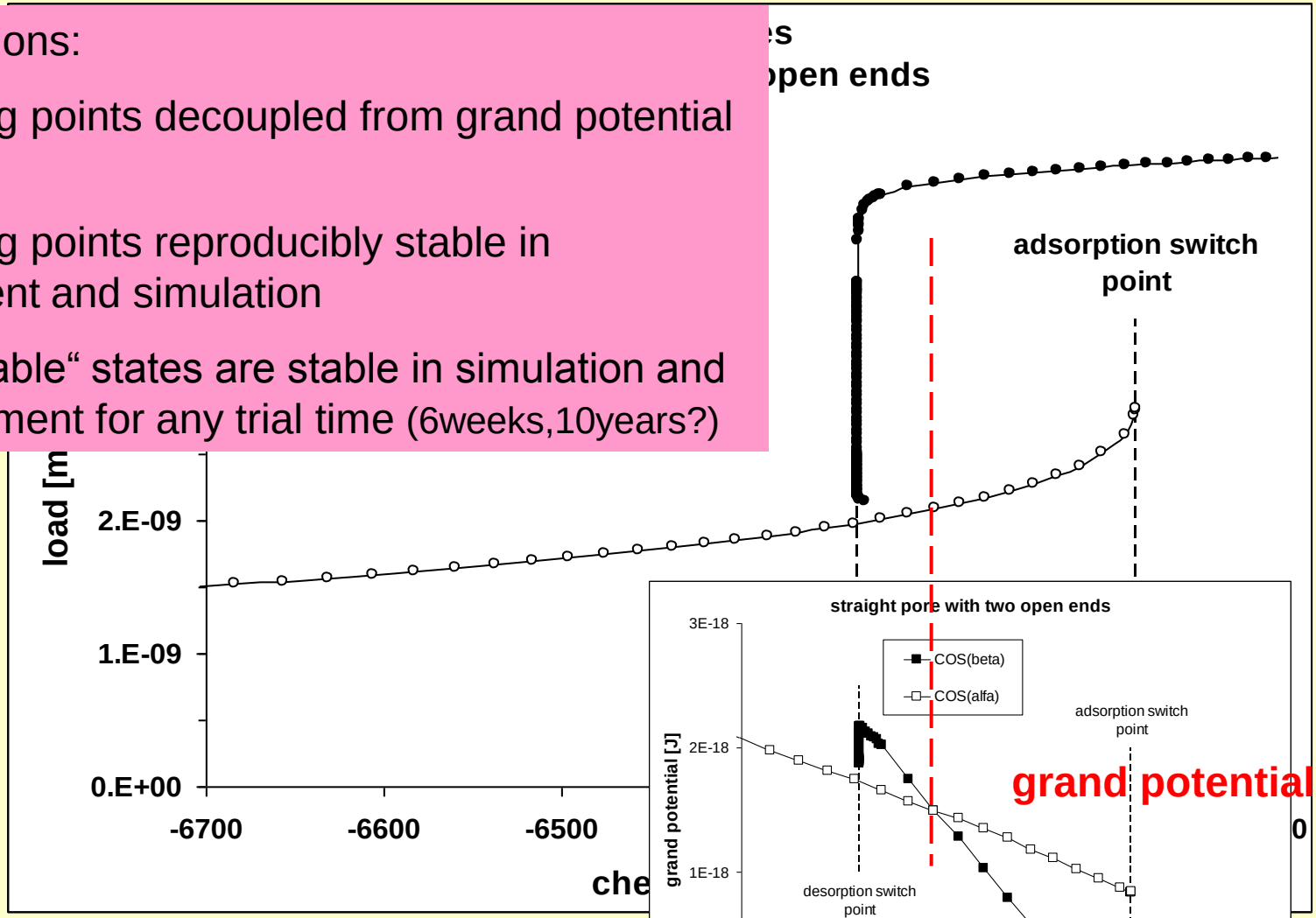
COS allow to retrieve isotherm

J. Chem. Chem. Eng. 5 (2011) 456 - 472

Curves of States (relation to thermodynamics)

observations:

- switching points decoupled from grand potential crossing
- switching points reproducibly stable in experiment and simulation
- „metastable“ states are stable in simulation and in experiment for any trial time (6weeks,10years?)



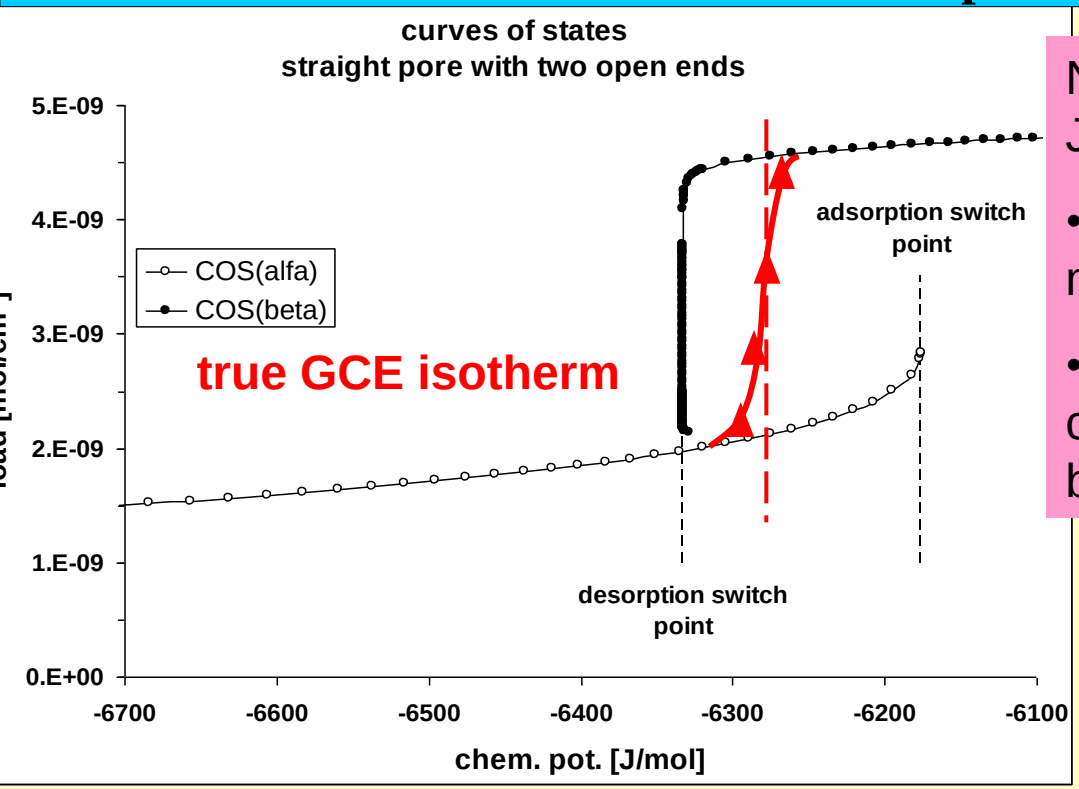
H. M

J. Cl - 472

COS and concept of applying canonical boundary conditions

COS allow to retrieve isotherm

literature: attempts to save thermodynamics



Neimark&Vishnyakov
J.Phys.Chem. B110 (2006) 9403-12

- both branches contain a set of microstates
- these sets are subsets of one common state (equilibrium). Thus, both branches form only one state

