Transport properties

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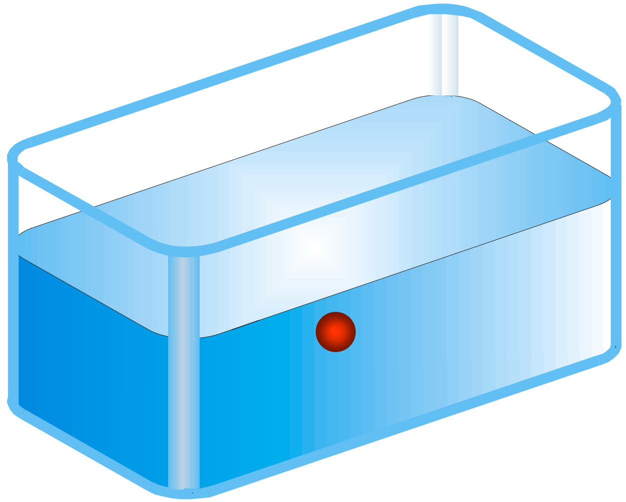
March 11, 2008

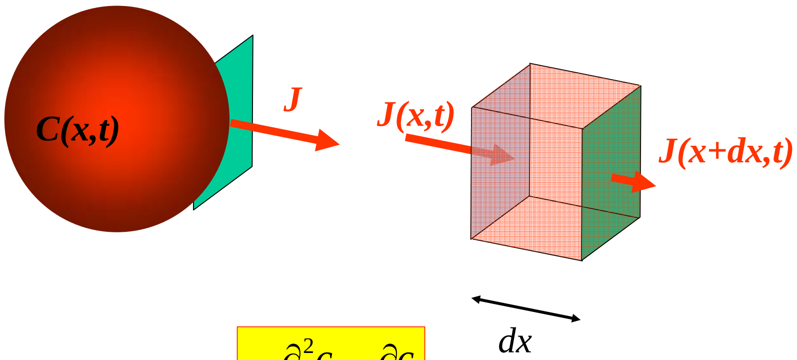
Diffusion



Fick's law — Equation of continuity

$$J = -D\frac{\partial c}{\partial x}$$

$$\frac{\partial c}{\partial t} + \frac{\partial J}{\partial x} = 0$$



$$D\frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t}$$

Diffusion equation

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

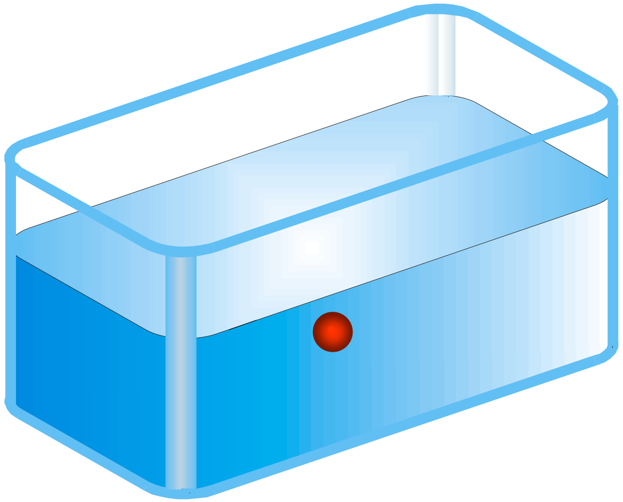
$$J = -D\frac{\partial c}{\partial x}$$

$$\frac{\partial c}{\partial t} + divJ = 0$$

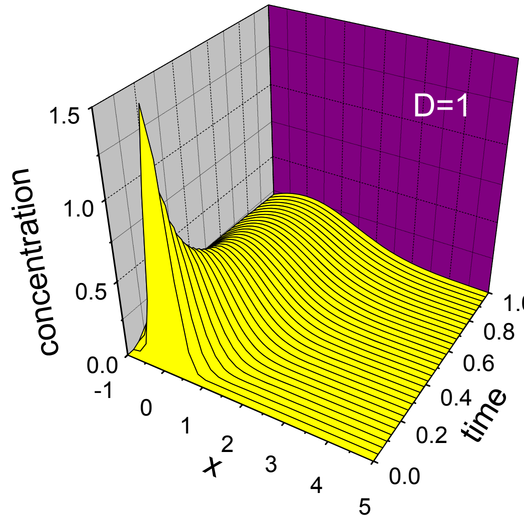
is clearly different from the wave equation

$$\frac{\partial^2 U}{\partial t^2} = v^2\frac{\partial^2 U}{\partial x^2}$$

Diffusion



Singularities decay immediately

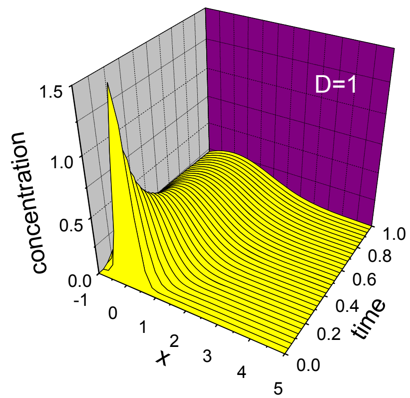


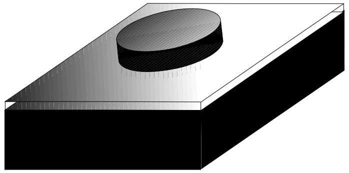
$$c = \frac{1}{2\sqrt{\pi D t}} e^{-\frac{x^2}{4Dt}}$$

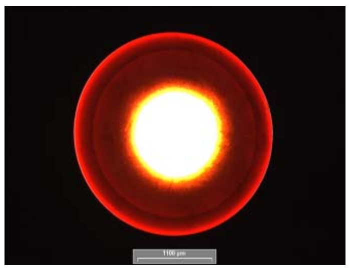
is a solution of

$$D\frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t}$$

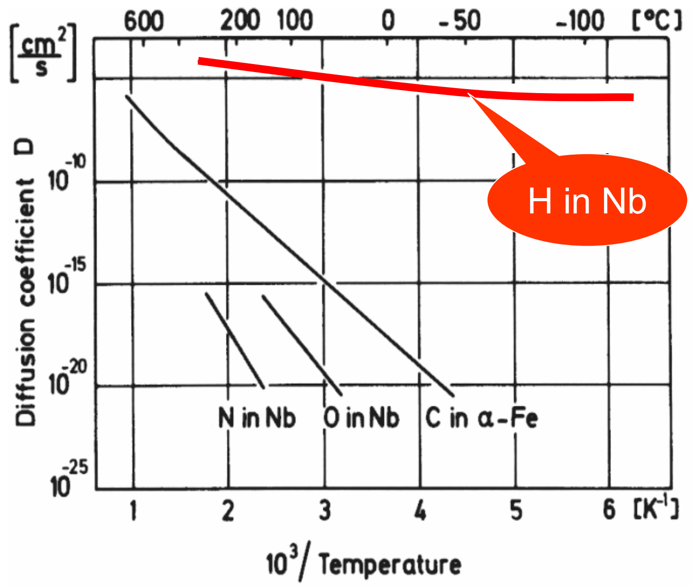
Radial diffusion of H as seen optically



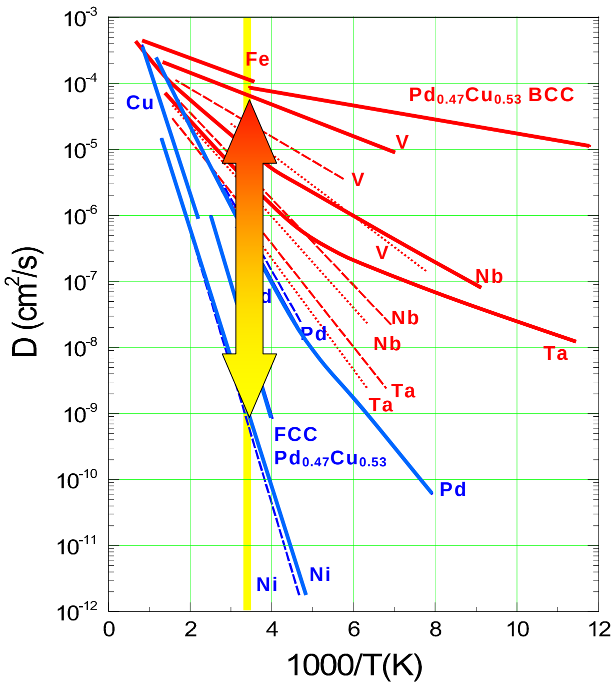




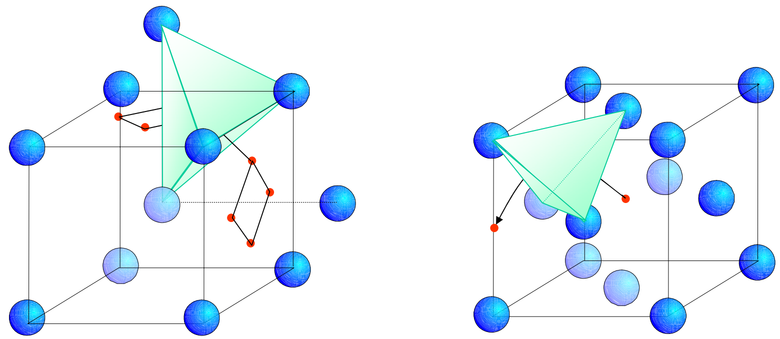
Diffusion coefficients of various interstitials

