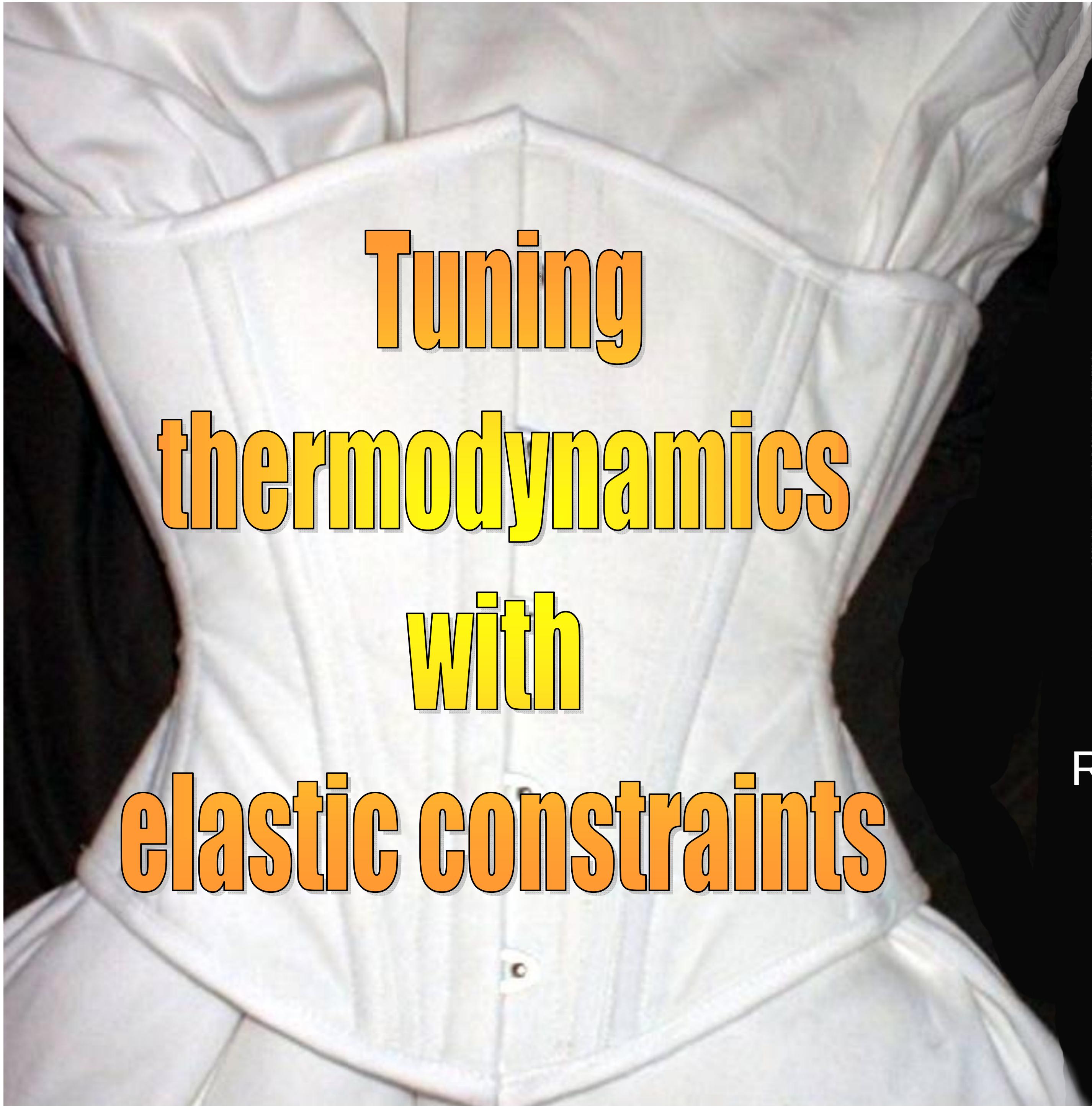
Tuning thermodynamics with elastic constraints



The Corset in the 18th Century.

Ronald Griessen
VU Amsterdam
Warsaw 2009

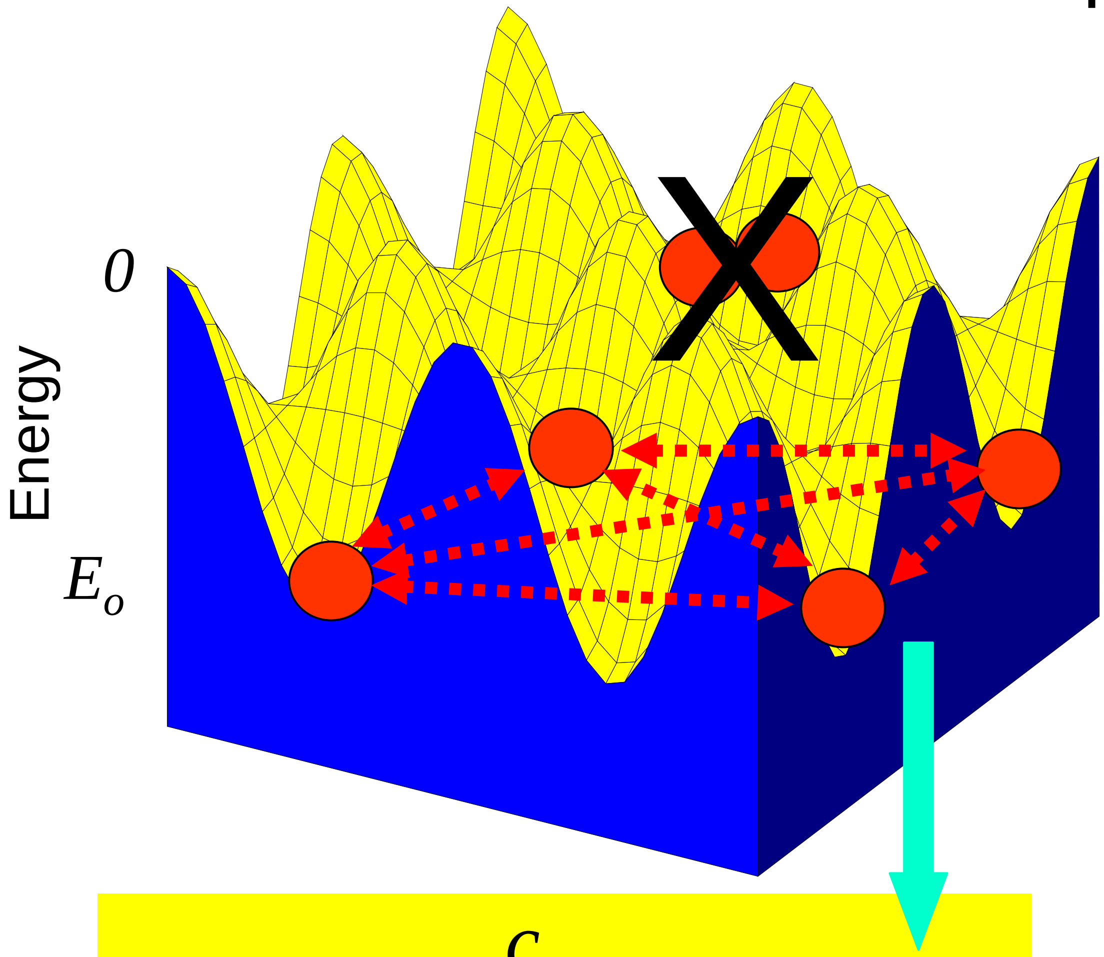
Tuning thermodynamics elastically

- Electronic and elastic interactions
- Constraints in 2D
- Layered Mg-Ti hydrides
  - Why Mg-Ti ?
  - Hydrogenography of layered Mg-Ti-H
  - Unexpected scenario for H-loading
  - The elastic scissor operator
- Layered Mg-TM hydrides
- Constraints in 3D: Mg/MgO nanocrystals

Tuning thermodynamics elastically

- Electronic and elastic interactions

H in M as a lattice gas



Fermi-Dirac statistics

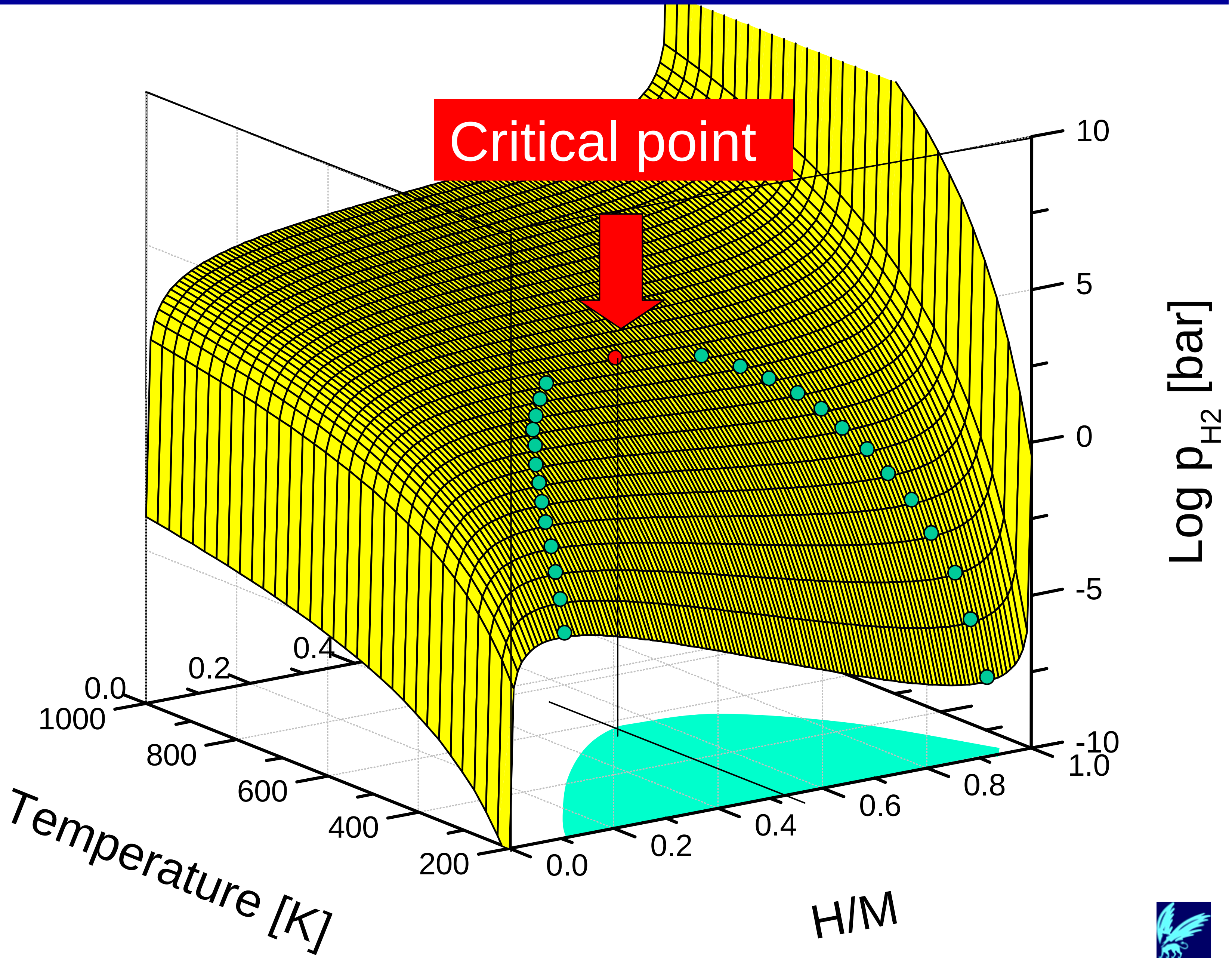
$$\langle n \rangle = \frac{1}{e^{\frac{E_o - \mu}{kT}} + 1}$$