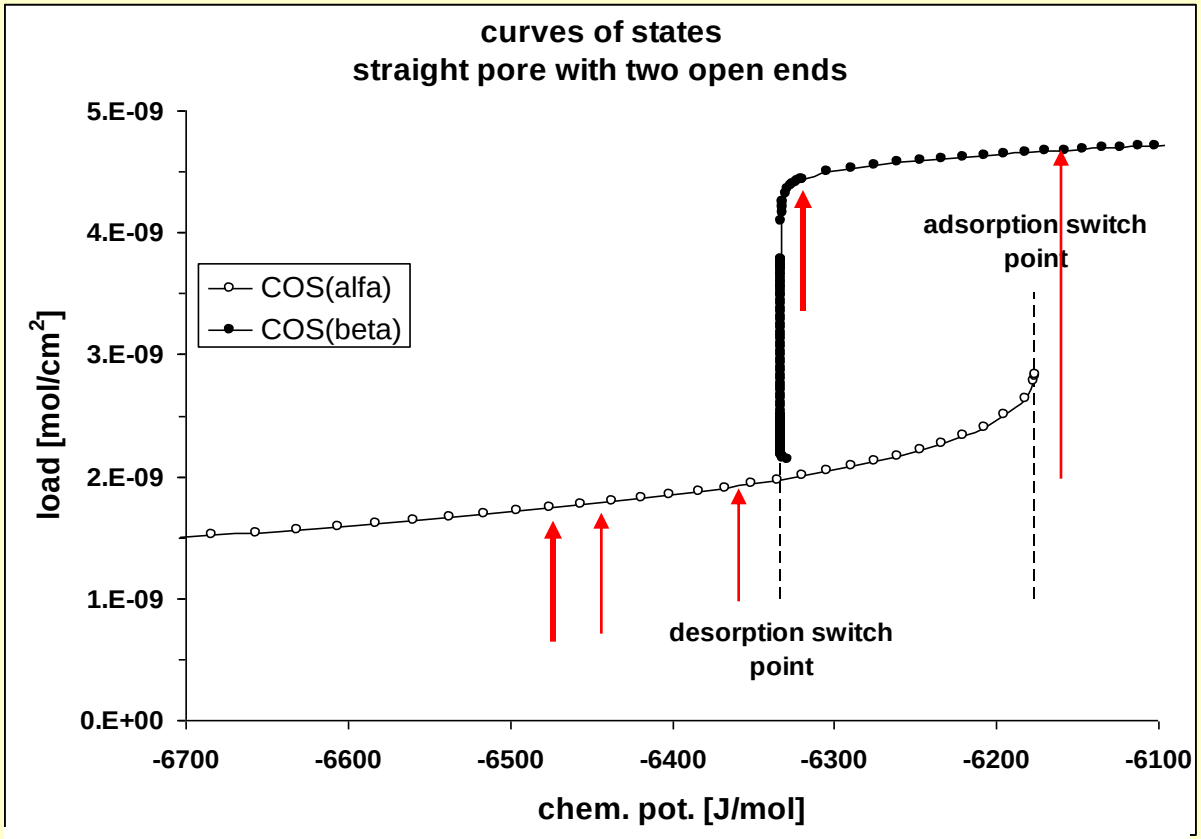
Neimark&Vishnyakov

J.Phys.Chem. B110
(2006) 9403-12

„….the true GCE isotherm cannot be sampled in practical simulations….“

$$N_{GCE}(\mu,V,T) = \frac{\bar{N}_v(\mu)\exp(-\Omega_v(\mu,V,T)/kT) + \bar{N}_l(\mu)\exp(-\Omega_l(\mu,V,T)/kT)}{\exp(-\Omega_v(\mu,V,T)/kT) + \exp(-\Omega_l(\mu,V,T)/kT)}$$

driving force: gradient of chemical potential



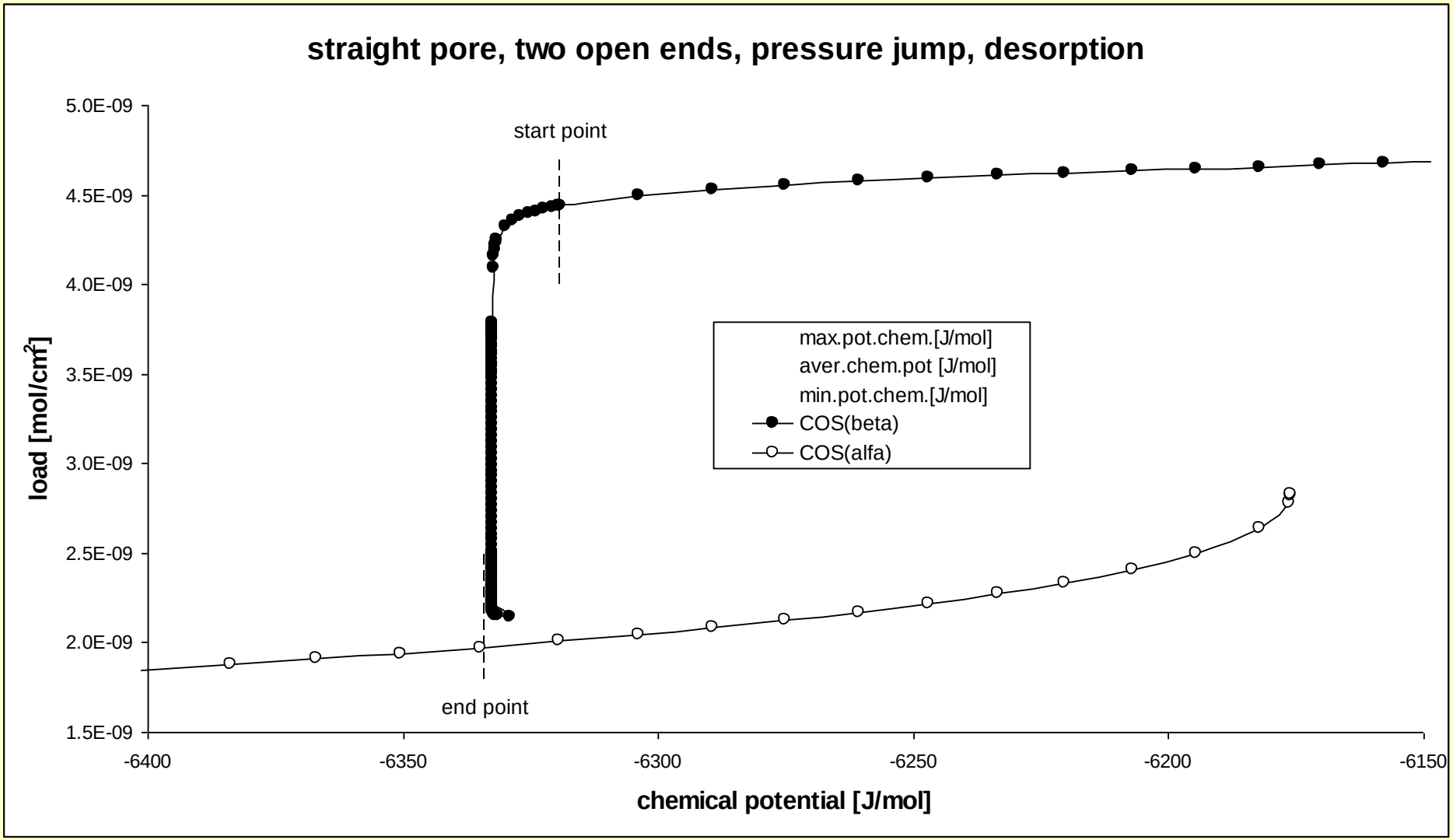
pressure in gas reservoir →

Diffusion treated by

Onsager ansatz

$$\vec{J} = -\frac{L}{T} \cdot grad\mu$$

desorption


straight pore, two open ends, pressure jump, desorption
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3.0E-09
2.5E-09
2.0E-09
1.5E-09
start point
end point
max.pot.chem.[J/mol]
aver.chem.pot [J/mol]
min.pot.chem.[J/mol]
COS(beta)
COS(alfa)
-6400
-6350
-6300
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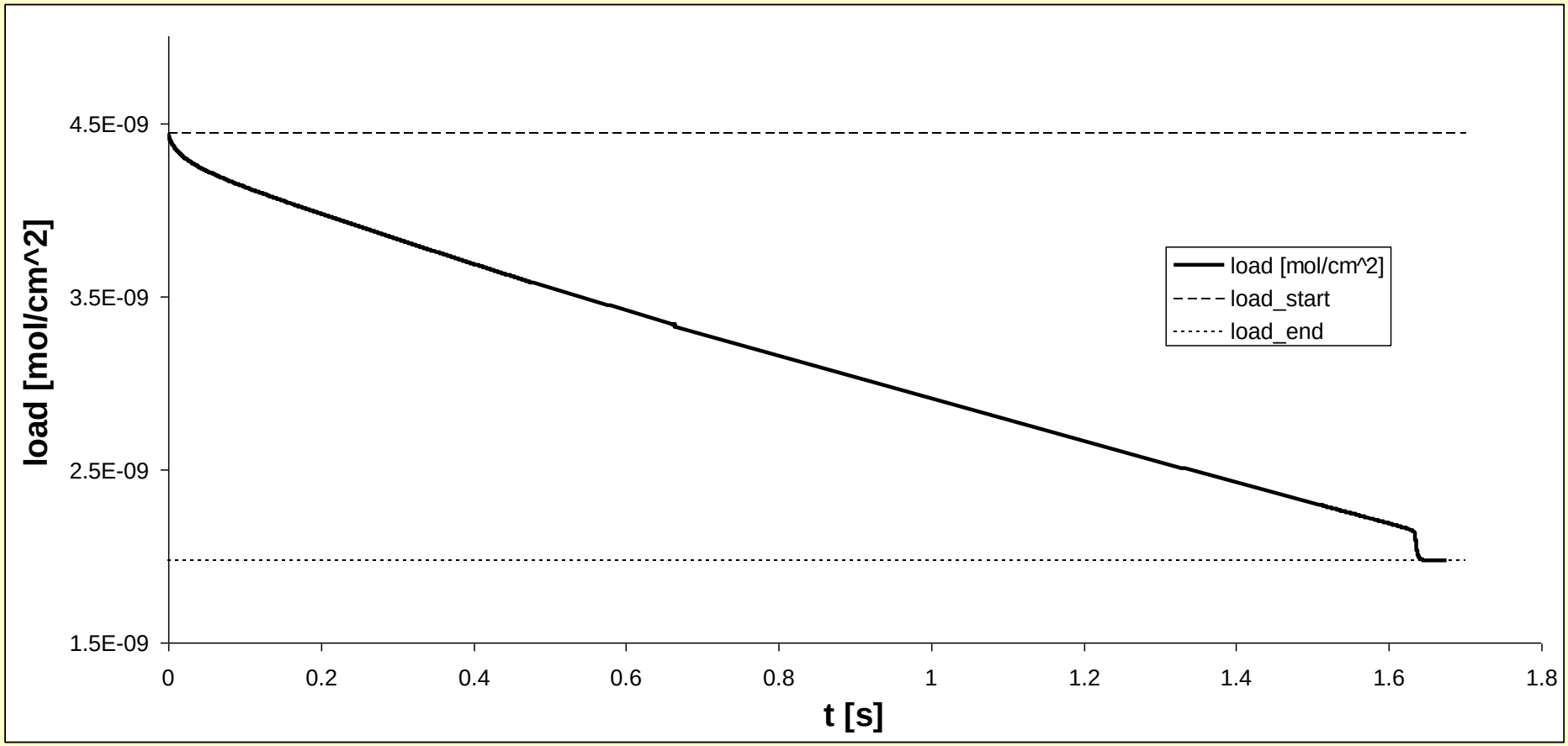
-6200
-6150
chemical potential [J/mol]