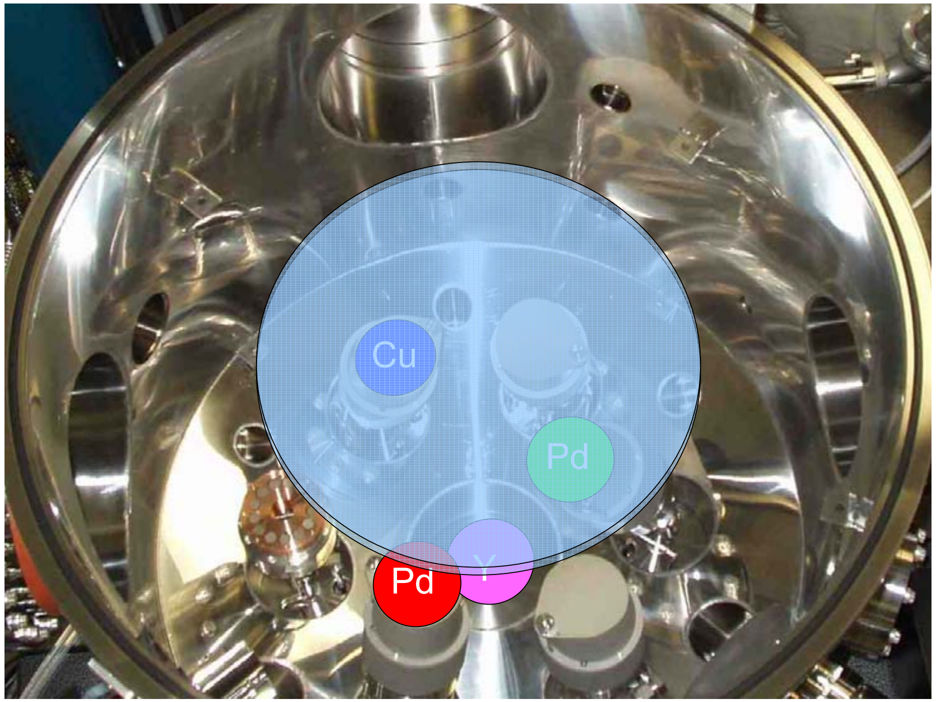


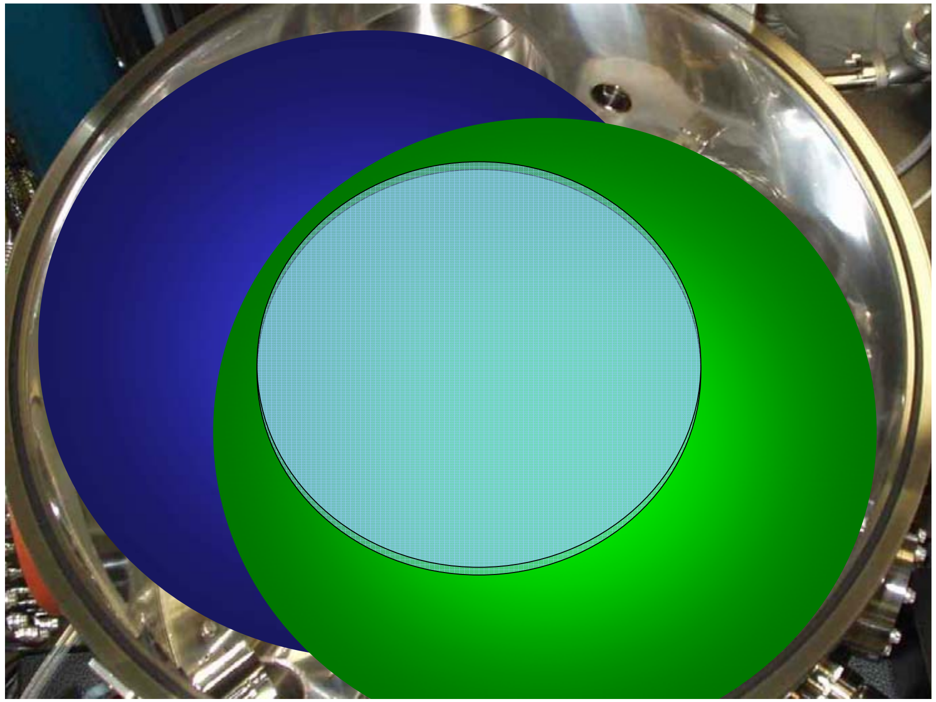
Diffusion coefficients of various interstitials

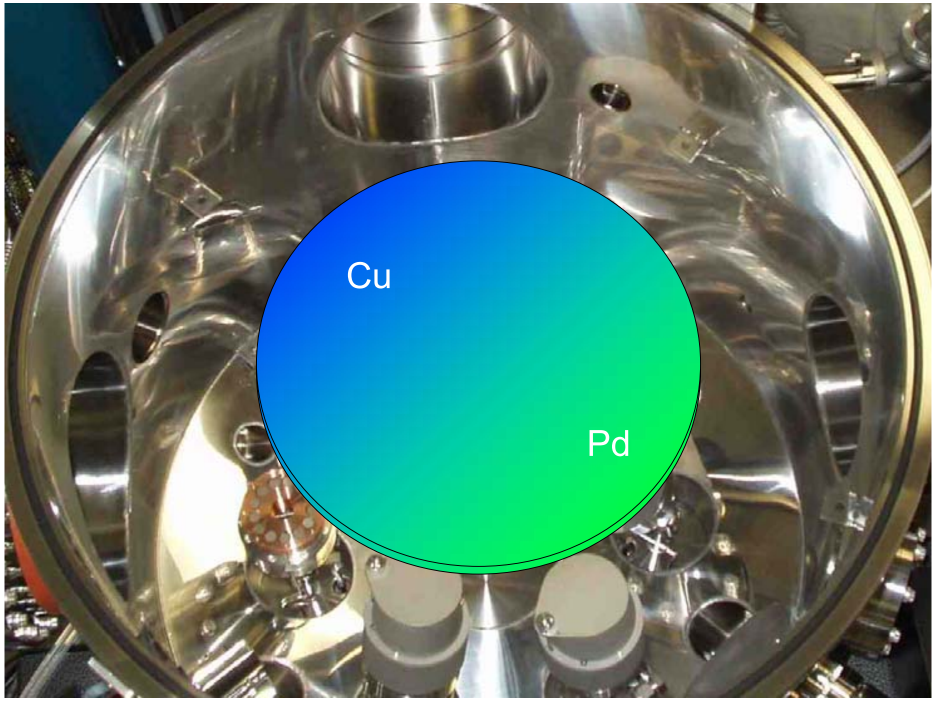


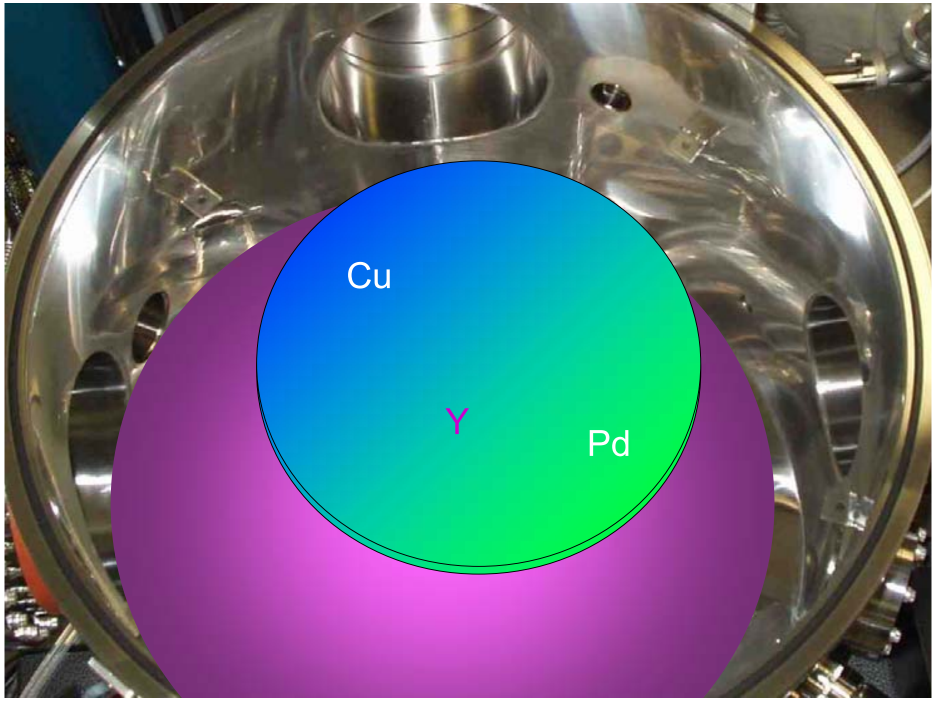
H diffusion is much faster in BCC than FCC metals