$$\mu = kT \ln\left(\frac{\langle n \rangle}{1 - \langle n \rangle}\right) + E_o$$

$$\mu_H = kT\, ln \frac{c_H}{1 - c_H} + E_o + \varepsilon n c_H$$

$$\mu_H = kT \ln\left(\frac{c_H}{1 - c_H}\right) + E_o$$

P-c isotherms of lattice gas



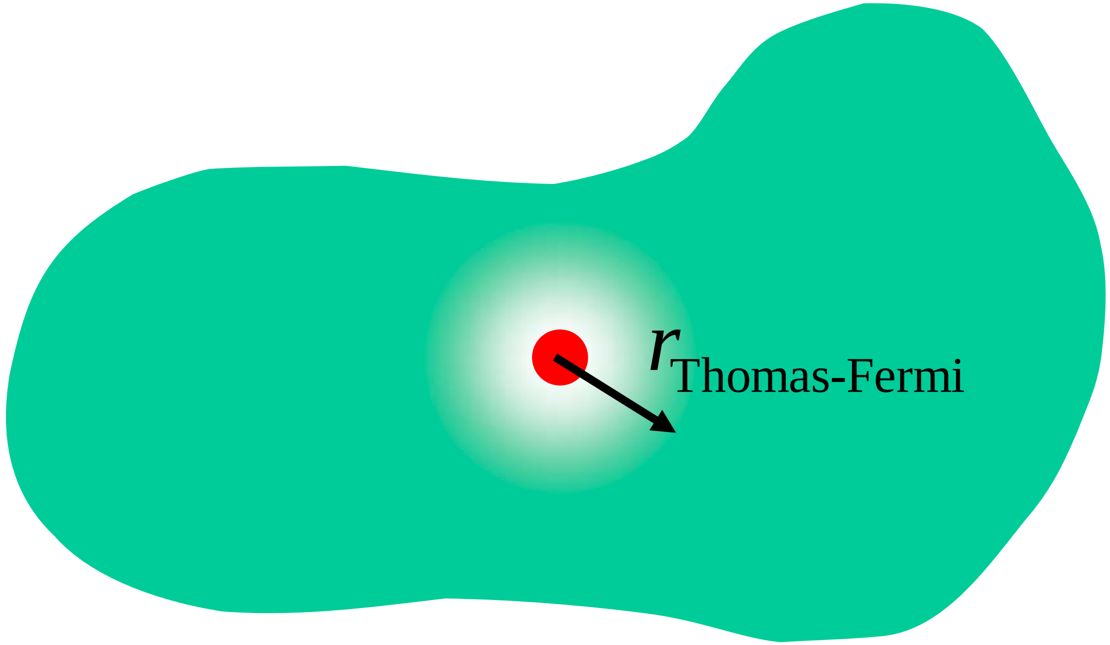
The interaction cannot be electronic

Potential of charge q in vacuum

$$V_0(r) = \frac{q}{r}$$

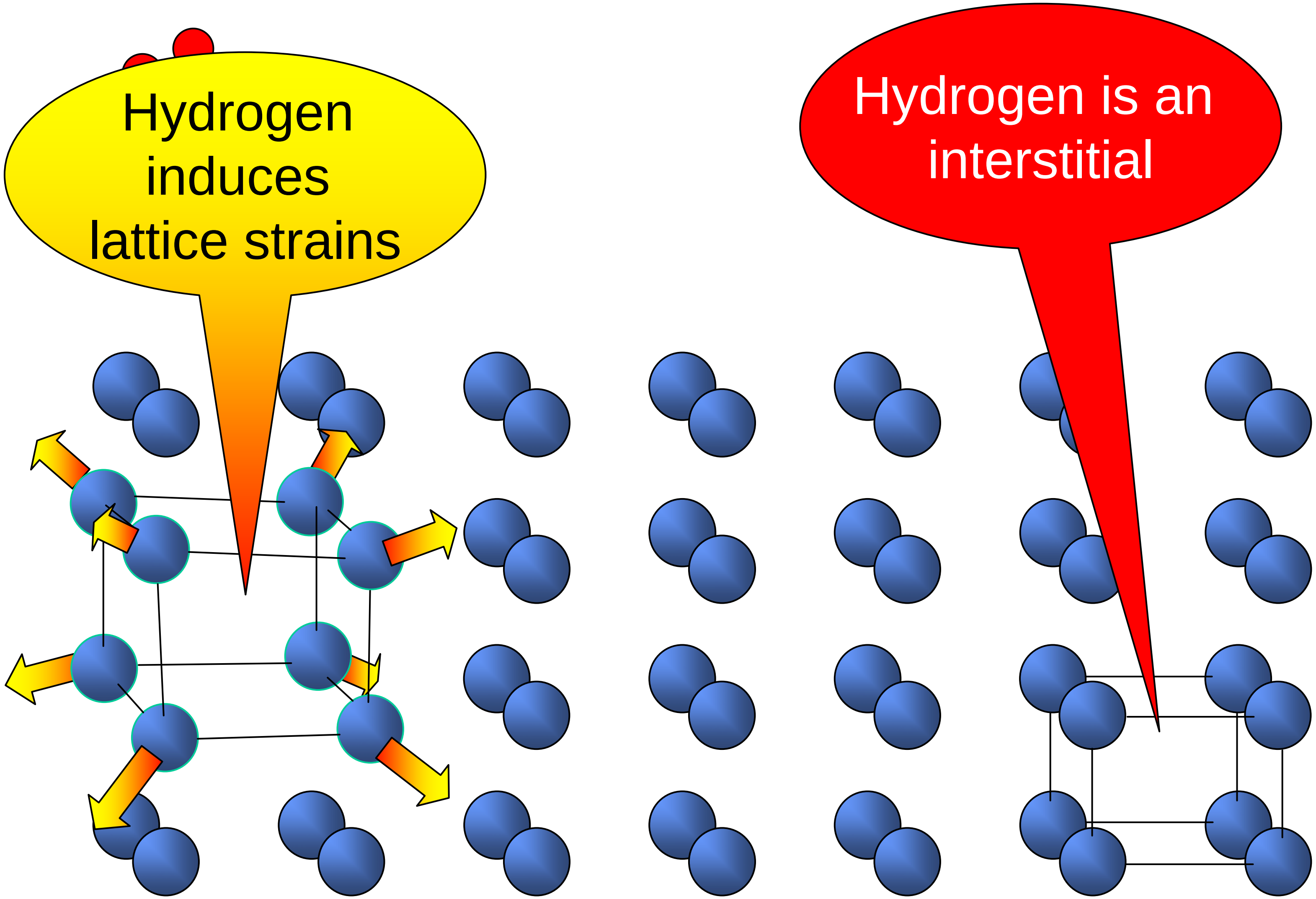
Potential of charge q in a metal

$$V_0(r) = \frac{q e^{-\frac{r}{r_{TF}}}}{r}$$



$$r_{TF} = \left(\frac{2\varepsilon_0 E_F}{3e^2 n} \right)^{\frac{1}{2}}$$ = typically 0.1 nm

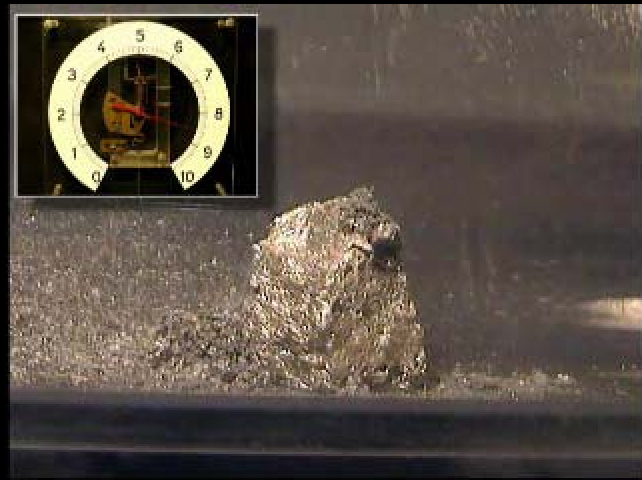
So,…what is it then?