desorption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0.4
0.6
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1.2
1.4
1.6
1.8
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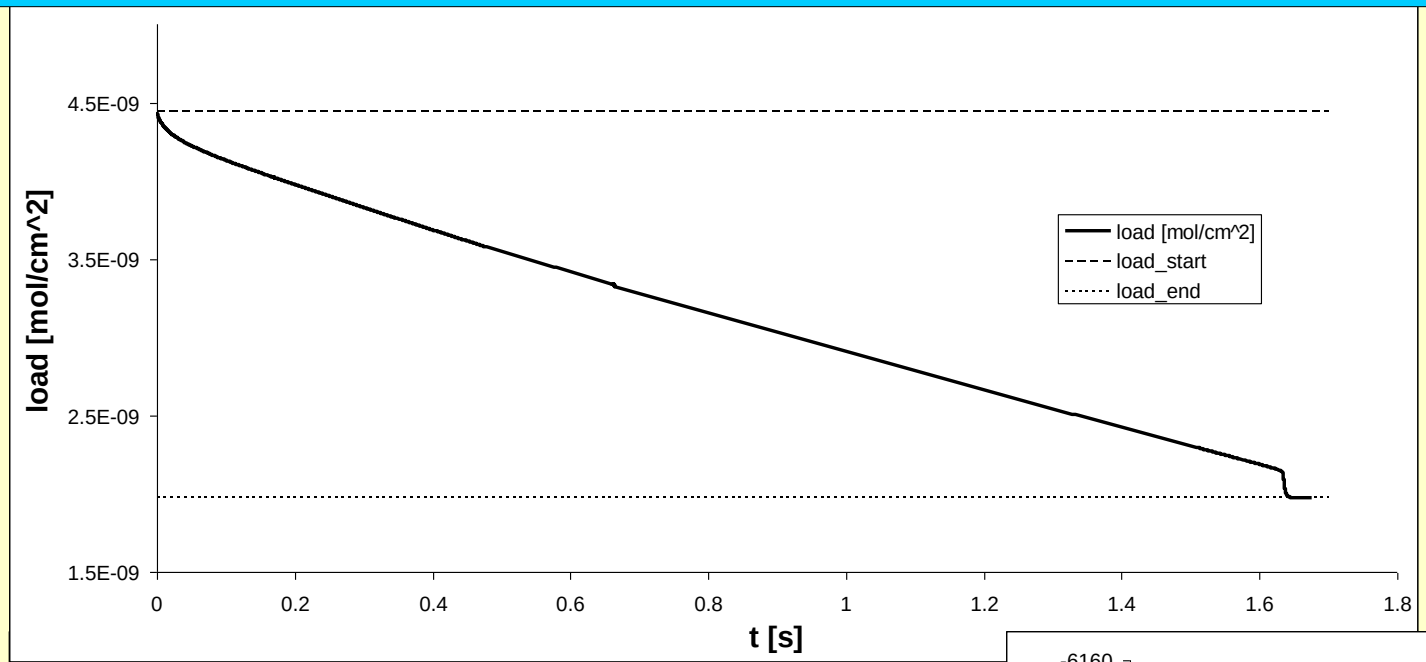
load_start
load_end

desorption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0.4
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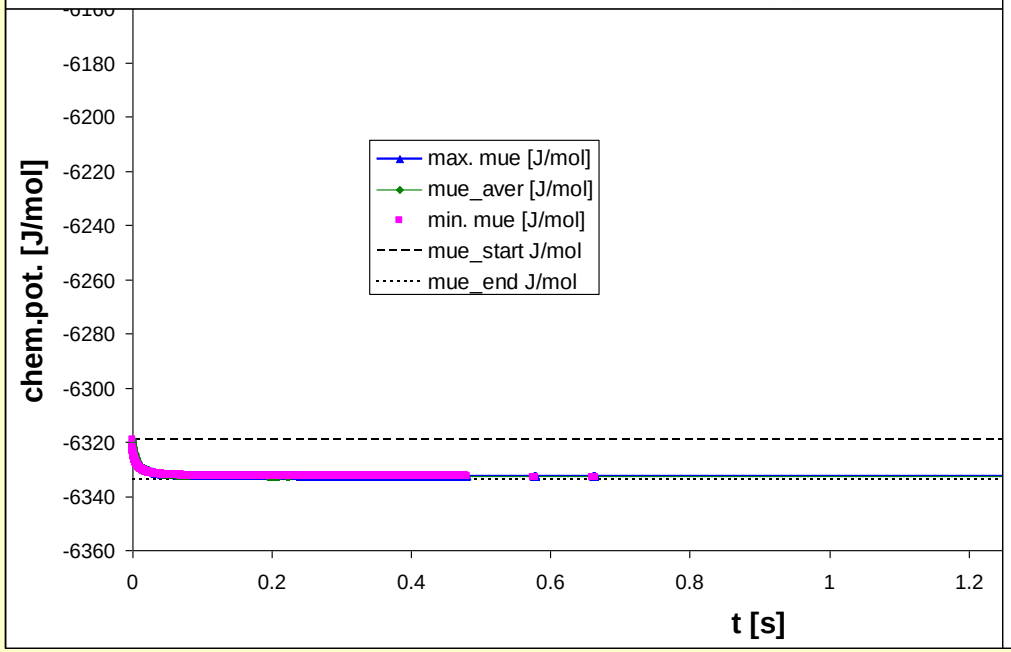
0.8
1
1.2
1.4
1.6
1.8
t [s]
load [mol/cm^2]
load_start
load_end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-6220
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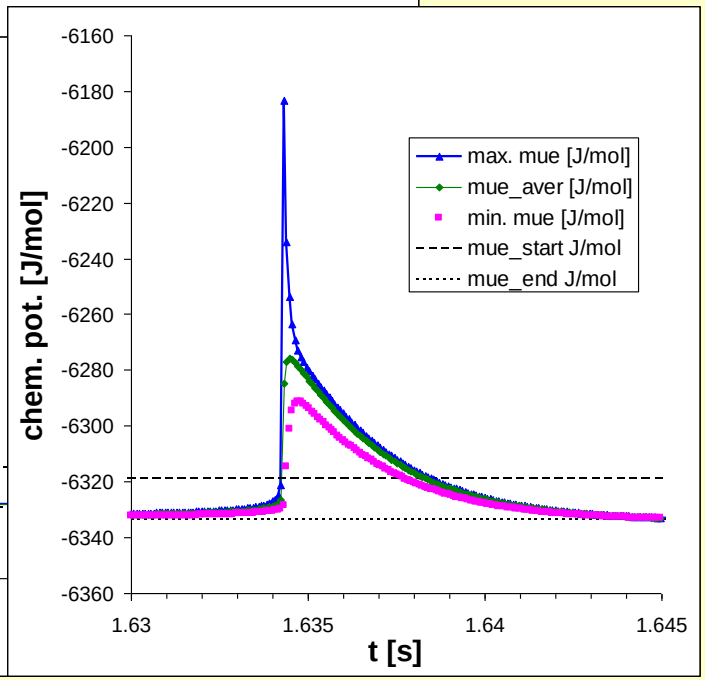
-6260
-6280
-6300
-6320
-6340
-6360
0
0.2
0.4
0.6
0.8
1
1.2
t [s]
max. mue [J/mol]
mue_aver [J/mol]
min. mue [J/mol]
mue_start J/mol
mue_end J/mol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-6300
-6320
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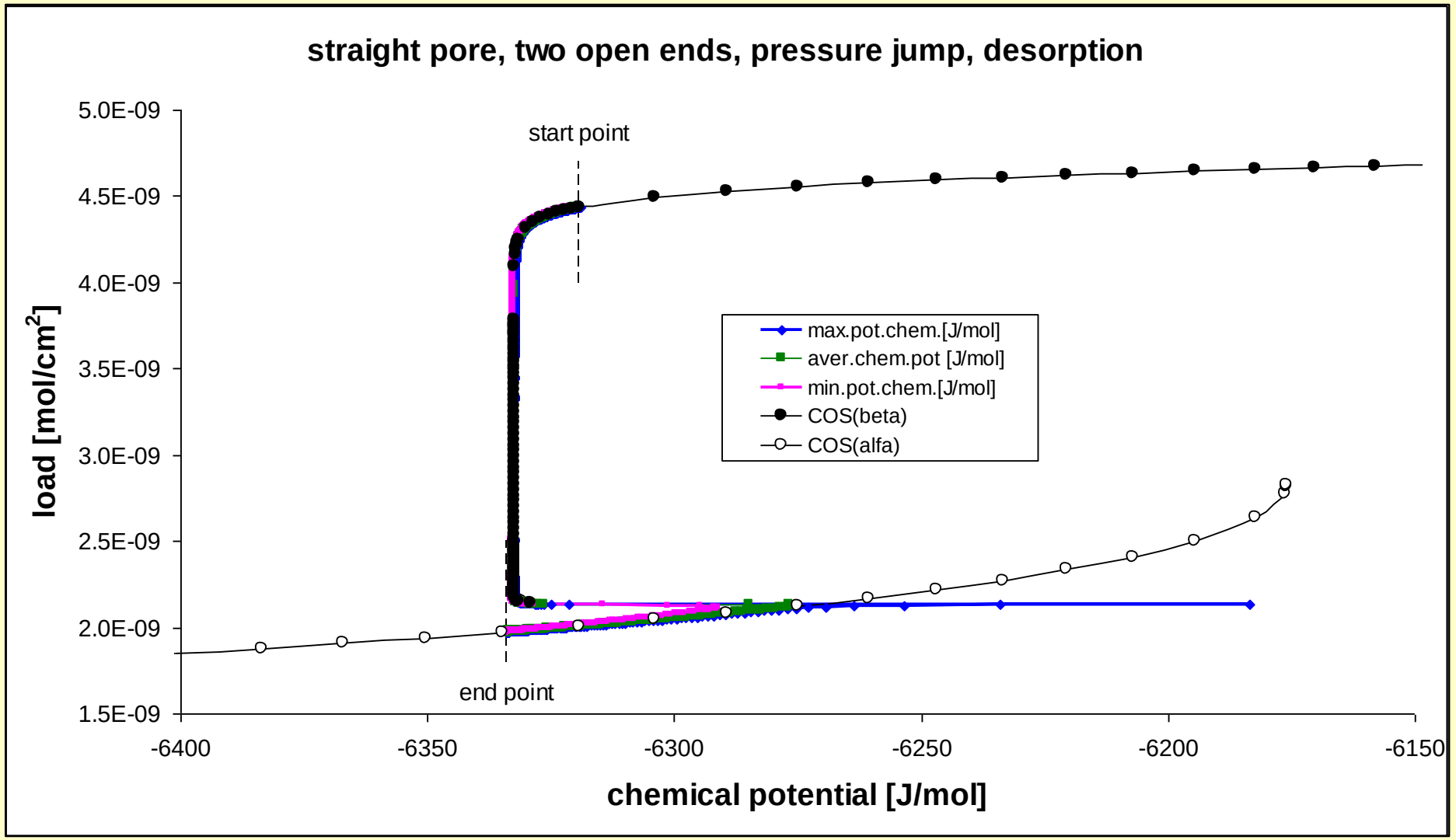
-6360
1.63
1.635
1.64
1.645
t [s]
max. mue [J/mol]
mue_aver [J/mol]
min. mue [J/mol]
mue_start J/mol
mue_end J/mol