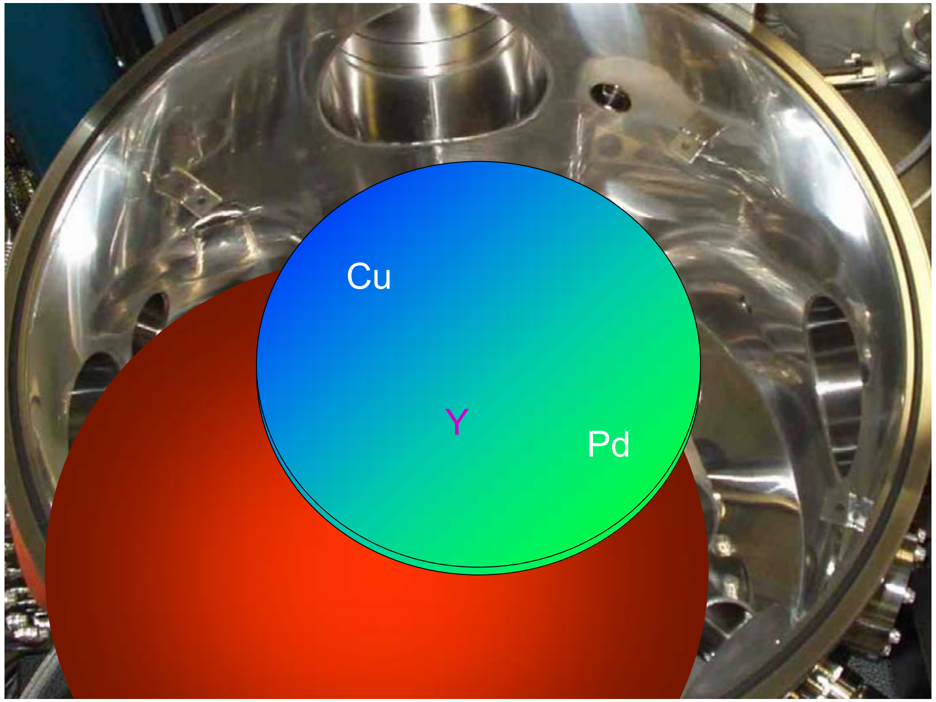


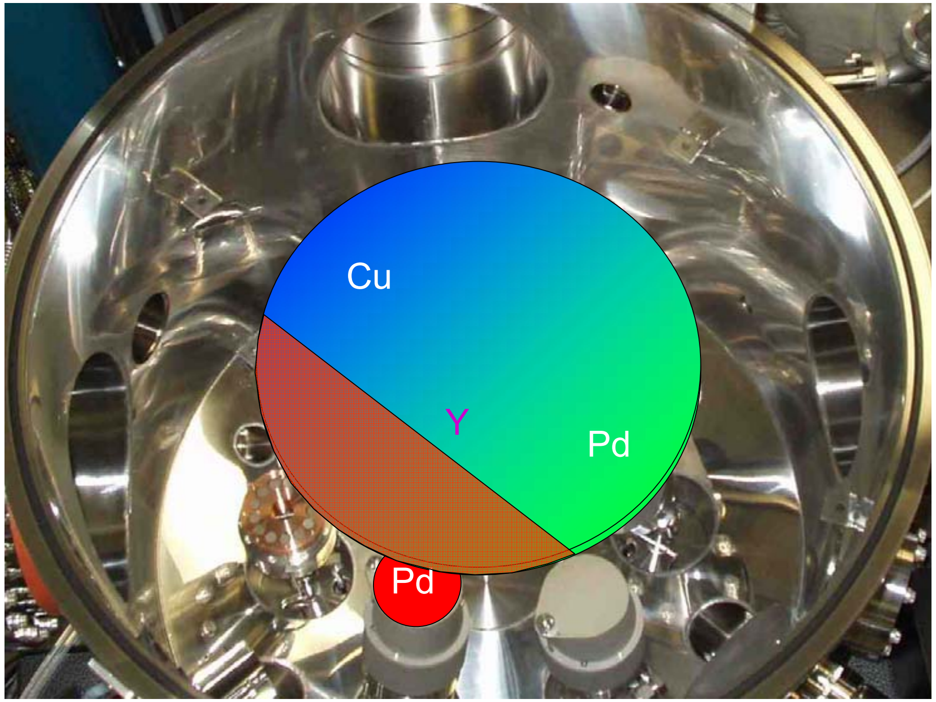


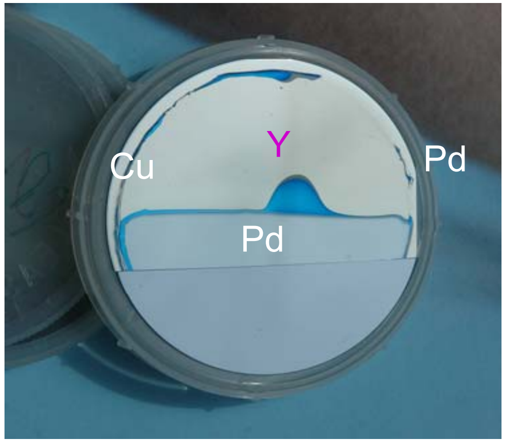



Cu
Pd

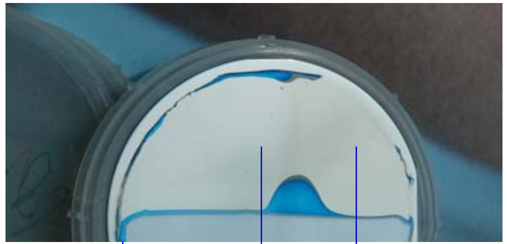

Cu
Y
Pd

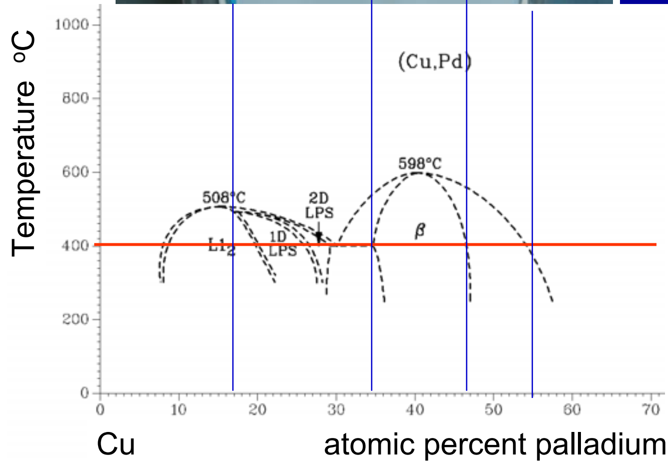

Cu
Y
Pd


Cu
Y
Pd
Pd



Fast H diffusion in bcc Pd-Cu

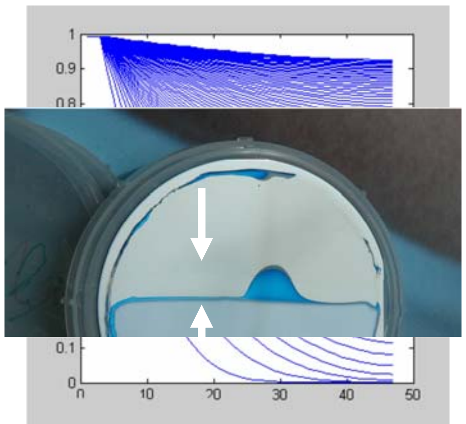




Fast H diffusion in bcc Pd-Cu

Diffusion length

$$D\frac{\partial^2 c}{\partial x^2}-\frac{\partial c}{\partial t}=0 \text{ with } c(0,t)=1 \qquad c=1-erf\left(\frac{x}{2\sqrt{Dt}}\right)$$



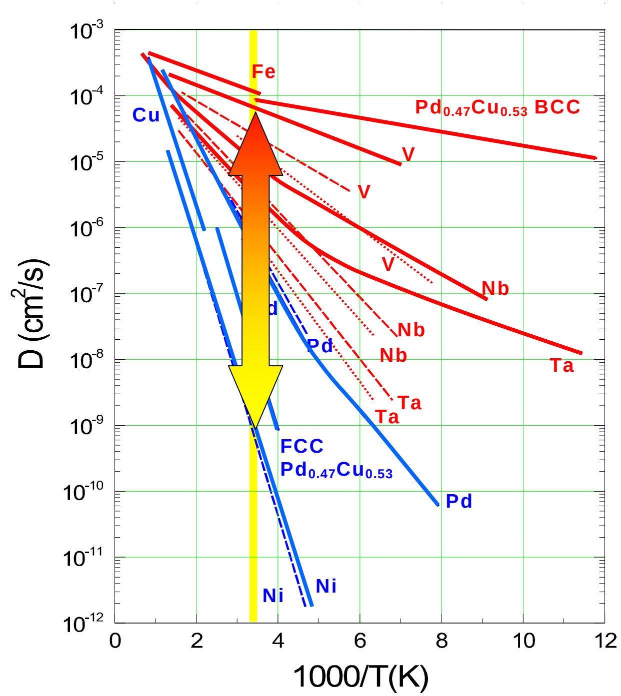
$$x^2 \cong Dt$$

In 10^4 s we have $x \cong 1$ cm

Thus

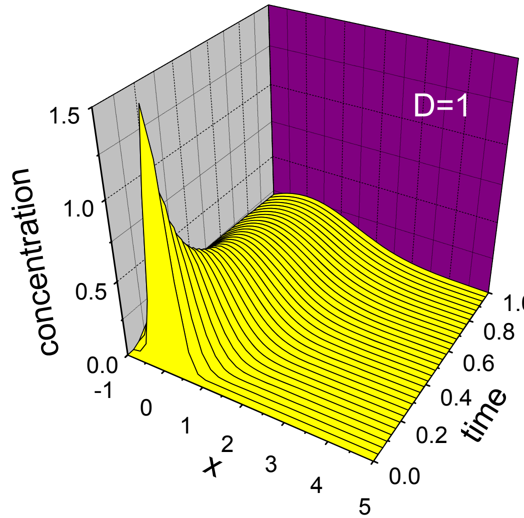
$D = 10^{-4}$ cm^2/s

Diffusion coefficients of various interstitials



Characteristic features of diffusion

Singularities decay immediately



$$c = \frac{1}{2\sqrt{\pi D t}} e^{-\frac{x^2}{4Dt}}$$

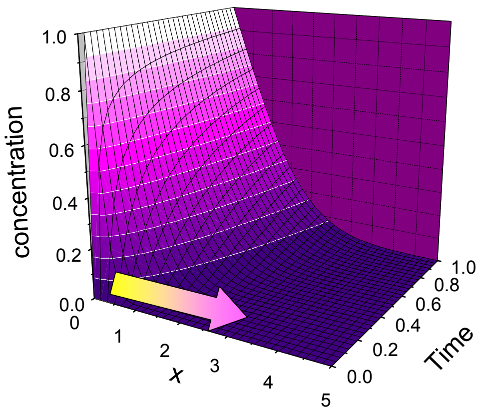
is a solution of

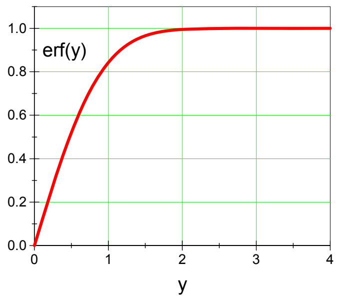
$$D\frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t}$$