Effect of lattice expansion during absorption of hydrogen in a metal

1

2

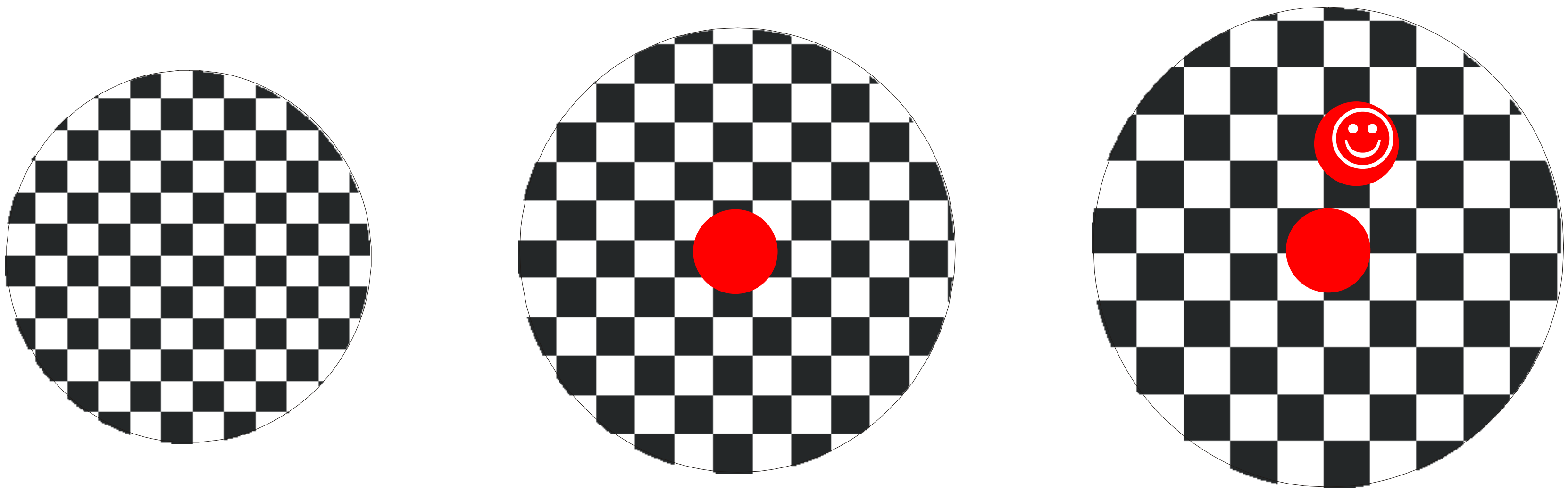


3

4

Andreas Zuettel, EMPA

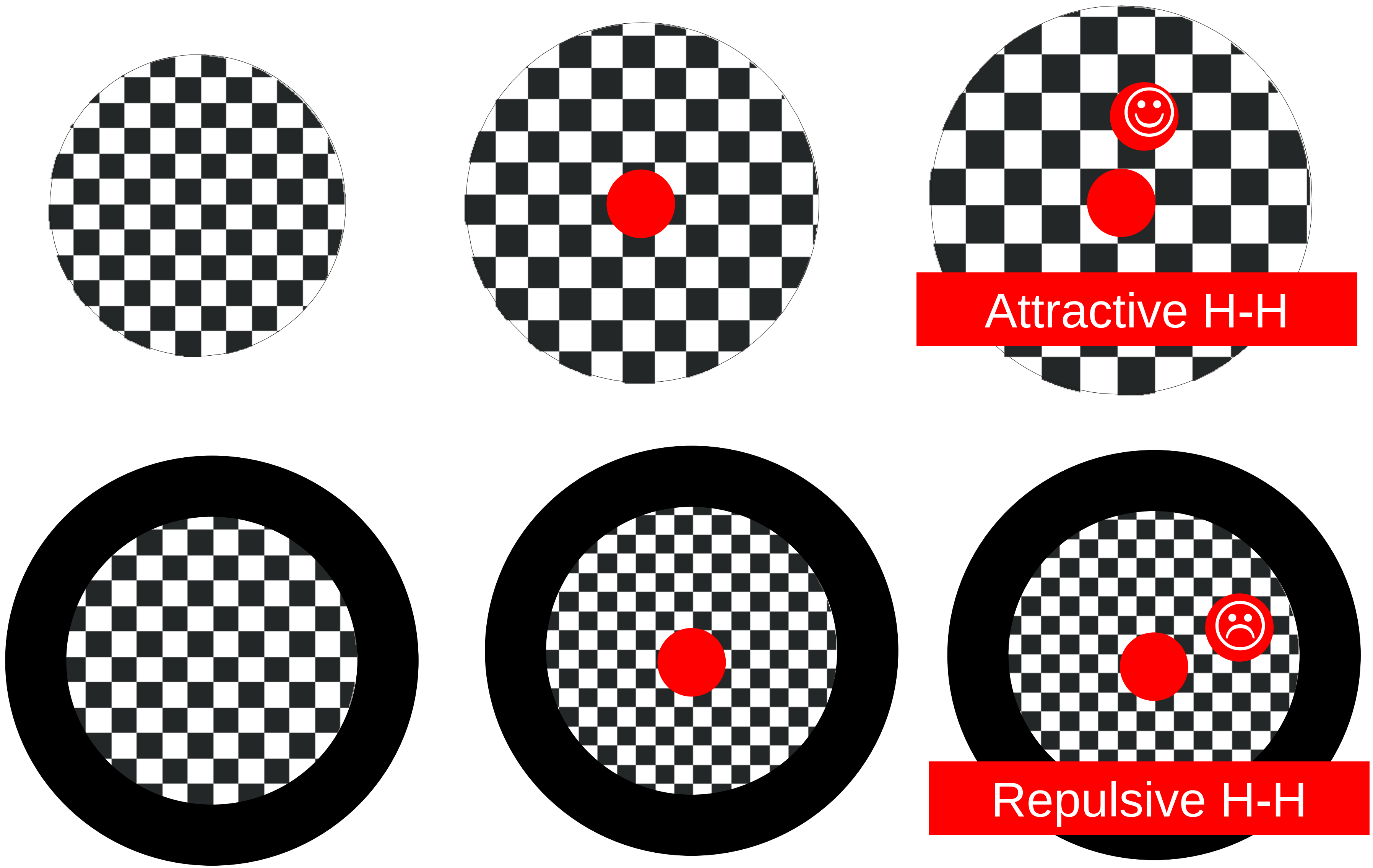
Volume dependence of the H-H interaction



$$\delta\left(\Delta\overline{H}\right) = -BV_H\left(\frac{\delta V}{V}\right)$$

For PdH_x $$\delta\left(\Delta\overline{H}\right) = -648\frac{\mathrm{kJ}}{\mathrm{molH_2}}\left(\frac{\delta V}{V}\right)$$

Boundary dependence of the H-H interaction



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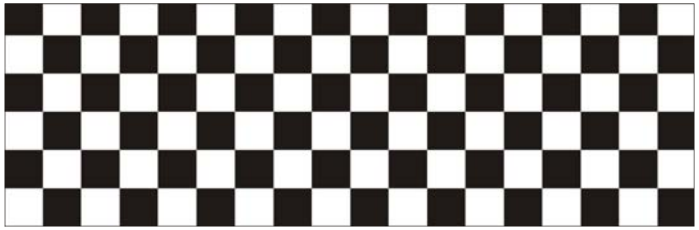
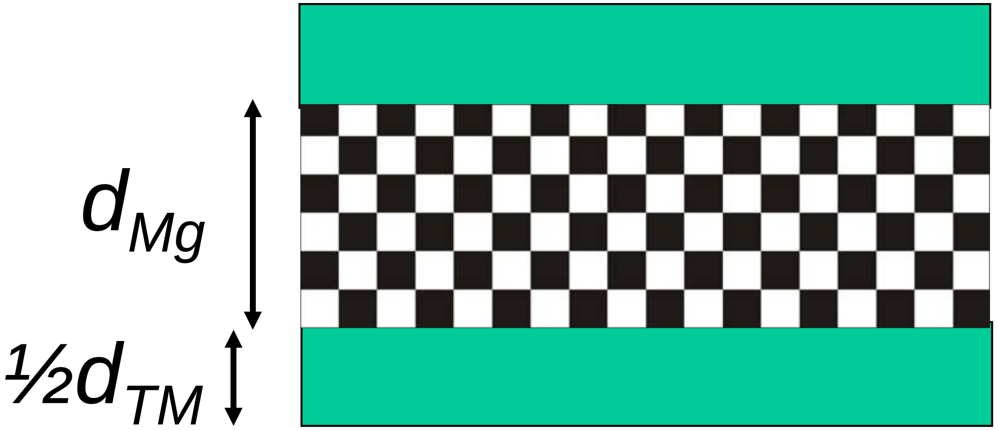
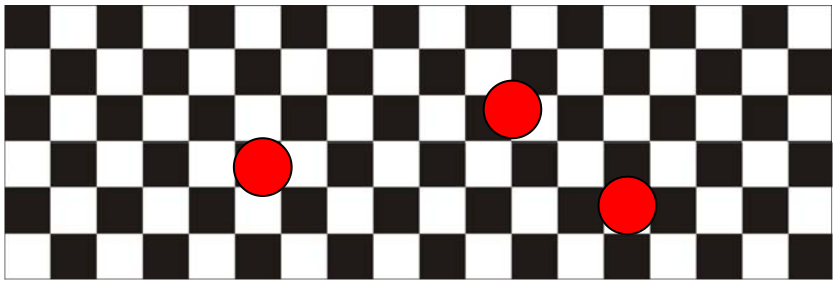
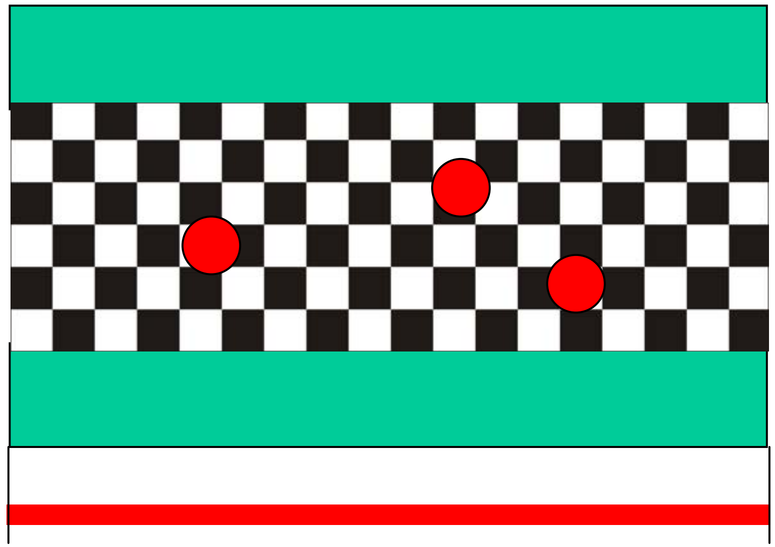
- Constraints in 2D

Elastic constraint in 2D



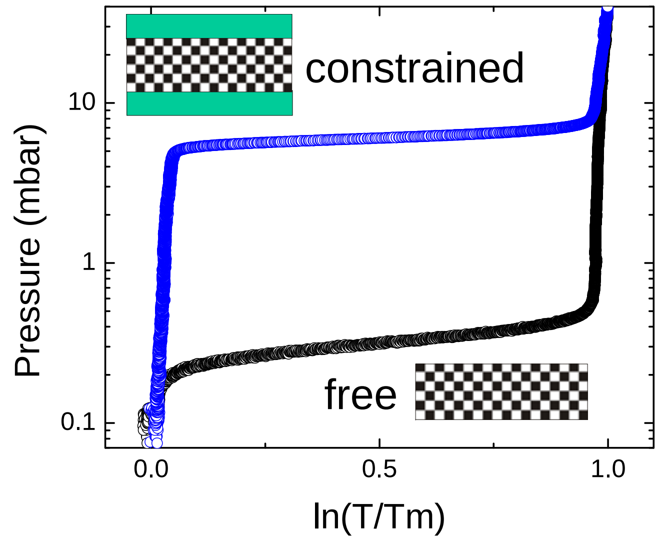






Elastic constraint in 2D

$$\frac{p_{constrained}}{p_{free}} = \exp\left(\frac{4E_{Mg}V_H^2}{9V_{Mg}RT} \frac{1}{\left(1-\nu_{Mg} + (1-\nu_{TM})\frac{E_{Mg}}{E_{TM}}\frac{d_{Mg}}{d_{TM}}\right)} \right)$$



$p_{constrained}$: plateau pressure of constrained Mg

p_{free} : plateau pressure of constrained Mg

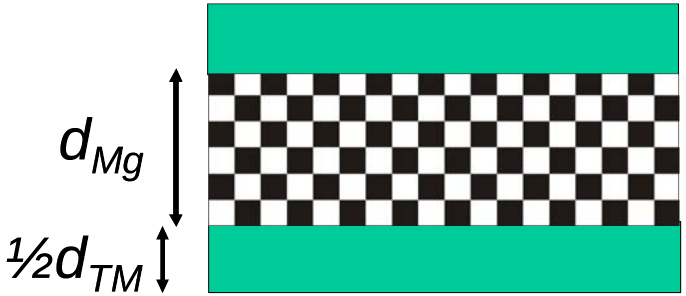
V_H : partial molar volume of H in Mg

V_{Mg} : molar volume of Mg

ν_{Mg}, ν_{TM} : Poisson ratio of Mg, TM

E_{Mg}, E_{TM} : Young modulus of Mg, TM

d_{Mg}, d_{TM} : thickness of Mg, TM-layer



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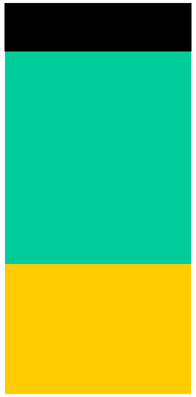
  - Why Mg-Ti ?