desorption


straight pore, two open ends, pressure jump, desorption
load [mol/cm²]
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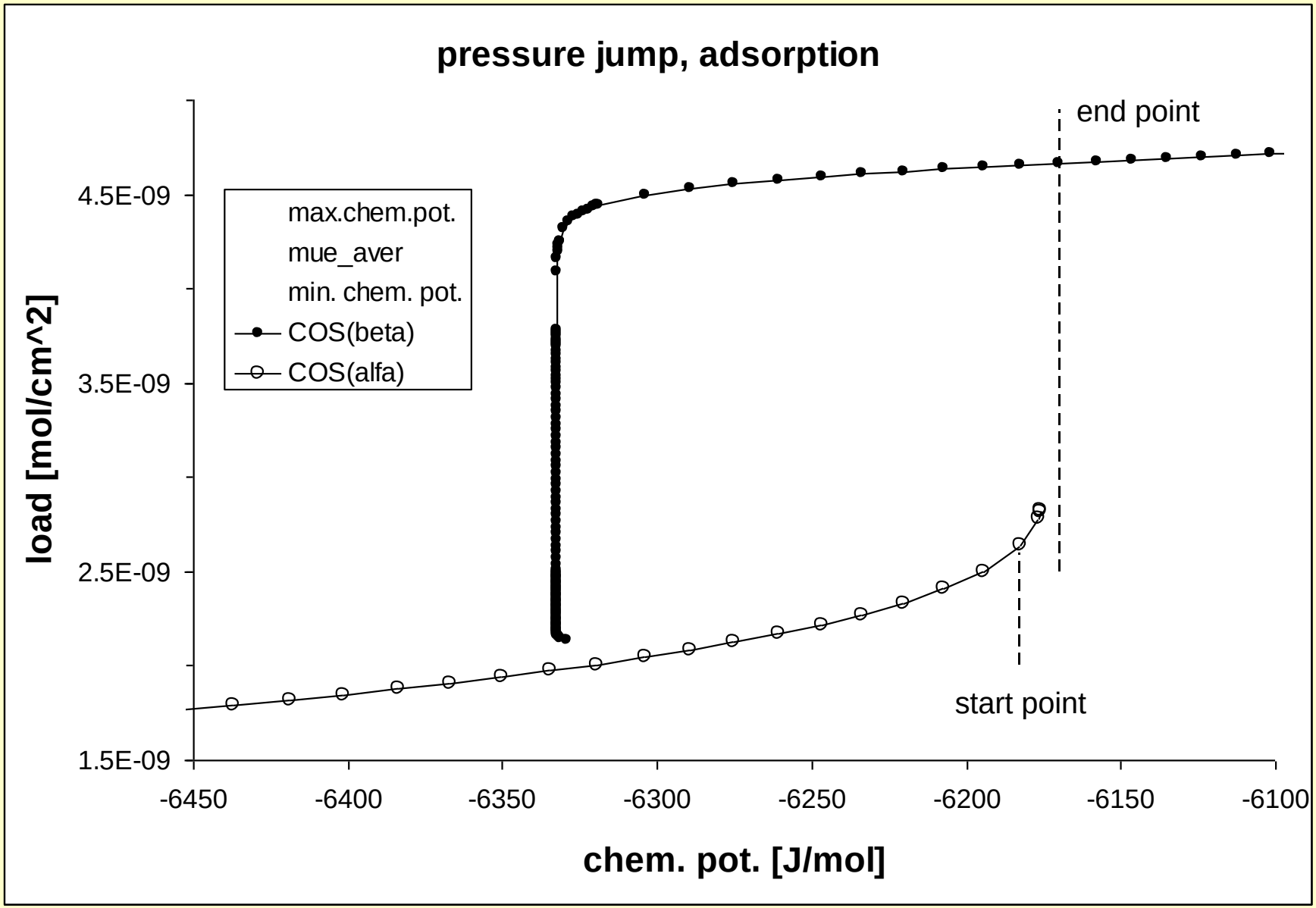
4.5E-09
4.0E-09
3.5E-09
3.0E-09
2.5E-09
2.0E-09
1.5E-09
start point
end point
max.pot.chem.[J/mol]
aver.chem.pot [J/mol]
min.pot.chem.[J/mol]
COS(beta)
COS(alfa)
-6400
-6350
-6300
-6250
-6200
-6150
chemical potential [J/mol]