Diffusion in semi-infinite space

$$D\frac{\partial^2 c}{\partial x^2} - \frac{\partial c}{\partial t} = 0 \text{ with } c(0,t) = 1 \qquad c = 1 - erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$erf(y) = \frac{2}{\sqrt{\pi}} \int_0^y e^{-p^2} dp$$



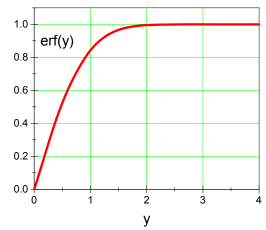


Infinite diffusion :a little numerical exercise

Typically in a solid $c_o = 10^{-10}\ m^{-1}$ at x=0.
The front at concentration $c = 10^{-12}\ m^{-1}$ is given by:

$$\frac{c}{c_0} = 1 - erf\left(\frac{x}{2\sqrt{Dt}}\right) = 10^{-2}$$

$$\frac{x}{2\sqrt{Dt}} = 1.8214 \quad \Rightarrow \quad \frac{x}{t} = 3.64\sqrt{\frac{D}{t}}$$

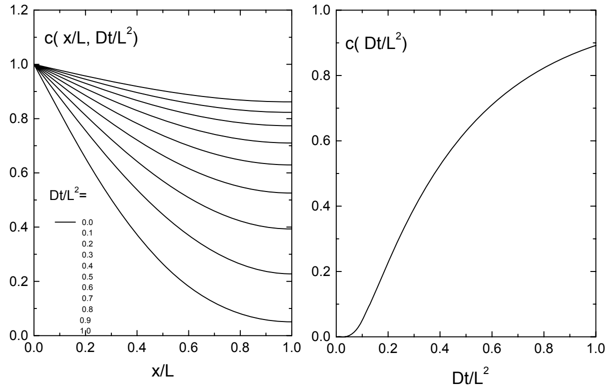


The velocity of light is reached at $t = 1.5\times10^{-24}$ s if $D = 10^{-8}\ m^2/s$. The average jump time is, however, with a=0.1 nm

$$\tau = \frac{a^2}{2D} = 5\times10^{-13} s \qquad \text{and} \qquad \frac{x}{\tau} = 3.64\sqrt{\frac{D}{\tau}} = 515\ \frac{\text{m}}{\text{s}}$$

Diffusion into a membrane of thickness *L*

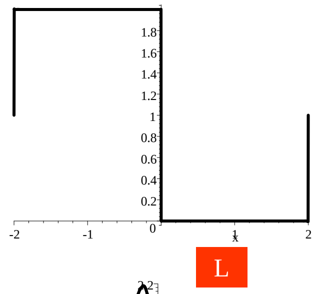
$$c(x,t) = 1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{1}{2n+1}\sin\left(\frac{(2n+1)\pi x}{2L}\right)e^{-\frac{(2n+1)^2\pi^2}{4}\frac{Dt}{L^2}}$$

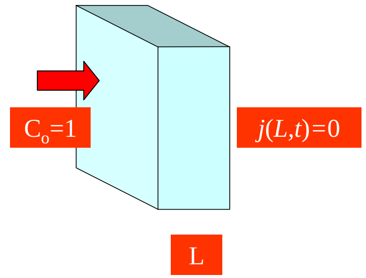


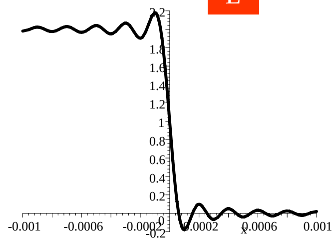
$$\frac{c_{HR}(t)}{c_{HL}} = 1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}e^{-\frac{(2n+1)^2\pi^2}{4}\frac{Dt}{L^2}}$$

diff_mu_edge1

Choosing the right Fourier series



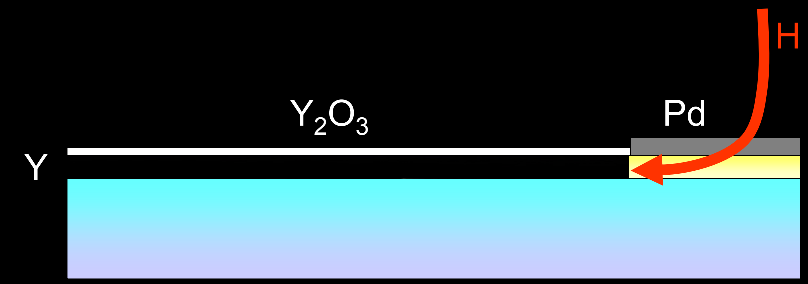




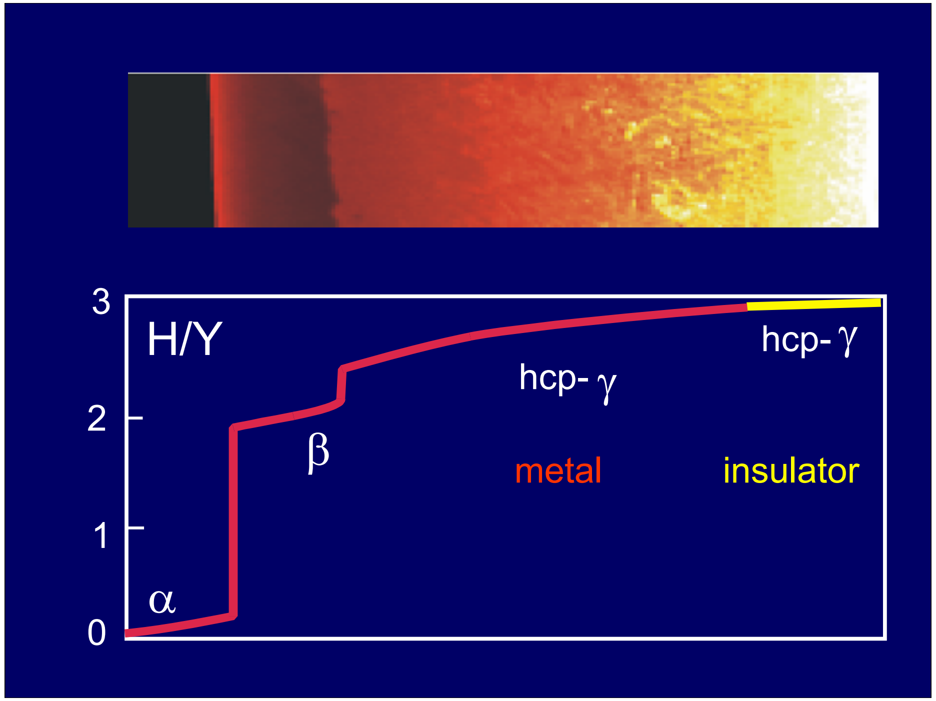
$$f(x) = 1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{1}{2n+1}\sin\left(\frac{(2n+1)\pi x}{2L}\right)$$