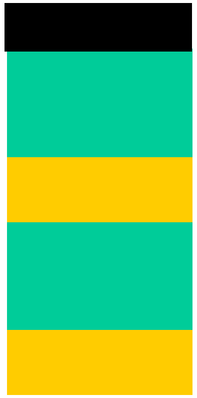

$Mg_{70}Ti_{30}$


$Mg_{70}Ti_{30}H_x$

Multilayers all nominally $Mg_{0.6}Ti_{0.4}$

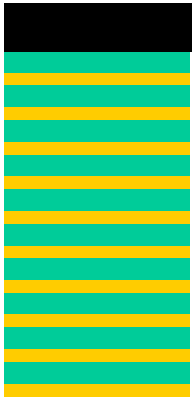


1 x [Ti(20nm)/Mg(40nm)]

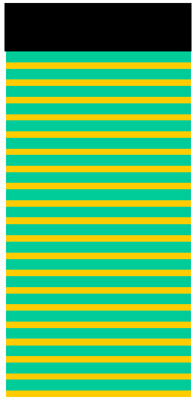


2 x [Ti(10nm)/Mg(20nm)]

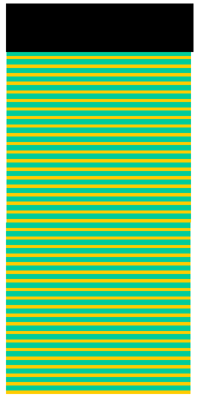
5 x [Ti(4nm)/Mg(8nm)]



10 x [Ti(2nm)/Mg(4nm)]

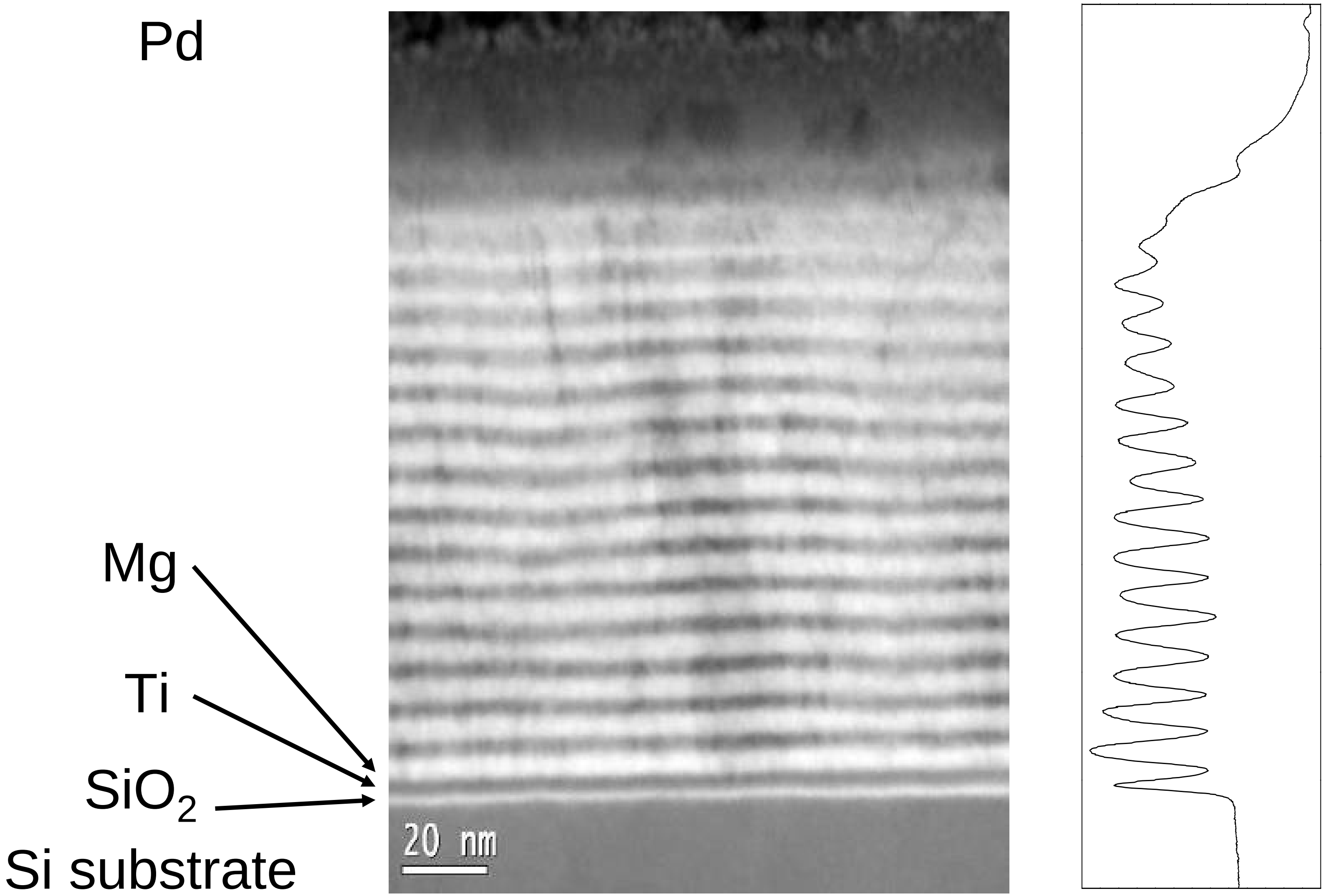


20 x [Ti(1nm)/Mg(2nm)]



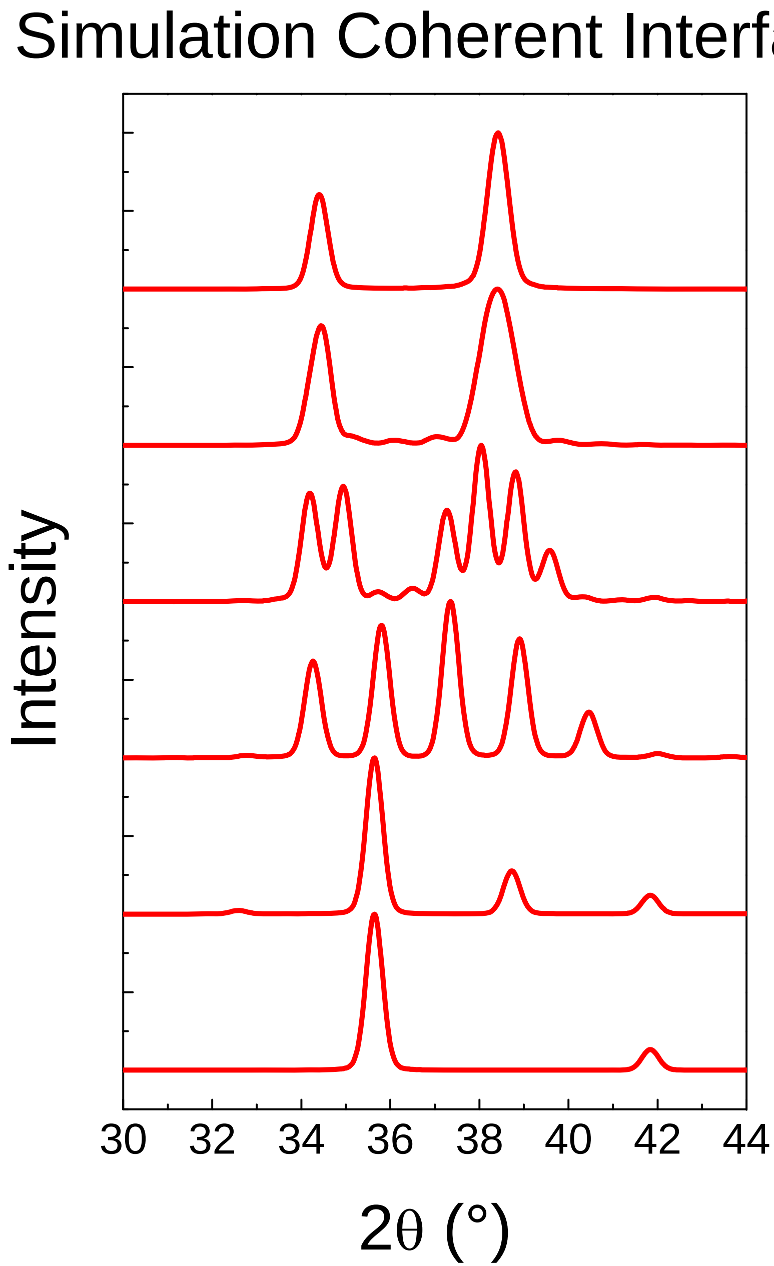
40 x [Ti(0.5nm)/Mg(1nm)]