pressure jump, adsorption
end point
start point
max.chem.pot.
mue_aver
min. chem. pot.
COS(beta)
COS(alfa)
load [mol/cm^2]
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3.5E-09
2.5E-09
1.5E-09
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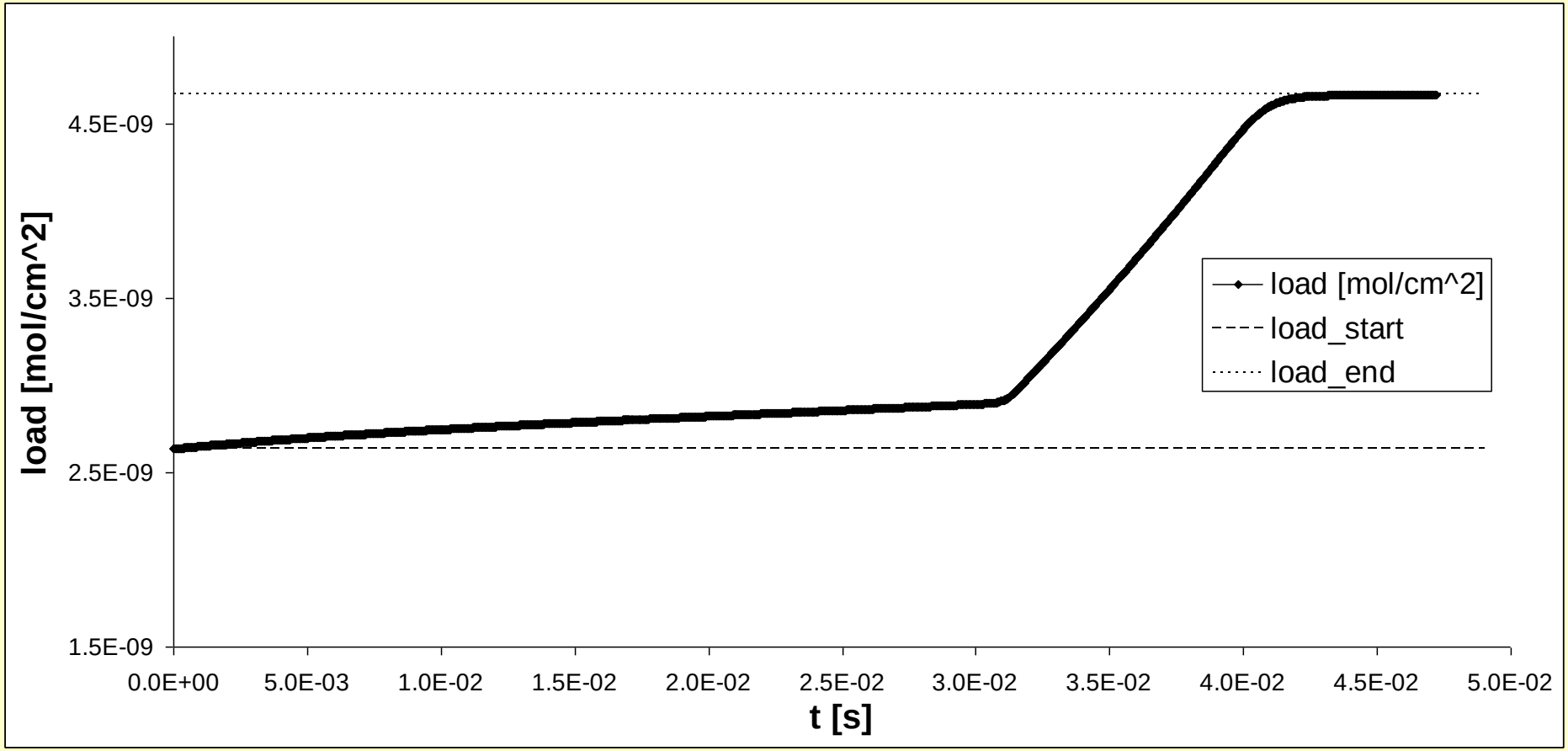
-6400
-6350
-6300
-6250
-6200
-6150
-6100
chem. pot. [J/mol]

adsorption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1.0E-02
1.5E-02
2.0E-02
2.5E-02
3.0E-02
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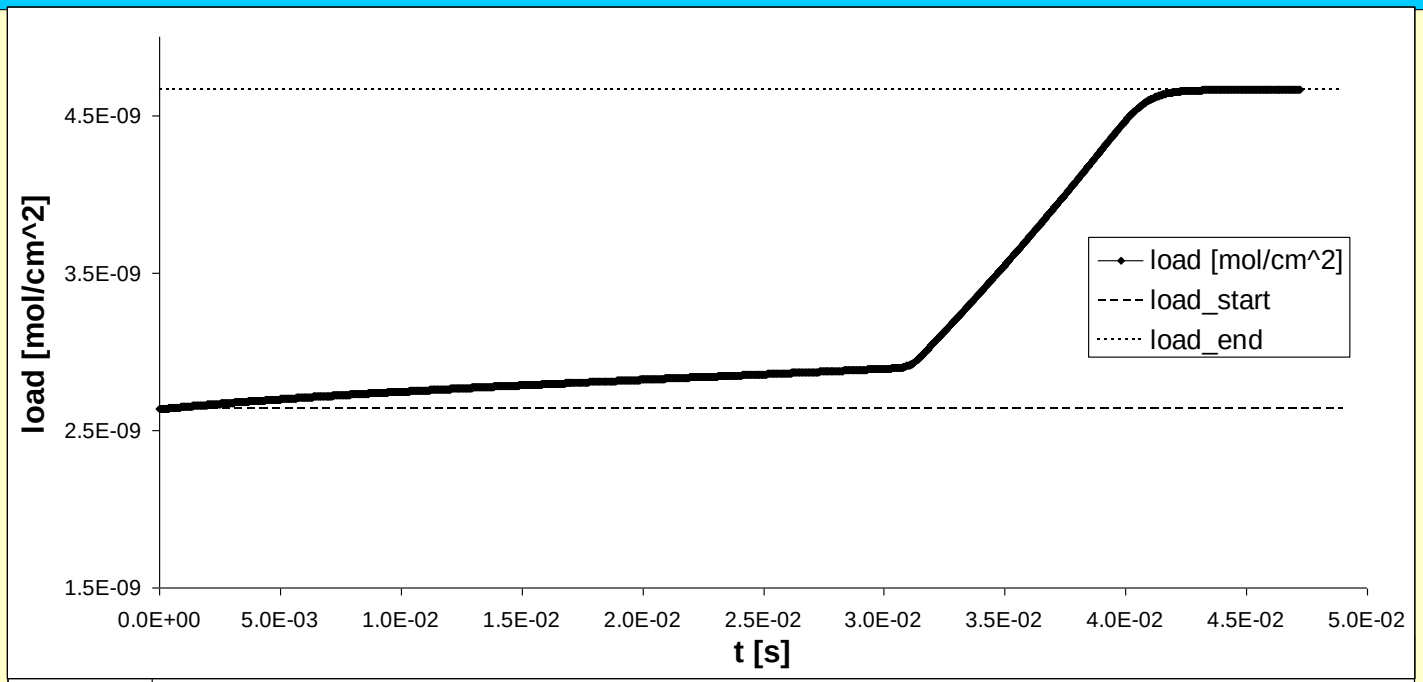
load_start
load_end