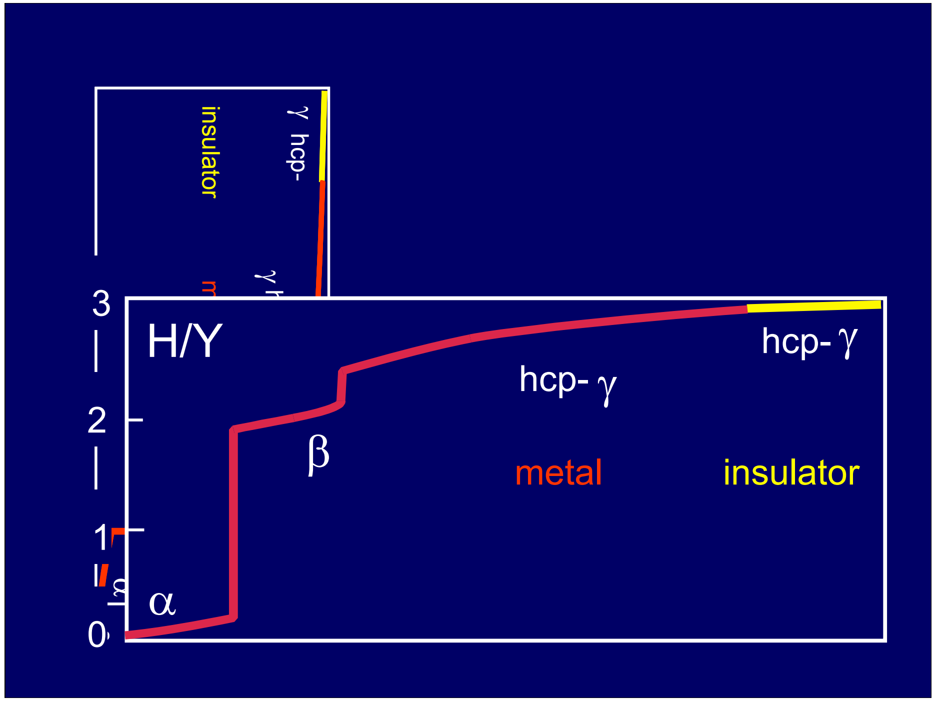
A real diffusion experiment

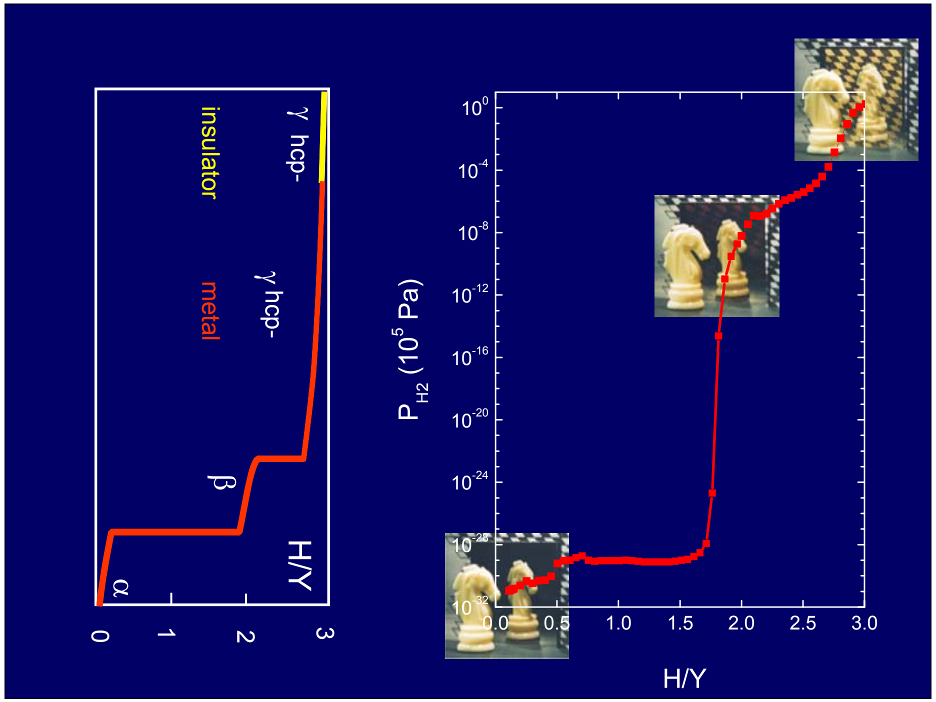
H diffusion in Y



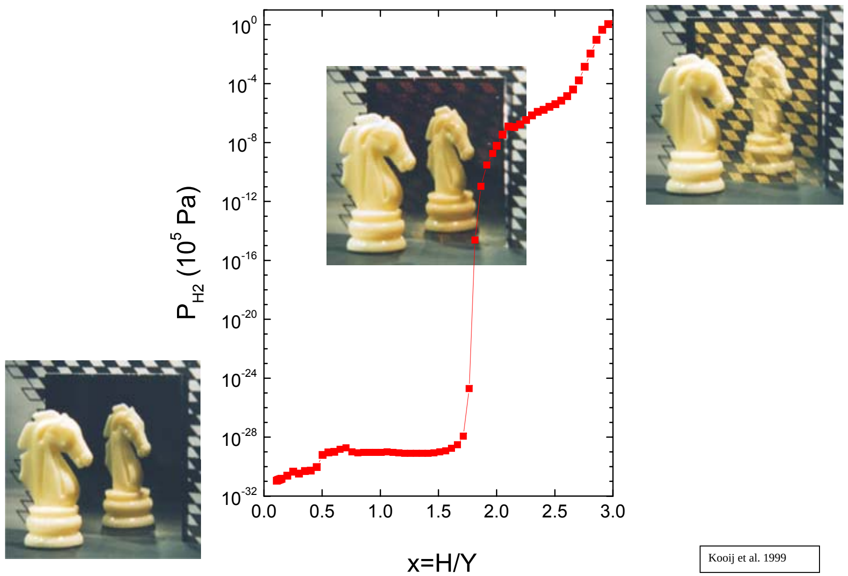
Den Broeder, van der Molen et al, Nature 394 (1998) 656



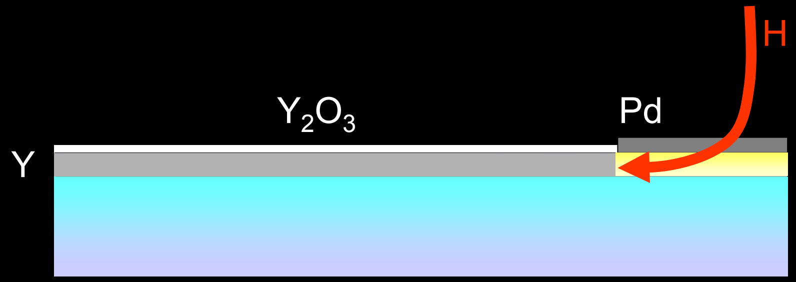




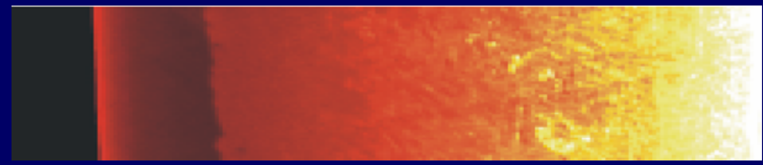
Pressure-composition isotherm of YH_x at T=293 K



Hydrogenography in Yttrium



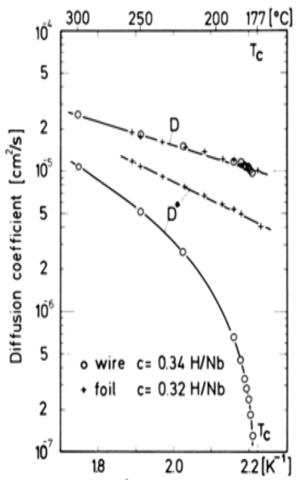
Den Broeder, van der Molen et al, Nature 394 (1998) 656

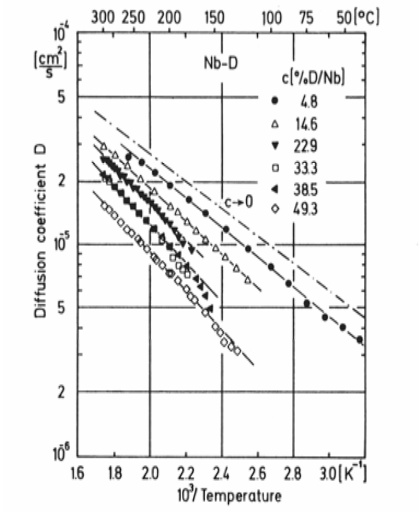


This picture demonstrates that

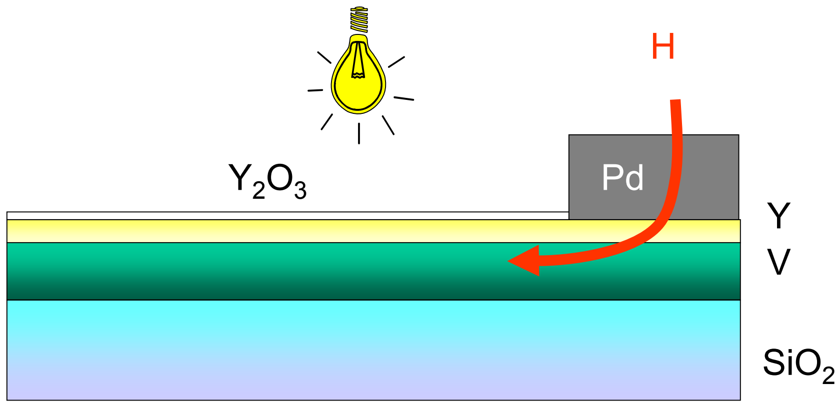
$$j = -L\frac{\partial \mu}{\partial x} \quad \text{instead of} \quad j = -D\frac{\partial c}{\partial x}$$