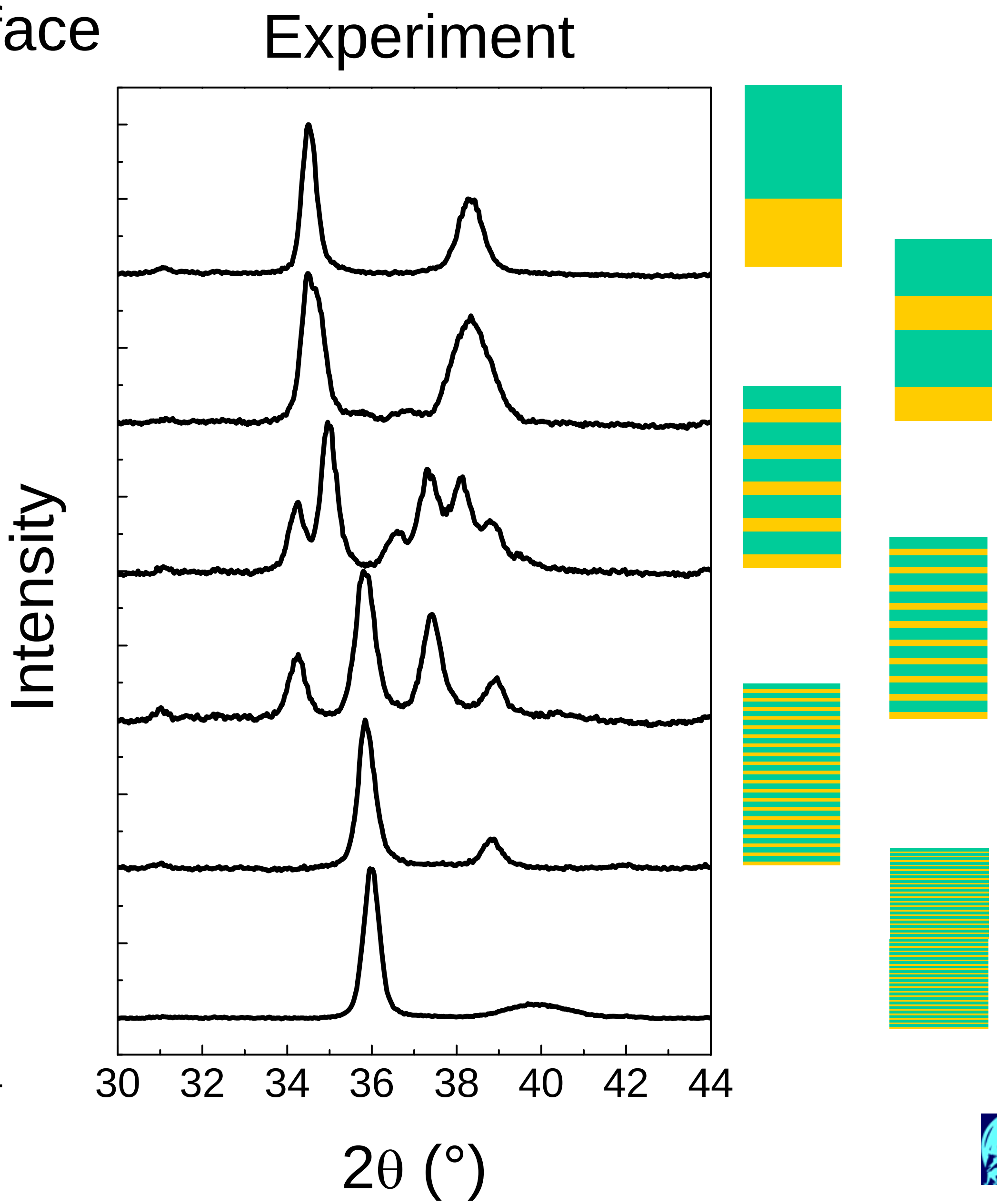
10nmPd / 20x[Ti(2nm)Mg(4 nm)] on Si(100)



Intensity profile

1st surprise: Mg/Ti multilayers are coherent





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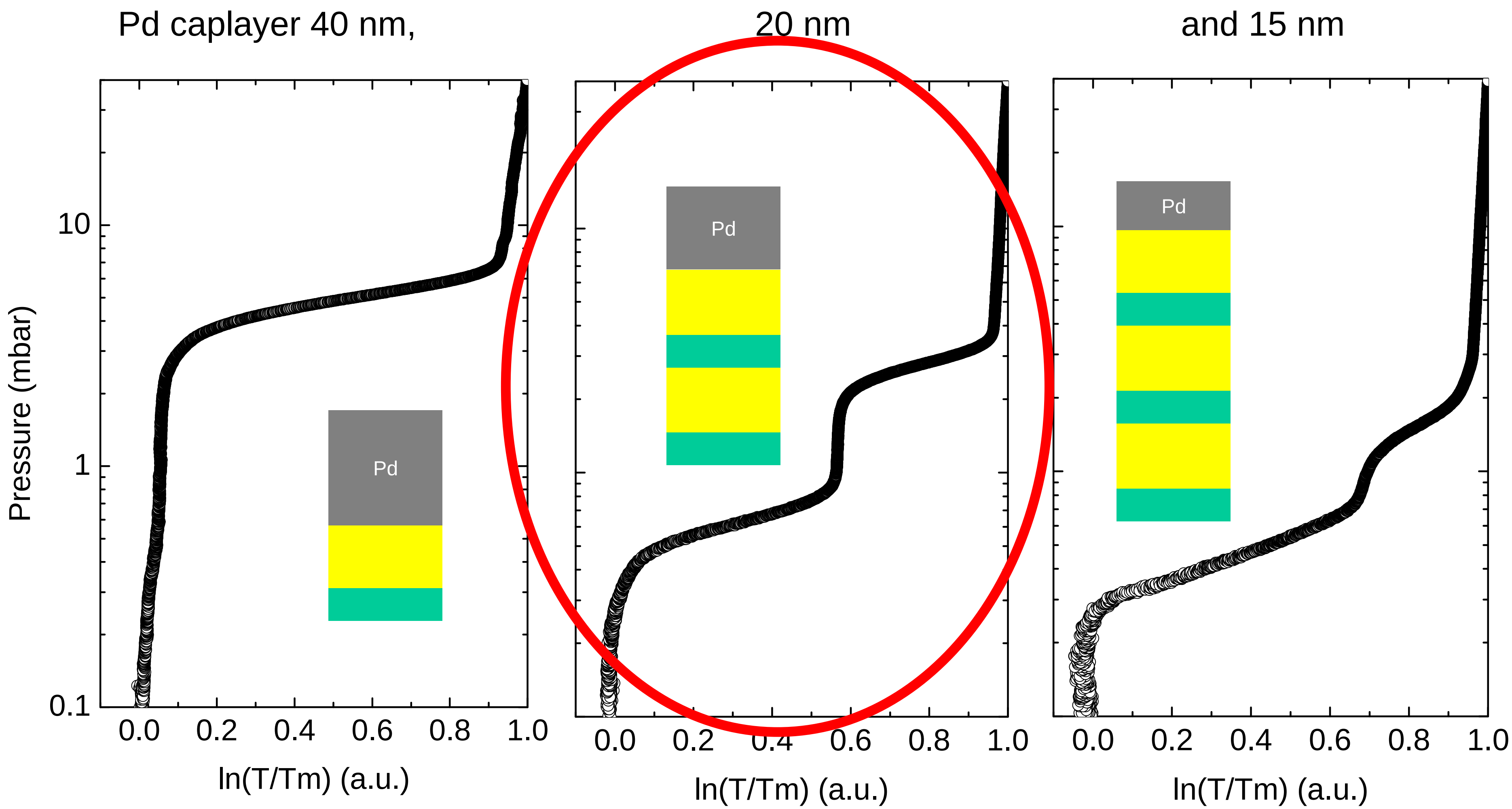
Mg(20nm)/Ti (10nm) multilayers



~Hydrogen concentration

A. Baldi, et al. Phys. Rev. Lett. 102 (2009) 226102.

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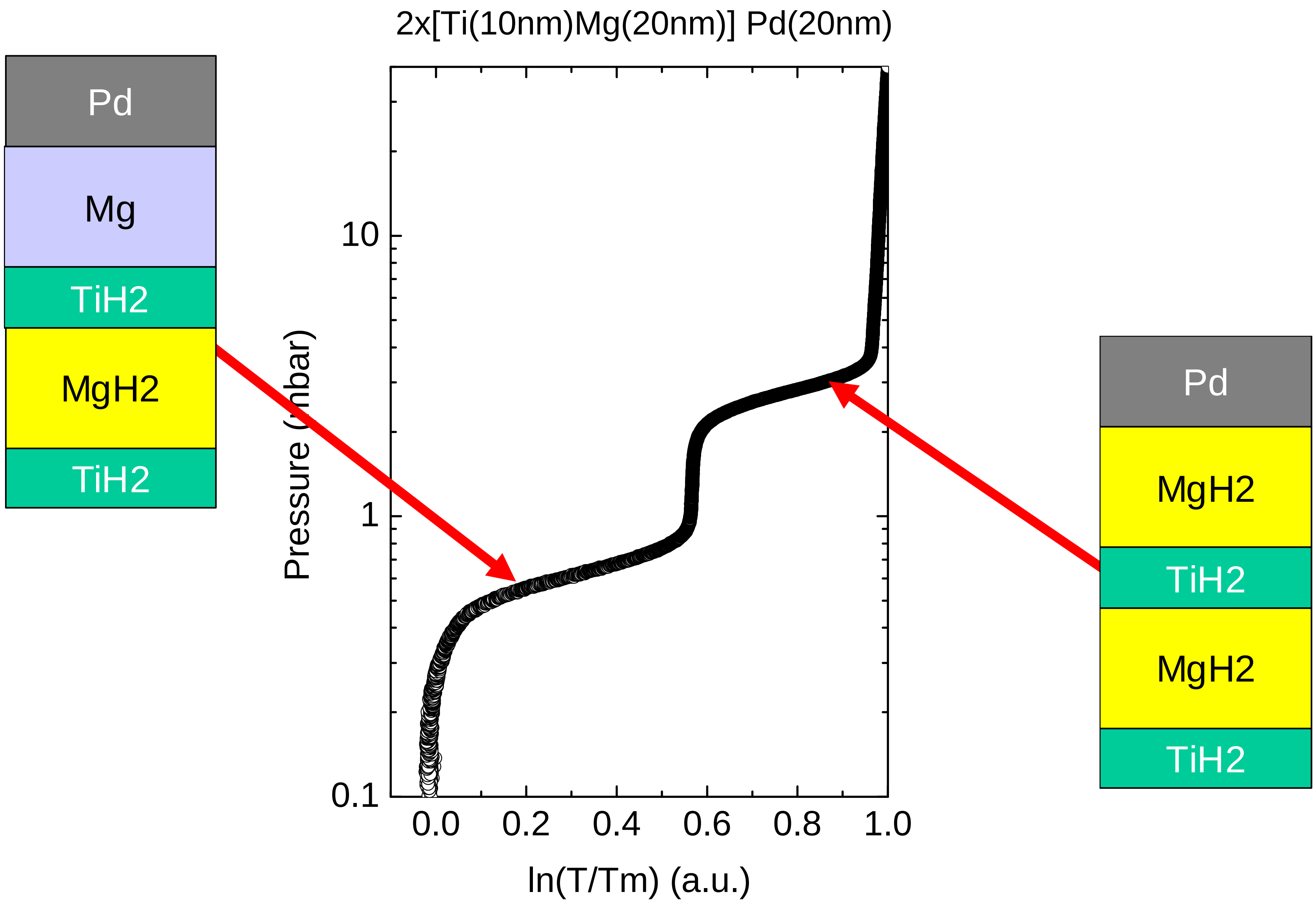
2nd surprise: Loading from the bottom