adsorption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0.0E+00
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1.0E-02
1.5E-02
2.0E-02
2.5E-02
3.0E-02
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load [mol/cm^2]
load_start
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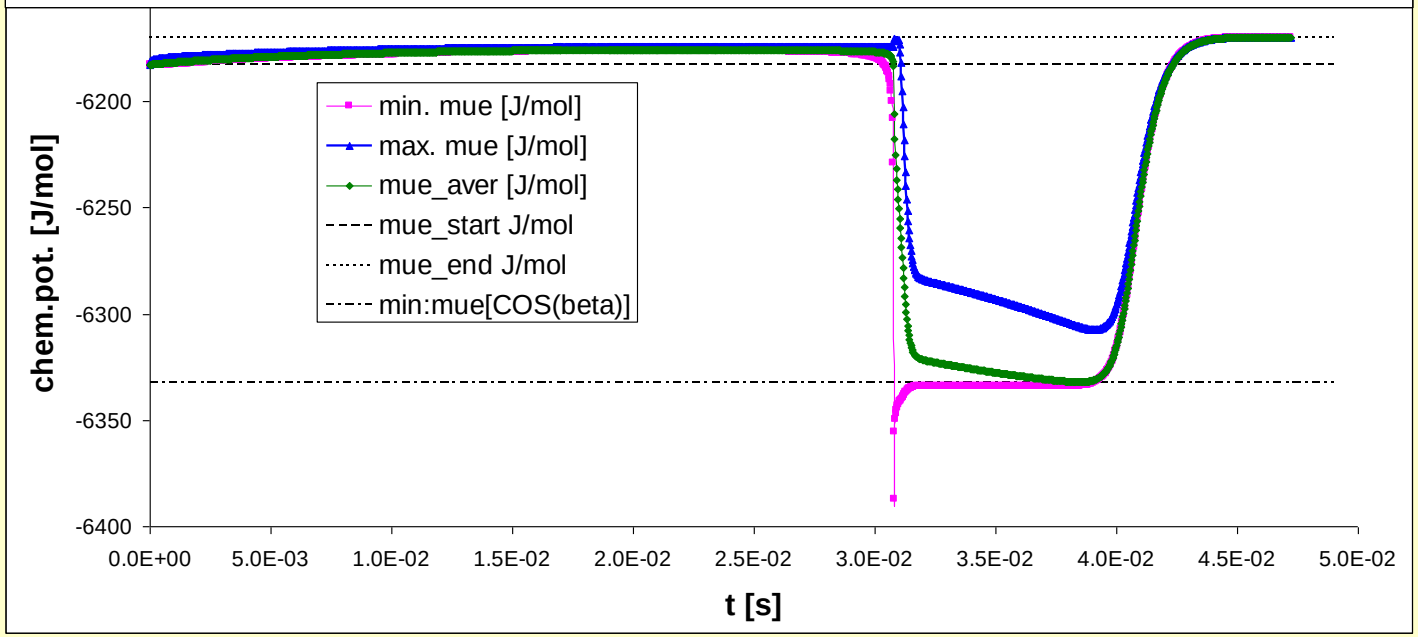
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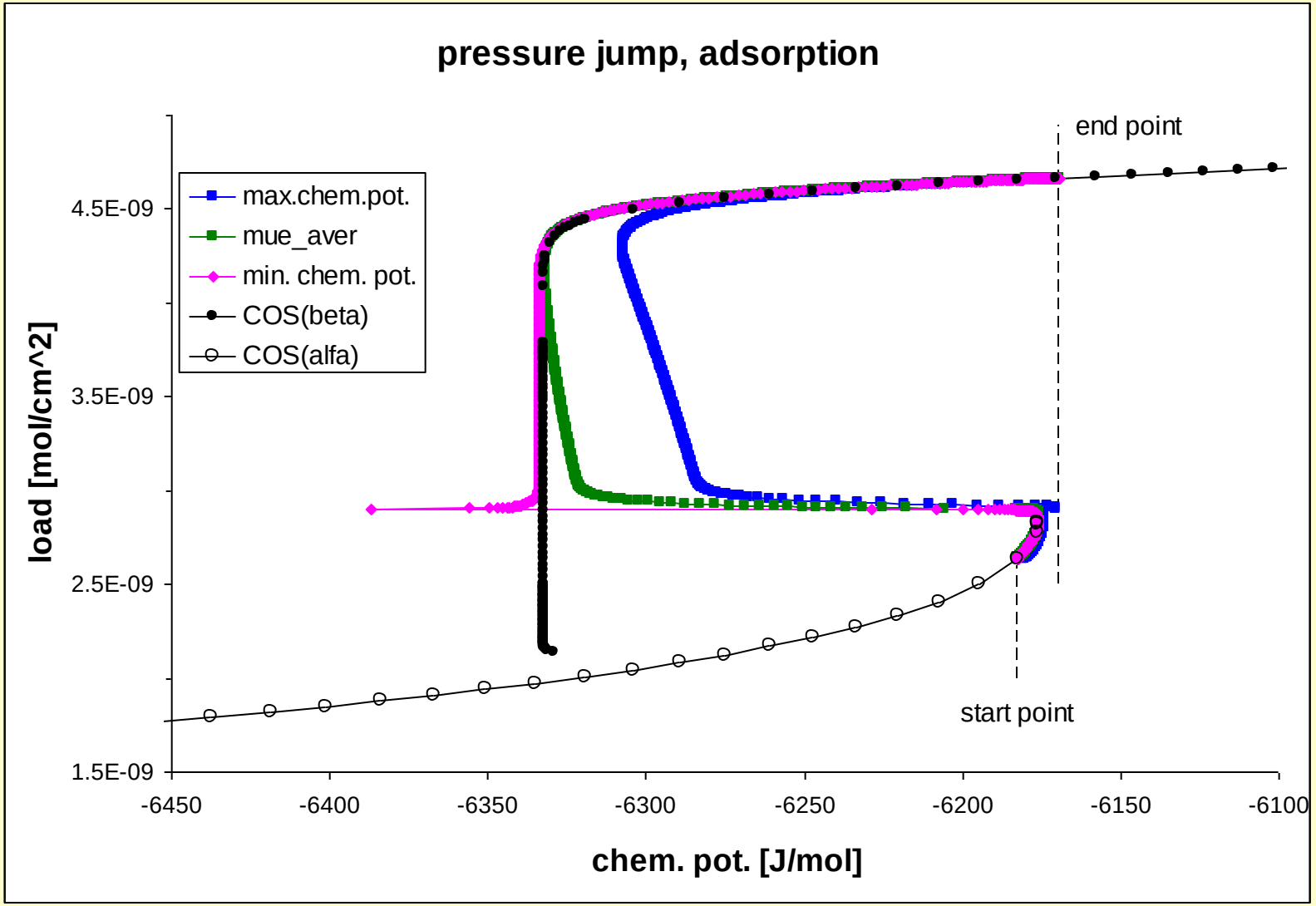
-6250
-6300
-6350
-6400
0.0E+00
5.0E-03
1.0E-02
1.5E-02
2.0E-02
2.5E-02
3.0E-02
3.5E-02
4.0E-02
4.5E-02
5.0E-02
t [s]
min. mue [J/mol]
max. mue [J/mol]
mue_aver [J/mol]
mue_start J/mol
mue_end J/mol
min:mue[COS(beta)]


pressure jump, adsorption
end point
start point
max.chem.pot.
mue_aver
min. chem. pot.
COS(beta)
COS(alfa)
load [mol/cm^2]
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3.5E-09
2.5E-09
1.5E-09
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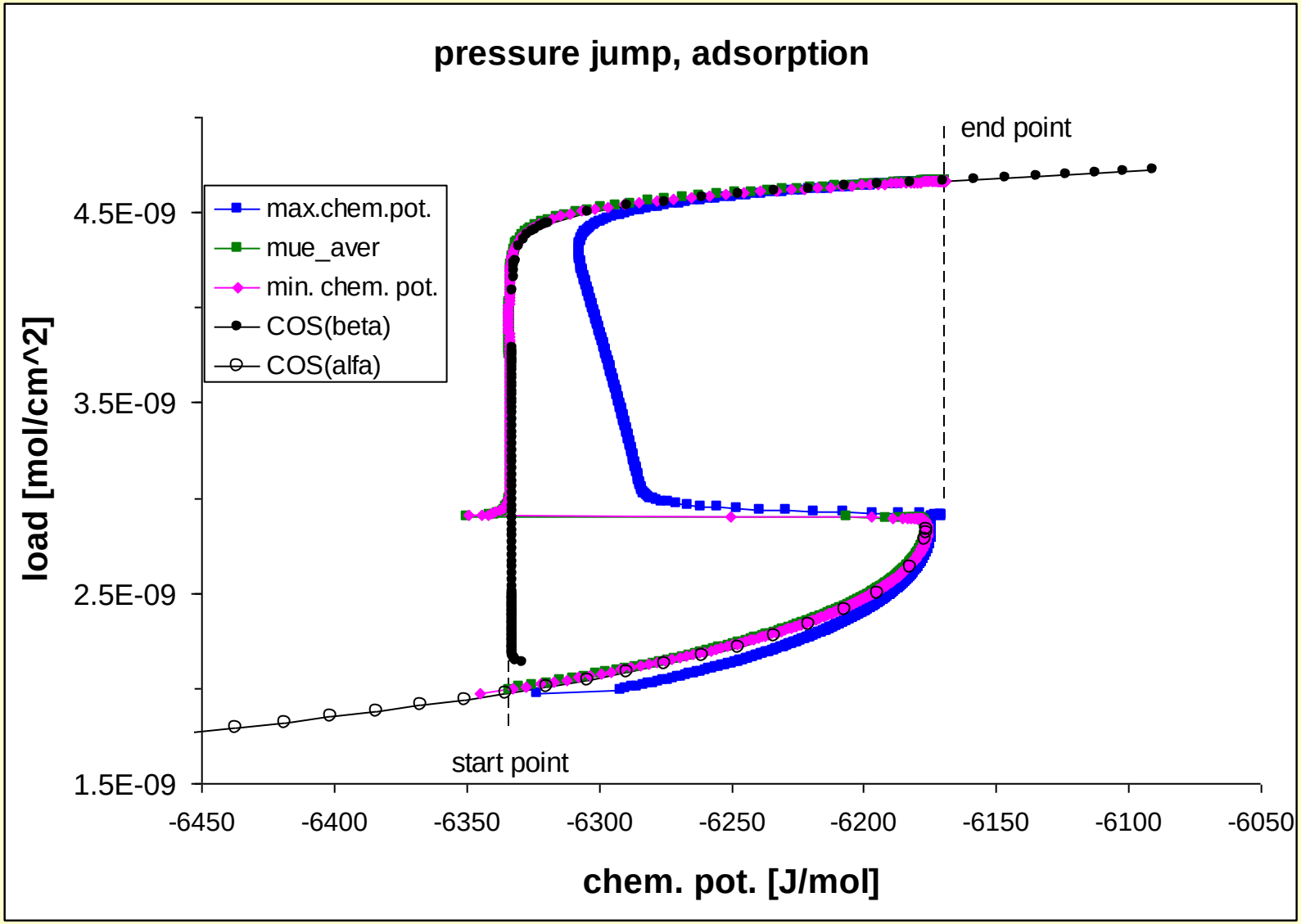
-6400
-6350
-6300
-6250
-6200
-6150
-6100
chem. pot. [J/mol]