Influence of the chemical factor

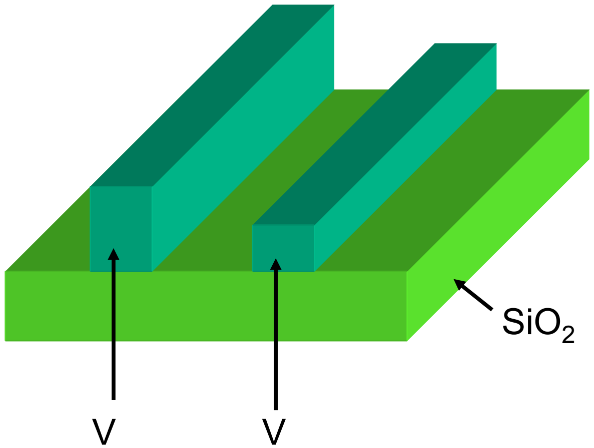




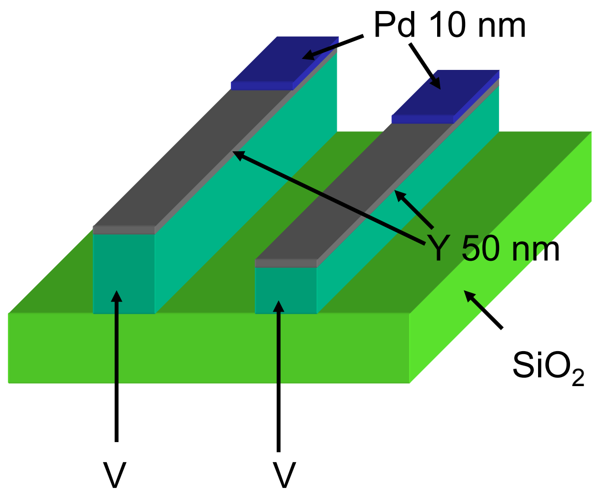
Switchable mirrors as indicators



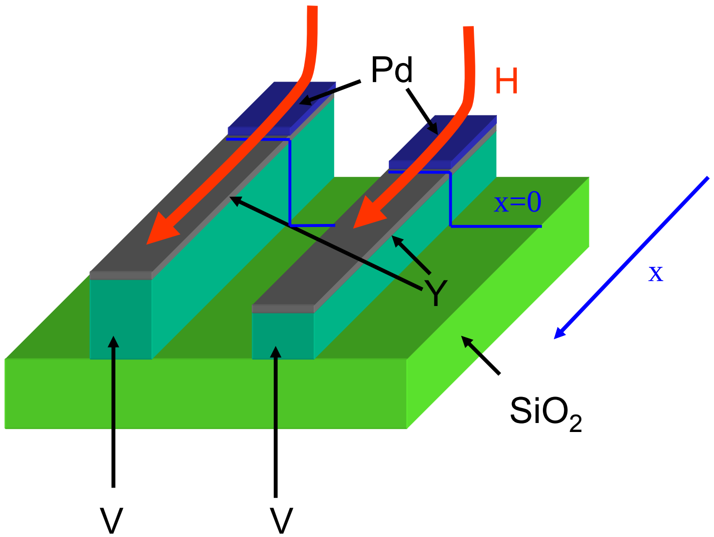
Sample architecture



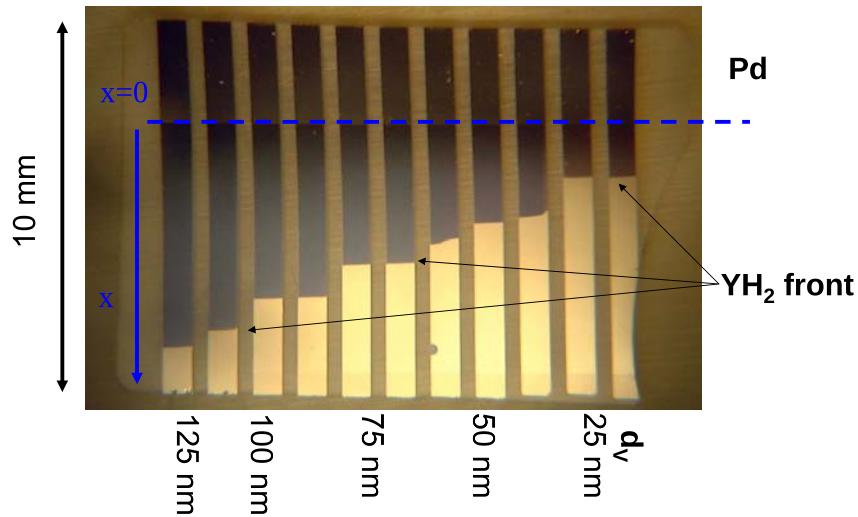
Sample architecture



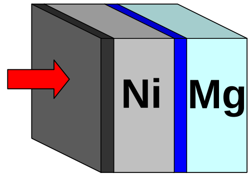
Hydrogen loading



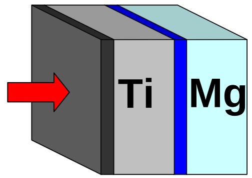
H-loading: 473K, 1mbar, 3h



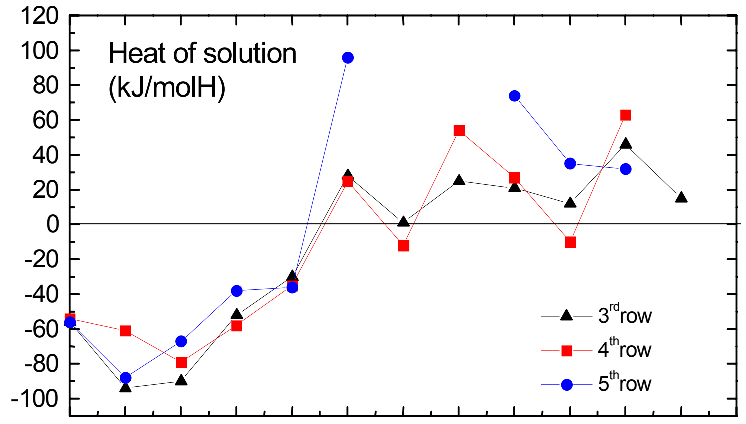
Diffusion in a multilayer



$$\Delta H_{Ti\text{-}H} < \Delta H_{Mg\text{-}H} < \Delta H_{Ni\text{-}H}$$



Heat of solution of metal-hydrides



K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd
Cs Ba La Hf Ta W Re Os Ir Pt Au Hg

Chemical potential: simplest model

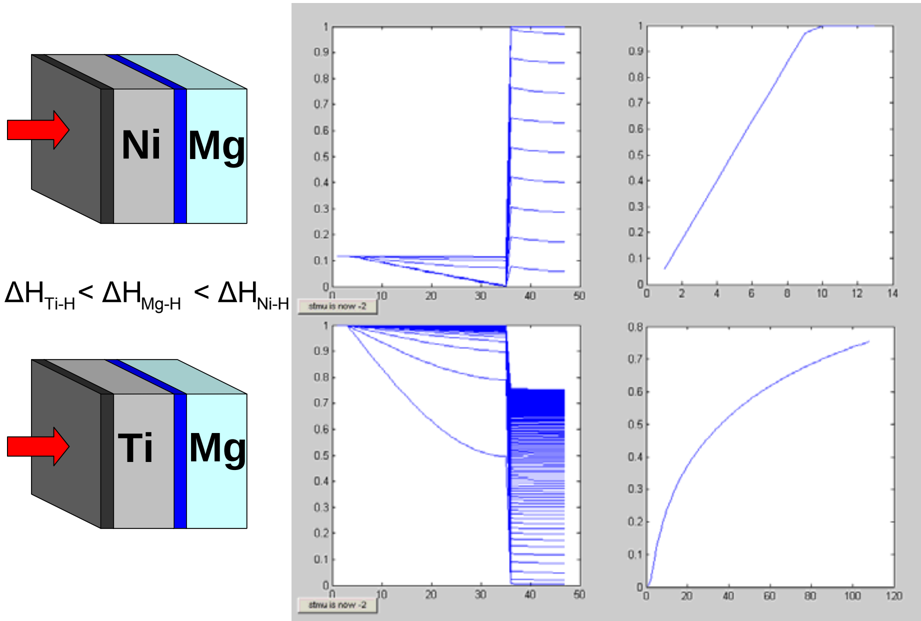
H_2 gas $$\mu_{H_2} = kT \ln\left(\frac{p}{p_o(T)}\right) + \varepsilon_b$$

H in metal $$\mu_H = kT \ln\left(\frac{c}{1-c}\right) + \varepsilon_o$$

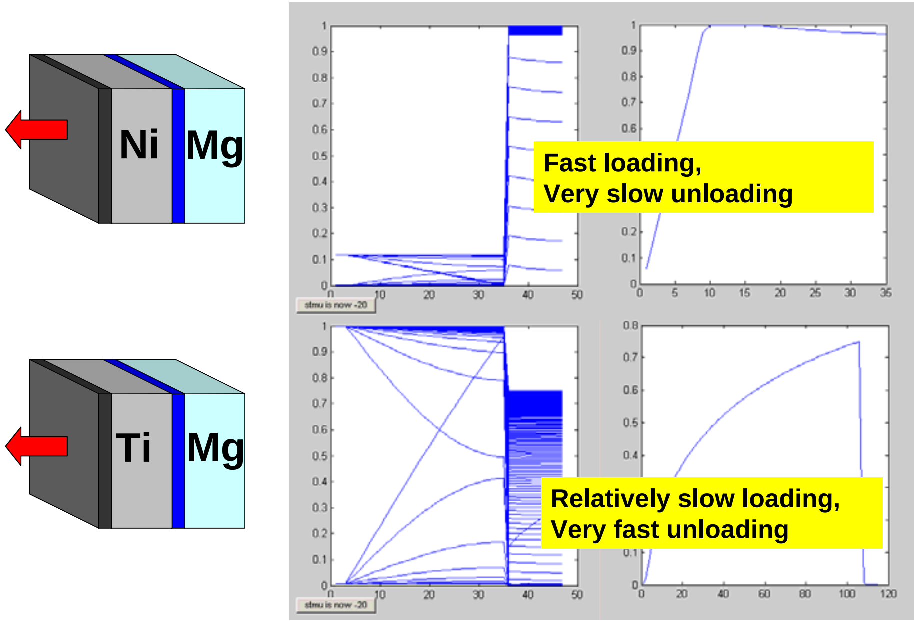
Diffusion $$J_H = -c(1-c) L_o \frac{\partial \mu}{\partial x}$$