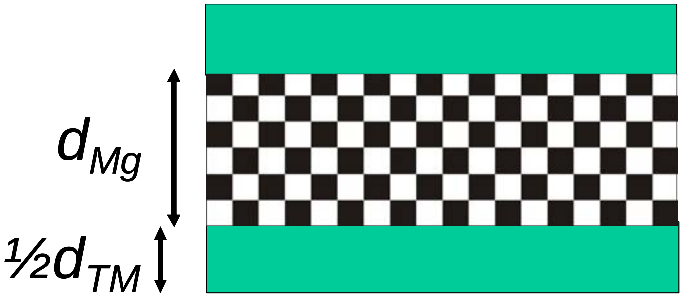
Elastic constraint in 2D

$$\left[\ln\left(\frac{p_{constrained}}{p_{free}}\right)\right]^{-1} = \left(\frac{1}{A} + \frac{B}{A}\frac{d_{Mg}}{d_{TM}}\right) = a + b\frac{d_{Mg}}{d_{TM}}$$

$$\frac{p_{constrained}}{p_{free}} = \exp\left(\frac{4E_{Mg}V_H^2}{9V_{Mg}RT}\frac{1}{\left(1-\nu_{Mg}+(1-\nu_{TM})\frac{E_{Mg}}{E_{TM}}\frac{d_{Mg}}{d_{TM}}\right)}\right)$$

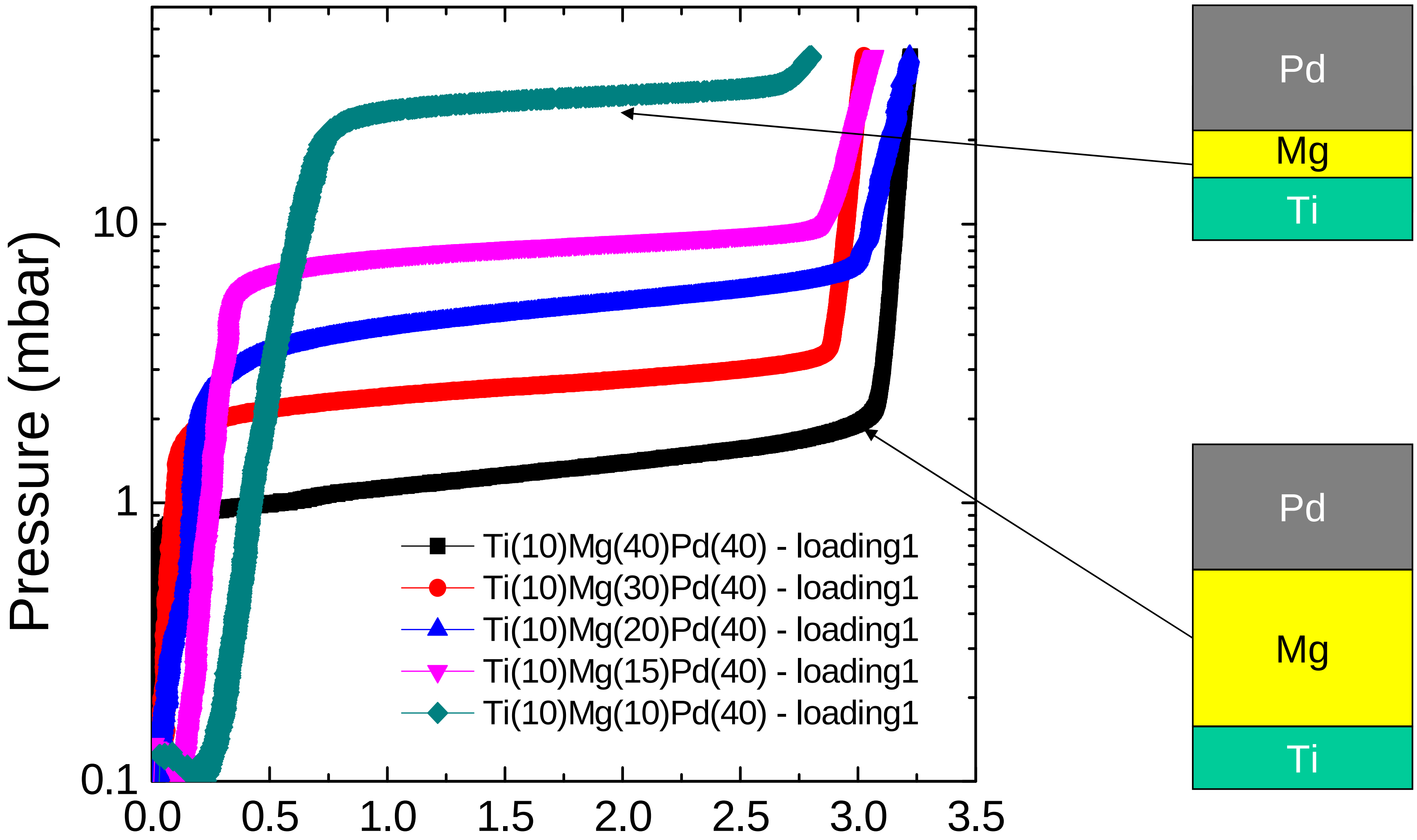
$$a = \left(\frac{4}{3}\left(\frac{1-2\nu_{Mg}}{1-\nu_{Mg}}\right)\frac{B_{Mg}V_H^2}{V_{Mg}RT}\right)^{-1}$$

$$a_{Mg} = 0.23$$



A. Baldi, M. Gonzalez-Silveira,
V. Palmisano, B. Dam and R. Griessen,
PRL 102 (2009) 226102

Effect of Mg thickness



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Test of the elastic model

$$\left[\ln\left(\frac{p_{constrained}}{p_{free}}\right)\right]^{-1} = \left(\frac{1}{A} + \frac{B}{A}\frac{d_{Mg}}{d_{TM}}\right) = a + b\frac{d_{Mg}}{d_{TM}}$$

$$a = \left(\frac{4}{3}\left(\frac{1-2\nu_{Mg}}{1-\nu_{Mg}}\right)\frac{B_{Mg}V_H^2}{V_{Mg}RT}\right)^{-1}$$

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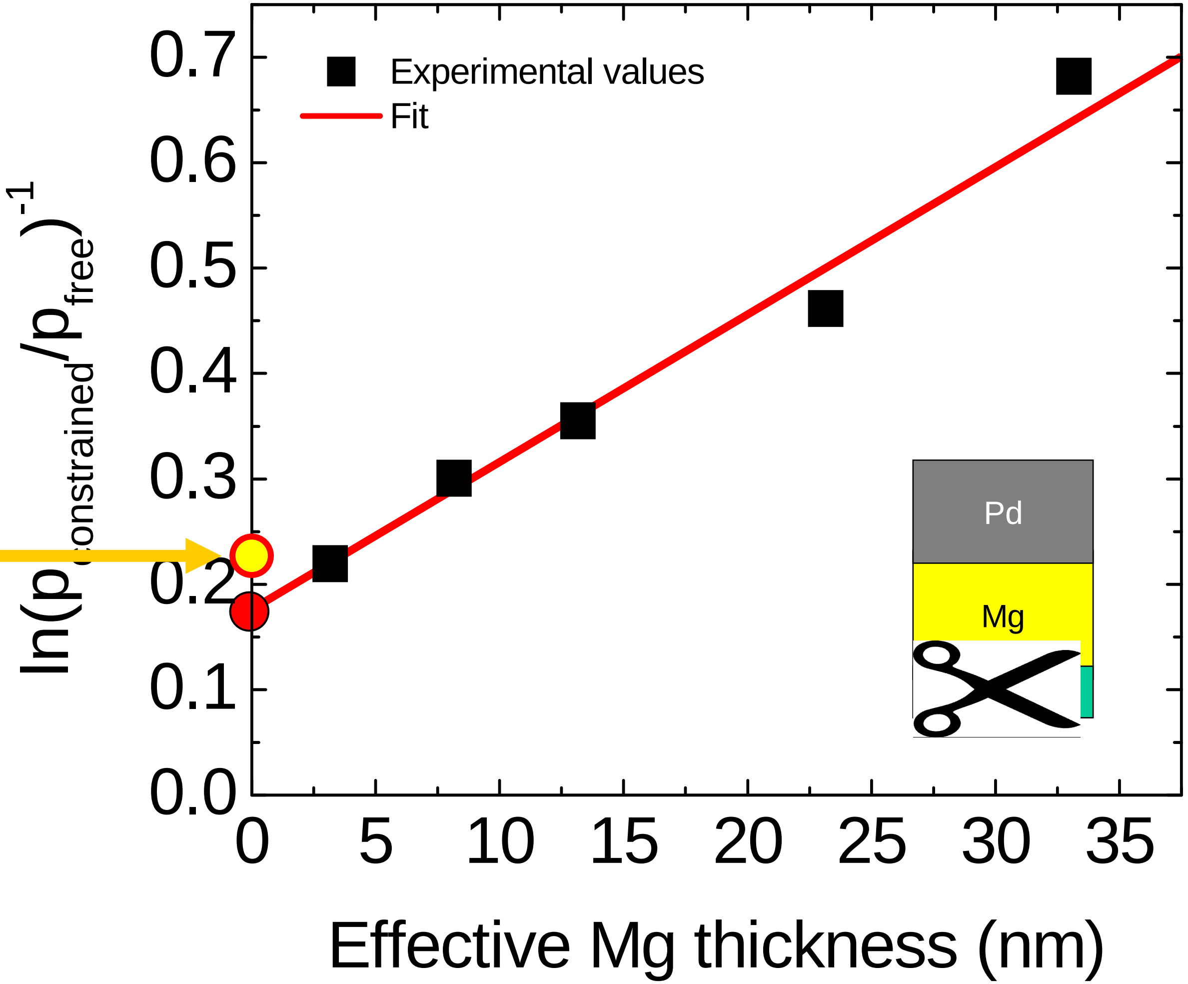