adsorption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mue_aver
min. chem. pot.
COS(beta)
COS(alfa)
load [mol/cm^2]
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1.5E-09
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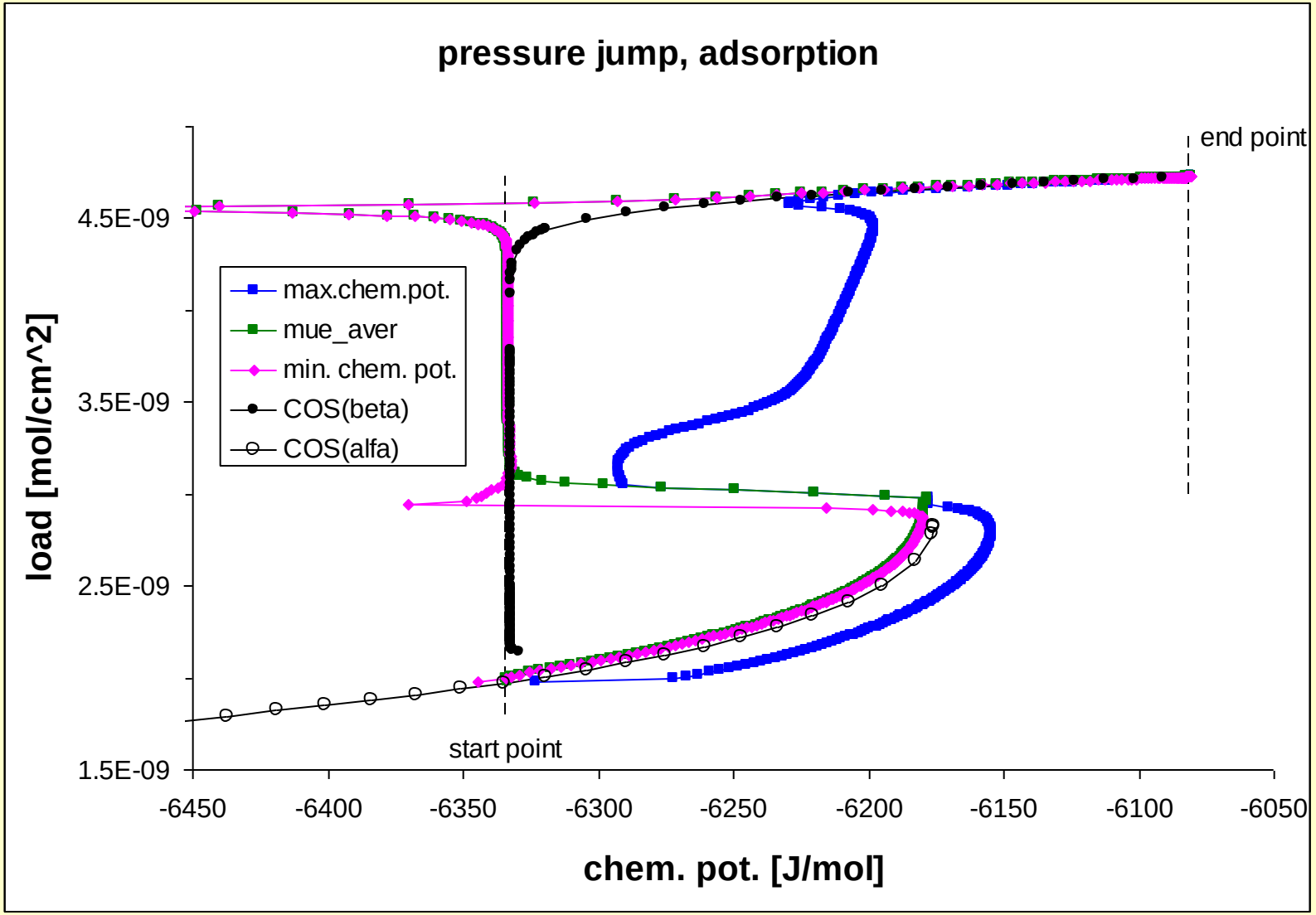
chem. pot. [J/mol]

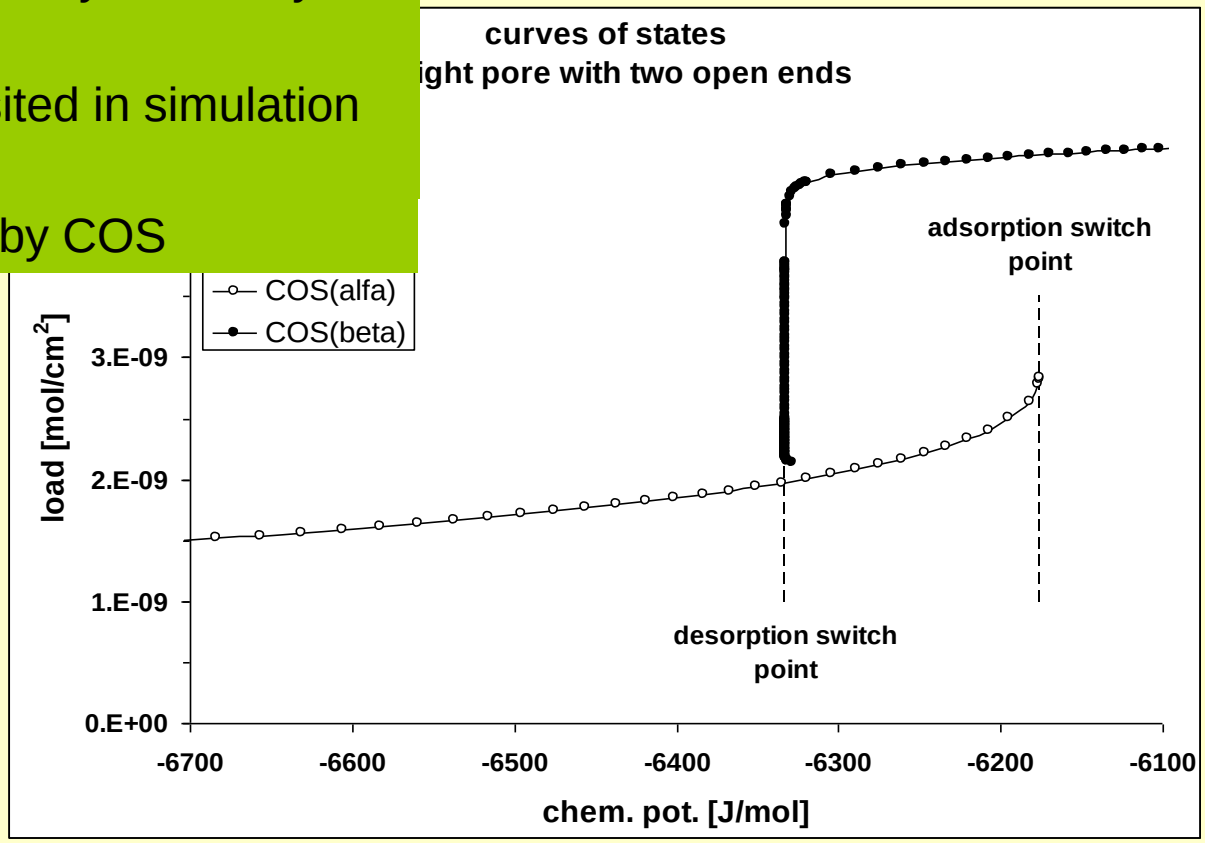

pressure jump, adsorption
end point
start point
max.chem.pot.
mue_aver
min. chem. pot.
COS(beta)
COS(alfa)
load [mol/cm^2]
4.5E-09
3.5E-09
2.5E-09
1.5E-09
-6450
-6400
-6350
-6300
-6250
-6200
-6150
-6100
-6050
chem. pot. [J/mol]

rules of new concept (Confined Thermodynamics):

- system is fully described by COS
- change within COS is always reversible
- switching between different COS is always irreversible, occurs only if required by boundary conditions
- all states of a system can be visited in simulation and experimentally
- dynamic behavior is dominated by COS

Thank you

critical remarks welcome !



Adsorption Hysteresis in Porous Material

Quotations from literature:

Metastable states ..... appear to be the most important aspect.[1]

.. in the experimental system the metastable states just do not have time enough to relax...[1]

...a failure of the system to equilibrate.[2]

This explains why hysteresis, although representing a departure from equilibrium, is so reproducible in experiment.[2]

[1] D.Wallacher et al., Phys. Rev. Lett. 92, (2004) 195704-1

[2] R.Valiullin et al., Nature Letters, 443 (2006) 965-8

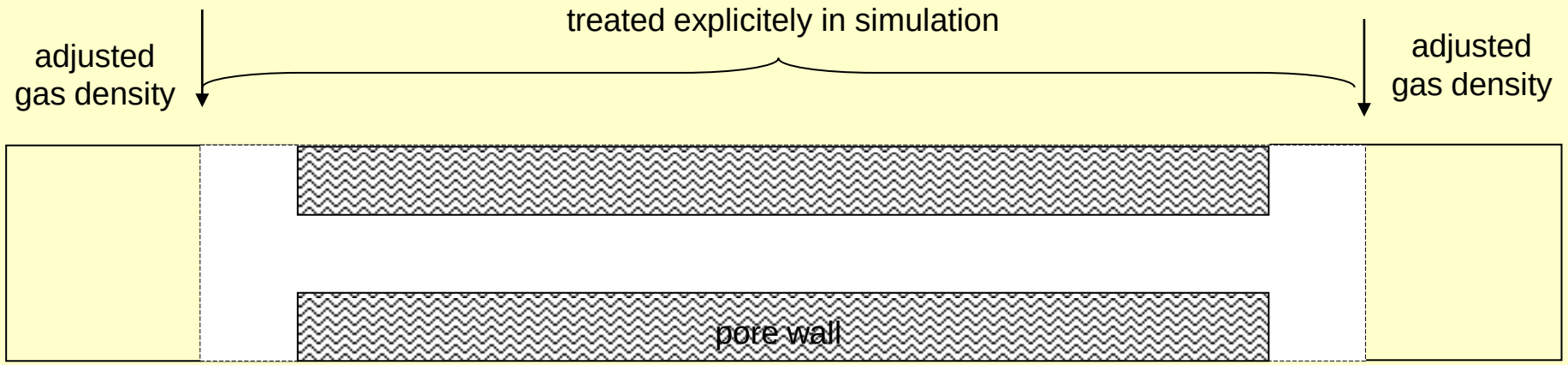
Adsorption Hysteresis in Porous Material