⇒ Development of a simulation model

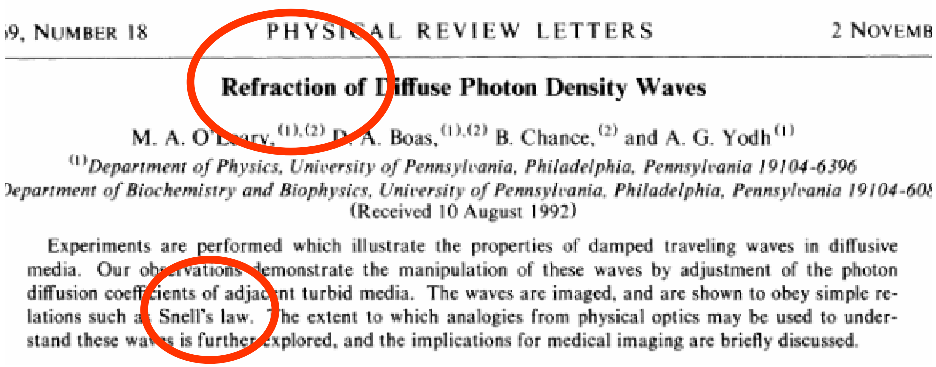
$c = c(x,t)$ $c_H = f(t)$



$c = c(x,t)$ $c_H = f(t)$



Diffusion and Snell's law



9, NUMBER 18 PHYSICAL REVIEW LETTERS 2 NOVEMB

Refraction of Diffuse Photon Density Waves

M. A. O'Leary,[1],[2] D. A. Boas,[1],[2] B. Chance,[2] and A. G. Yodh[1]
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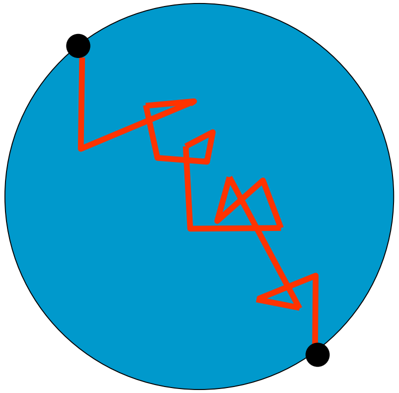
(Received 10 August 1992)

Experiments are performed which illustrate the properties of damped traveling waves in diffusive media. Our observations demonstrate the manipulation of these waves by adjustment of the photon diffusion coefficients of adjacent turbid media. The waves are imaged, and are shown to obey simple relations such as Snell's law. The extent to which analogies from physical optics may be used to understand these waves is further explored, and the implications for medical imaging are briefly discussed.

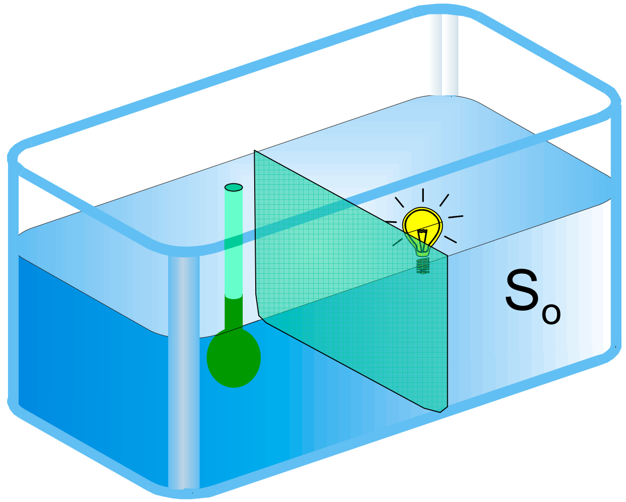
Random walk of a photon

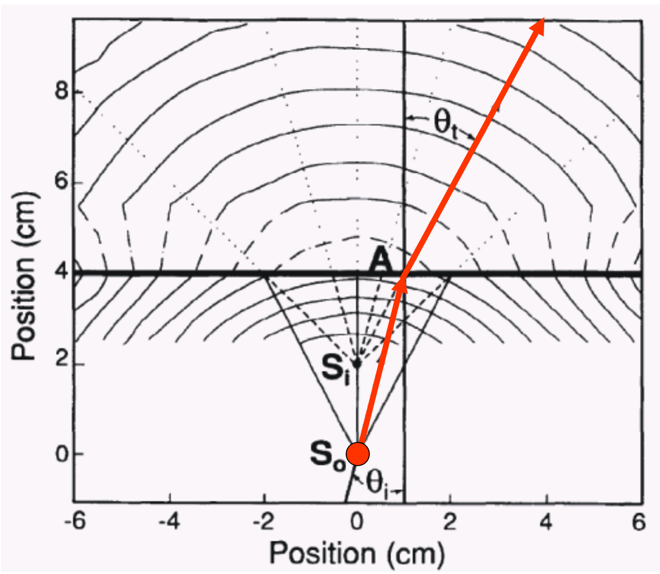
$$\frac{\partial U}{\partial t} = D\Delta U - v\mu_a U$$