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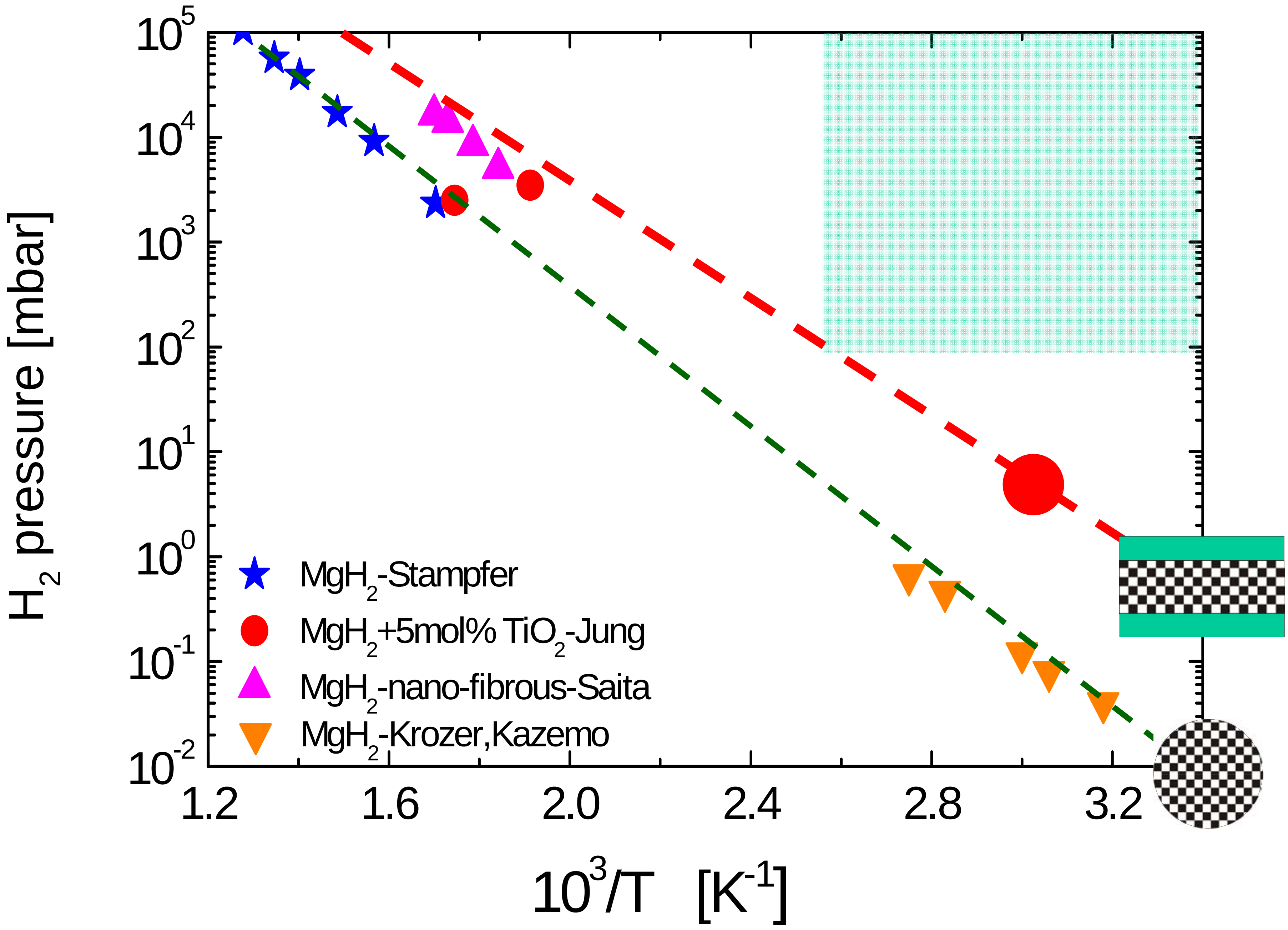
Free and 2D-constrained Mg-H



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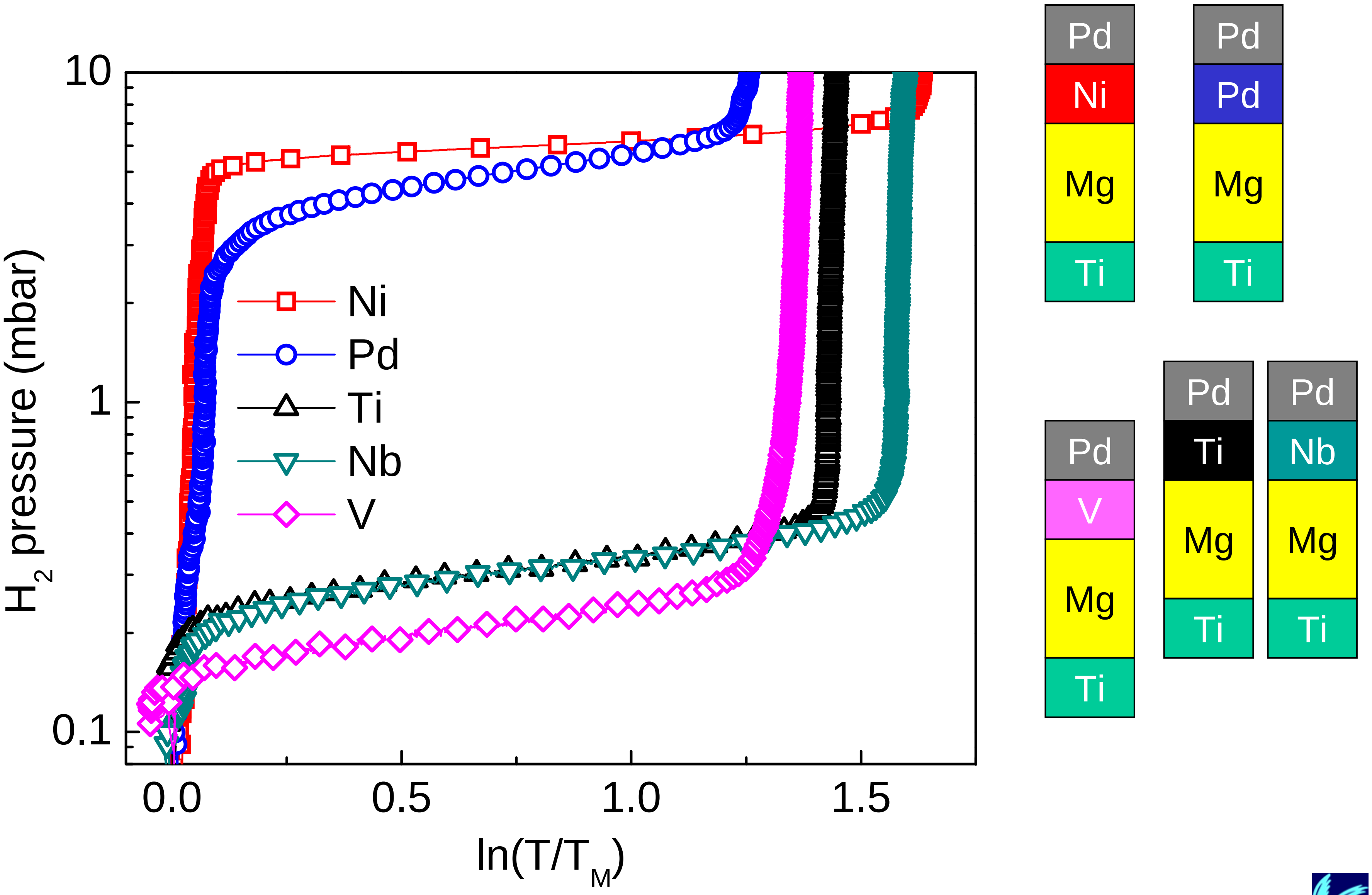
Influence of caplayer metal



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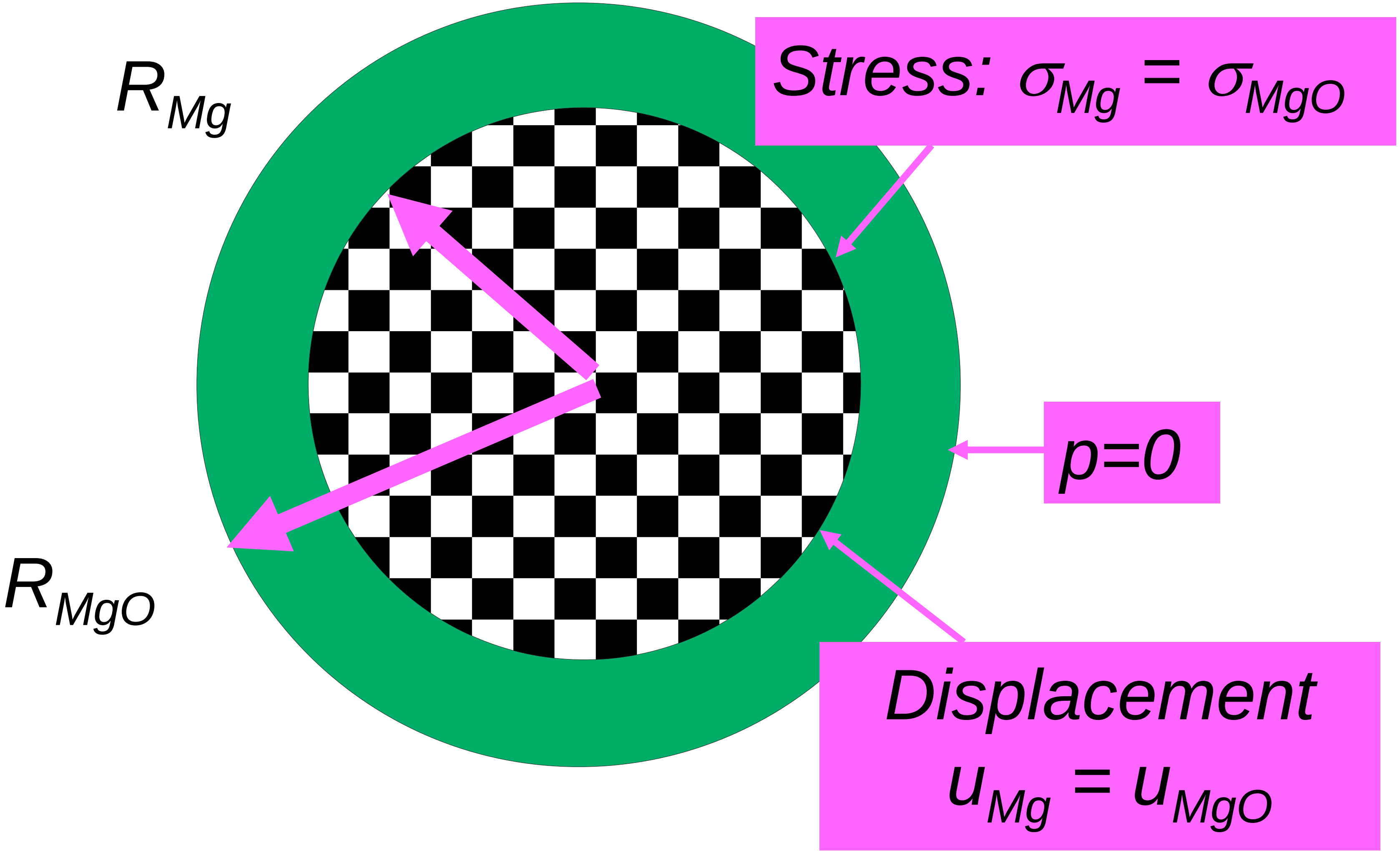
Elastic boundary conditions