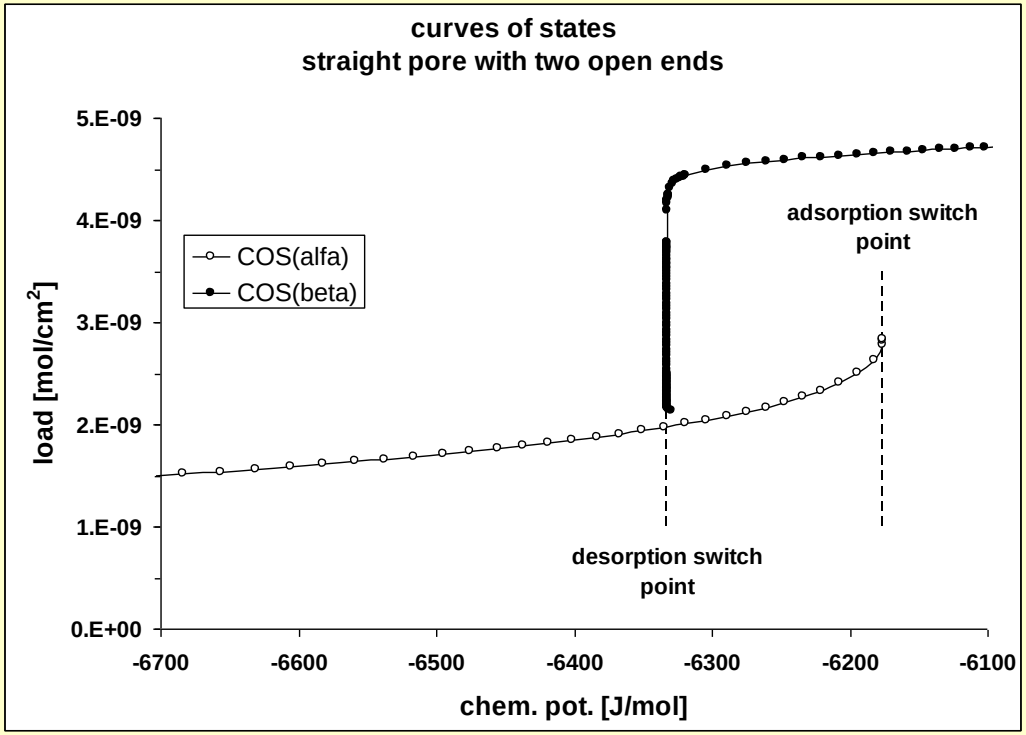
Quotations from literature:

However, even in experiments in which accessible observation times are much longer than in simulations, a hysteresis is usually observed, whose properties are quite reproducible.[1]

[1] J. Puibasset et al. J.Chem.Phys. **131** (2009) 124123-1/10

Simulated system





shape of pore

isotherm of pores with two open ends

crossing of grand potential curves

$$E_{pot}(\vec{r}) = \int_{volume} g(|\vec{r}-\vec{r}'|)\cdot V(|\vec{r}-\vec{r}'|)\rho(\vec{r}')d^3r'$$

potential energy

Homogeneous case:

$$E_{pot}^{\hom} = \rho\cdot \int_{volume} g(|\vec{r}-\vec{r}'|)\cdot V(|\vec{r}-\vec{r}'|)d^3r'$$

$$E_{pot}^{\hom} = \rho\cdot \int_0^{\infty}\int_0^{2\pi}\int_{-\pi}^{\pi} g(r)\cdot V(r) r^2 \sin(\theta) d\theta d\varphi dr$$

$$E_{pot}^{\hom} = \rho\cdot 4\pi \int_0^{\infty} g(r)\cdot V(r) r^2 dr$$

Radial convolution function

$$f_r(r) = \frac{g(r)\cdot V(r)}{E_{pot}^{\hom}(\rho)\cdot \rho^{-1}}$$

with $$1 = 4\pi \int_0^{\infty} f_r(r)\cdot r^2 dr$$

Inhomogeneous case:

$$E_{pot}^{inh}(\vec{r}) = \int_{volume} E_{pot}^{\hom}(\rho(\vec{r})) \cdot \rho^{-1}(\vec{r}) \cdot f_r(|\vec{r} - \vec{r}'|) \cdot \rho(\vec{r}') d^3 r'$$

$$E_{pot}^{inh}(\vec{r}) = \frac{E_{pot}^{\hom}(\rho(\vec{r}))}{\rho(\vec{r})} \cdot \int_{volume} f_r(|\vec{r} - \vec{r}'|) \cdot \rho(\vec{r}') d^3 r'$$

$$E_{pot}^{inh}(\vec{r}) = \frac{E_{pot}^{\hom}(\rho(\vec{r}))}{\rho(\vec{r})} \cdot \bar{\rho}(\vec{r})$$

with $$\bar{\rho}(\vec{r}) = \int_{volume} f_r(|\vec{r} - \vec{r}'|) \cdot \rho(\vec{r}') d^3 r'$$

Specializing to van der Waals fluid:

$$E_{pot}^{\hom}(\rho(\vec{r})) = -a \cdot \rho(\vec{r}) \quad \Rightarrow \quad E_{pot}^{inh}(\vec{r}) = -a \cdot \bar{\rho}(\vec{r})$$

Employing the potential energy as internal energy (o.k. for isothermal systems) we can write the free energy:

$$A_m(\vec{r}) = U_m^{\text{hom}}(\rho(\vec{r})) \cdot \frac{\bar{\rho}(\vec{r})}{\rho(\vec{r})} - T \cdot S_m(\rho(\vec{r}))$$ depends on $\bar{\rho}(\vec{r})$ and on $\rho(\vec{r})$

The chemical potential can then be shown to be:

$$\mu(\vec{r}) = -T \cdot S_m(\vec{r}) - T \cdot \rho(\vec{r}) \cdot \left(\frac{\partial S_m}{\partial \rho}(\vec{r}) \right) + \left(\frac{\partial U_m^{\text{hom}}}{\partial \rho}(\vec{r}) \right) \cdot \bar{\rho}(\vec{r})$$

$$+ \int_{-\infty}^{\infty} f(\vec{r}' - \vec{r}) \cdot U_m^{\text{hom}}(\rho(\vec{r}')) d^3 r'$$

Specializing to van der Waals fluid:

$$\mu(\vec{r}) = -TR \cdot \left(\ln\left(\frac{1}{\rho(\vec{r})} - b \right) - \frac{1}{1 - b\rho(\vec{r})} \right) - 2a \cdot \bar{\rho}(\vec{r})$$

For 2D and 3D simulation:
Convolution function as sum of Gaussians

$$f(r) = f\left(\left|\vec{r} - \vec{r}'\right|\right) = \sum_k \alpha_k G_k\left(\left|\vec{r} - \vec{r}'\right|\right) \qquad \text{with} \quad \sum_k \alpha_k = 1$$

where $$G_k\left(\left|\vec{r} - \vec{r}'\right|\right) = G_{z,k}\left(\left|z - z'\right|\right) \cdot G_{y,k}\left(\left|y - y'\right|\right) \cdot G_{x,k}\left(\left|x - x'\right|\right)$$

$$4\pi \int_0^\infty G_k(r) \cdot r^2 d^3 r = 1$$

Factorization of Gaussians saves computer time
~ 1 order of magnitude for 2D, ~2 orders of magnitude for 3D

$$\bar{\rho}(\vec{r}) = \int_{vol} f\left(\left|\vec{r}-\vec{r}'\right|\right)\cdot\rho(\vec{r}')\cdot d^3r'$$

$$= \sum_k \alpha_k \int_{vol} G_k\left(\left|\vec{r}-\vec{r}'\right|\right)\cdot\rho(\vec{r}')\cdot d^3r'$$

$$= \sum_k \alpha_k \cdot \int dz'\cdot G_{z,k}\left(\left|z-z'\right|\right)\cdot \underbrace{\int dy'\cdot G_{y,k}\left(\left|y-y'\right|\right)\cdot \underbrace{\int dx'\cdot G_{x,k}\left(\left|x-x'\right|\right)\cdot\rho(x',y',z')}_{\bar{\rho}_k(x,y',z')}}_{\bar{\rho}_k(x,y,z')}$$

$$\bar{\rho}_k(x,y,z)$$

$$\bar{\rho}(\vec{r}) = \sum_k \alpha_k \cdot \bar{\rho}_k(x',y',z')$$

Further savings in computer time:

•in region of mild inhomogeneity:

Cahn Hilliard approximation

square gradient method

$$\bar{\rho}(z) = \int_{-\infty}^{\infty} f_r(z - z') \cdot \rho(z') dz' \approx \rho(z) + m \cdot \frac{\partial^2 \rho}{\partial z^2}(z)$$

$$E_{pot}^{inh}(z) = \frac{E_{pot}^{\hom}(\rho(z))}{\rho(z)} \cdot \bar{\rho}(z) = E_{pot}^{\hom}(\rho(z)) \cdot \left(1 + \frac{m}{\rho(z)} \cdot \frac{\partial^2 \rho}{\partial z^2}(z)\right)$$

•adaptive grid

large gain in computer time possible compared to grid of fixed resolution