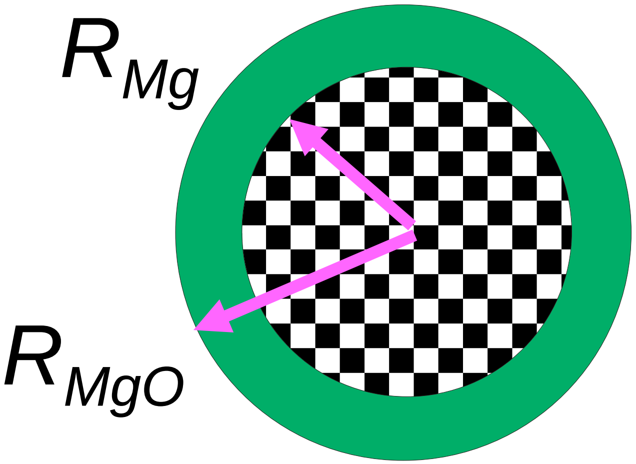


Elastic constraint in 3D

$$\frac{p_{constrained}}{p_{free}} = \exp\left(\frac{4B_{Mg}V_H^2}{V_{Mg}RT} \frac{y\left(r^3-1\right)}{\left(2+r^3\left(\frac{1+\nu}{1-2\nu}\right)+2y\left(r^3-1\right)\right)} \right)$$

$$y = \frac{E_{MgO}}{E_{Mg}}$$

$$r = \frac{R_{MgO}}{R_{Mg}}$$



Mg nanocrystal with MgO caplayer

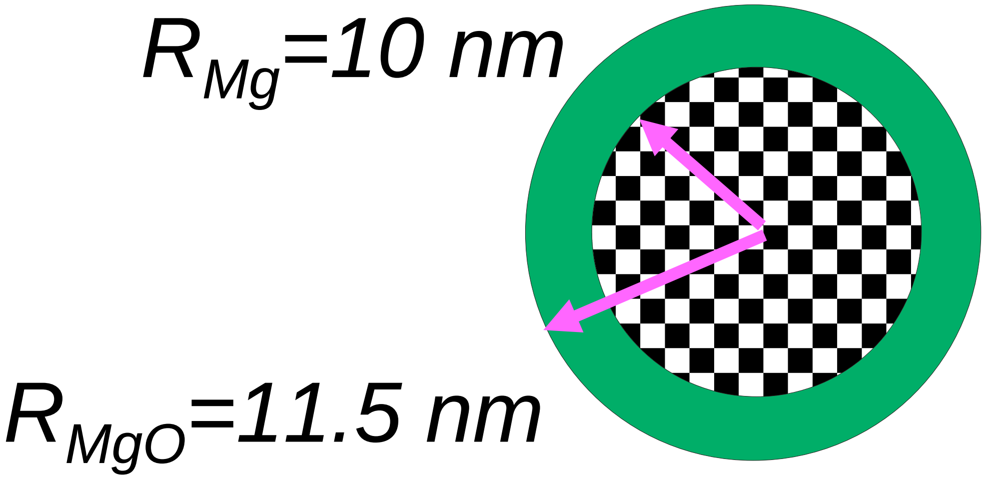
$$\frac{p_{constrained}}{p_{free}} = \exp\left(\frac{4B_{Mg}V_H^2}{V_{Mg}RT} \frac{y\left(r^3-1\right)}{\left(2+r^3\left(\frac{1+\nu}{1-2\nu}\right)+2y\left(r^3-1\right)\right)} \right)$$

$$y = \frac{E_{MgO}}{E_{Mg}} = 10$$

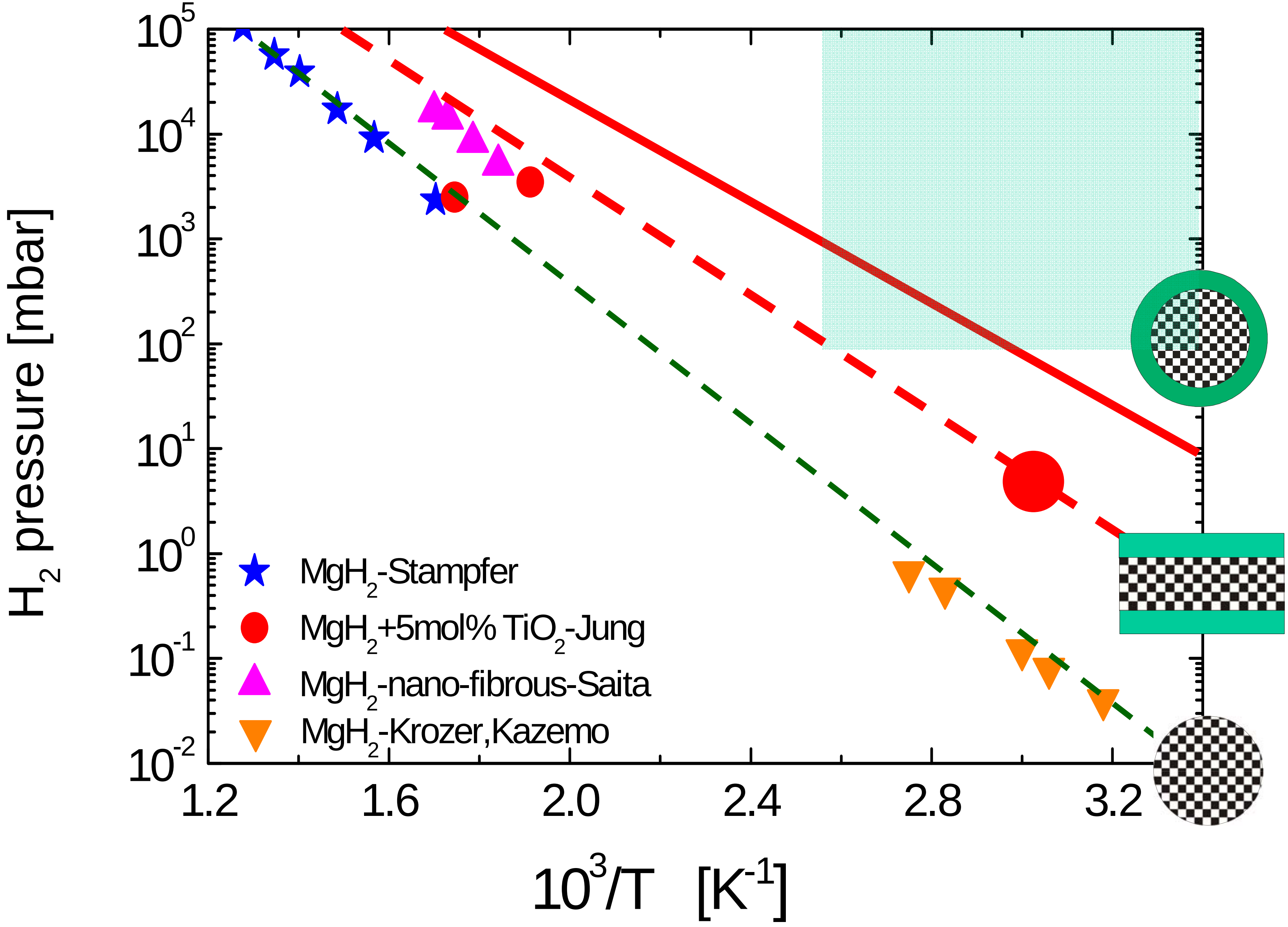
$$r = \frac{R_{MgO}}{R_{Mg}} = 1.15$$

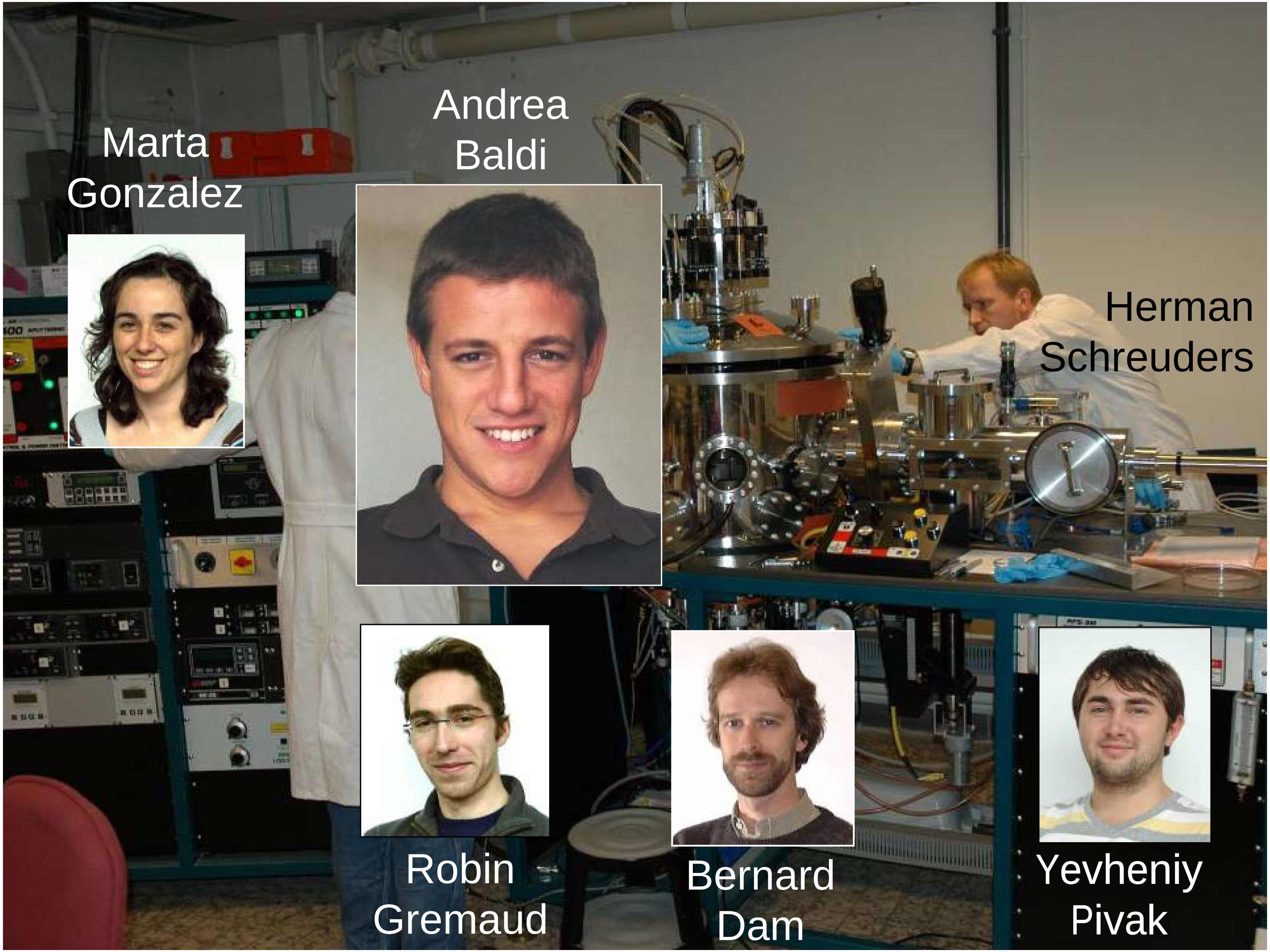
At 60°C this gives

$$\frac{p_{constrained}}{p_{free}} = 227$$



Free, 2D and 3D-constrained Mg-H




Marta
Gonzalez
Andrea
Baldi
Herman
Schreuders
Robin
Gremaud
Bernard
Dam
Yevheniy
Pivak

Thank you !

Ronald Griessen
VU Amsterdam
Warsaw 2009