With
v the velocity of light
μ_a the absorption coefficient

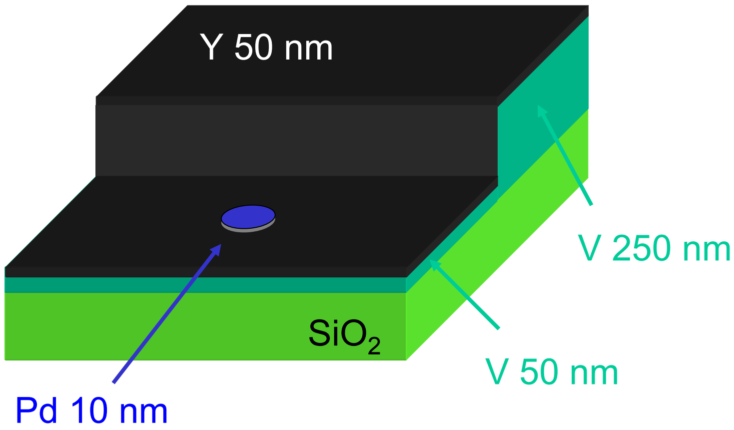
The aquarium experiment

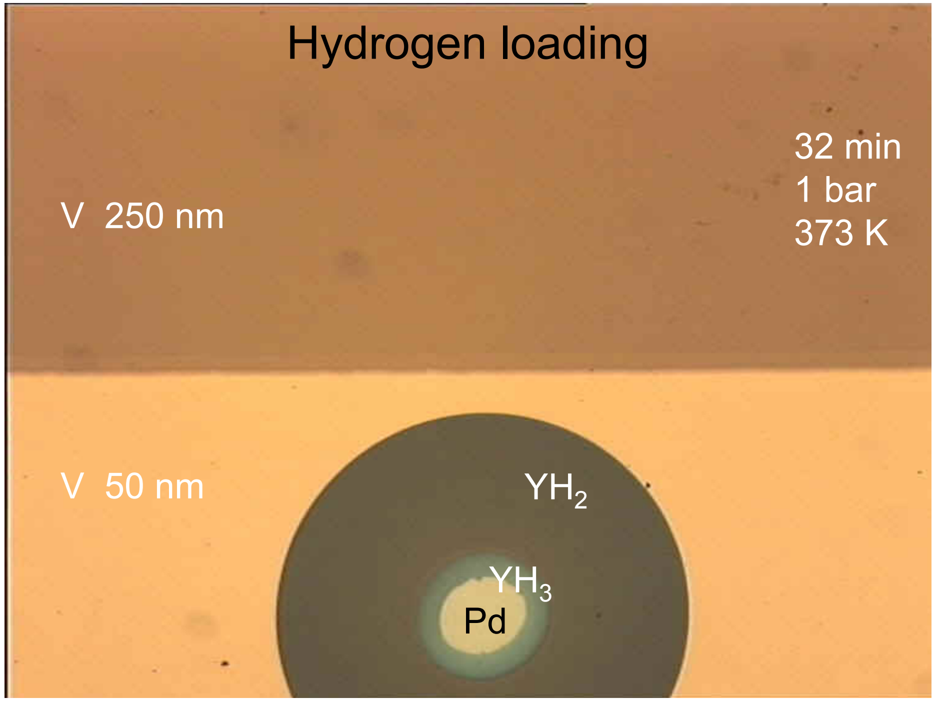


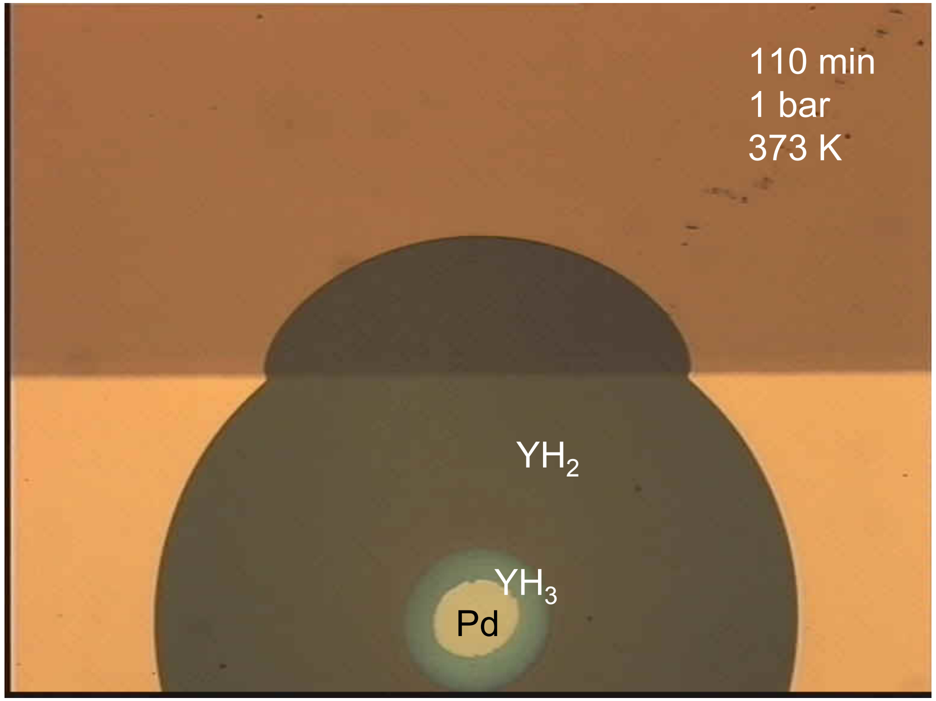


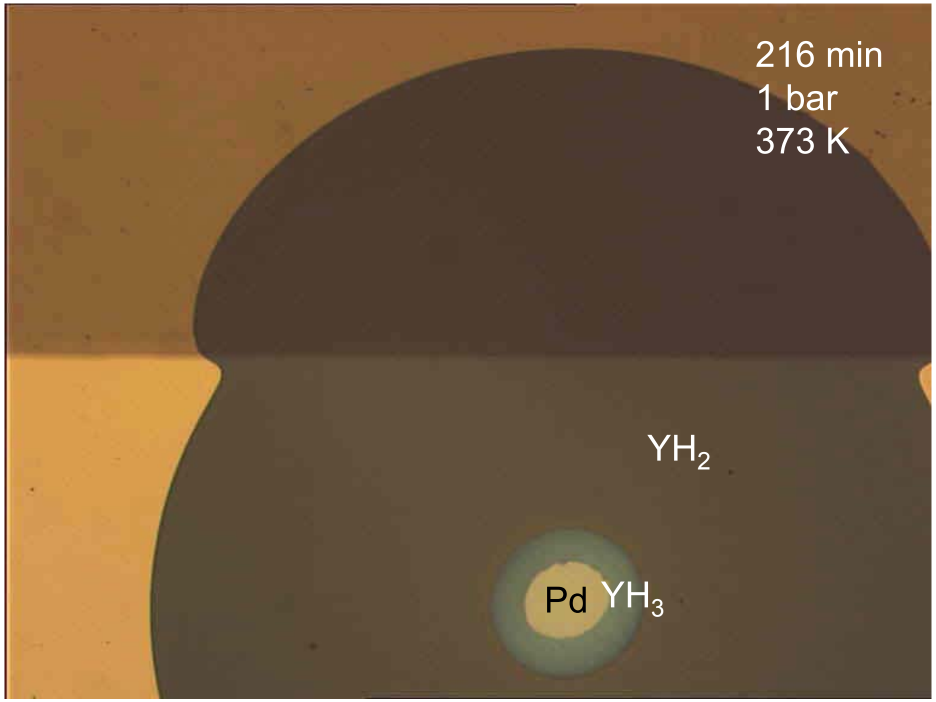
O'Leary et al., Phys. Rev. Lett. 69 (1992) 2658

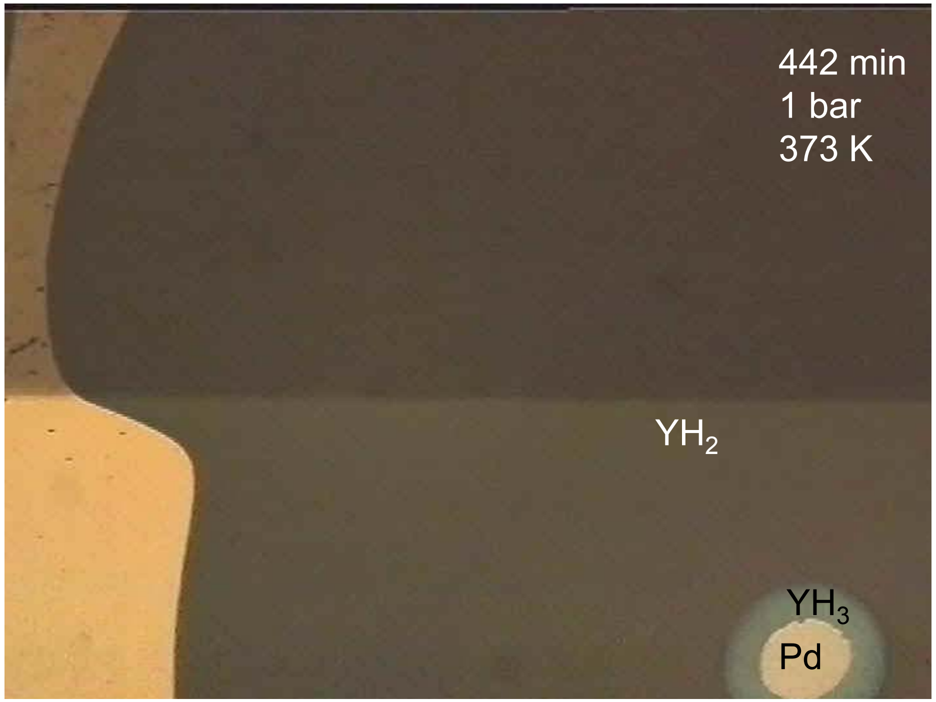
Sample architecture



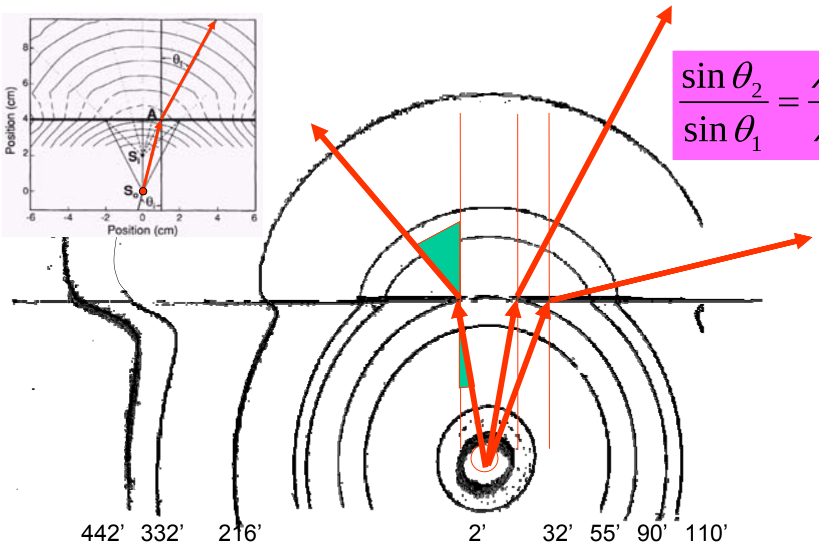

Hydrogen loading
32 min
1 bar
373 K
V 250 nm
V 50 nm
YH2
YH3
Pd


110 min
1 bar
373 K
YH2
YH3
Pd


216 min
1 bar
373 K
YH2
Pd YH3

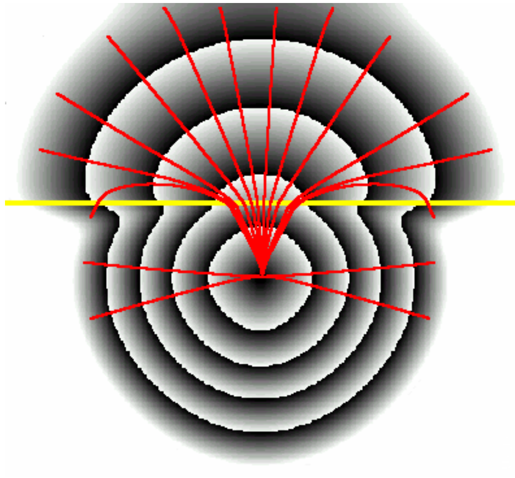

442 min
1 bar
373 K
YH2
YH3
Pd

Time evolution of contours



$$\frac{\sin\theta_2}{\sin\theta_1} = \frac{\lambda_2}{\lambda_1}$$

Snell's law for diffusion !

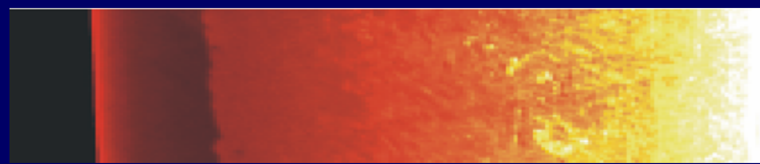


Ray tracing along the phase – gradient at small angles

$$\frac{\sin\theta_2}{\sin\theta_1} = \frac{\lambda_2}{\lambda_1} = \sqrt{\frac{D_2}{D_1}}$$

Remhof, R. J. Wijngaarden, and R. Griessen, *Refraction and reflection of diffusion fronts*, Phys. Rev. Lett., **90** (2003) 145502

Electromigration



In presence of an electric field

$$\mathbf{j} = -L\left(\frac{\partial\mu}{\partial x} - eZ\mathbf{E}\right)$$

Usual diffusion

$$J = -D\frac{\partial c}{\partial x}$$

$$\mu = ?$$

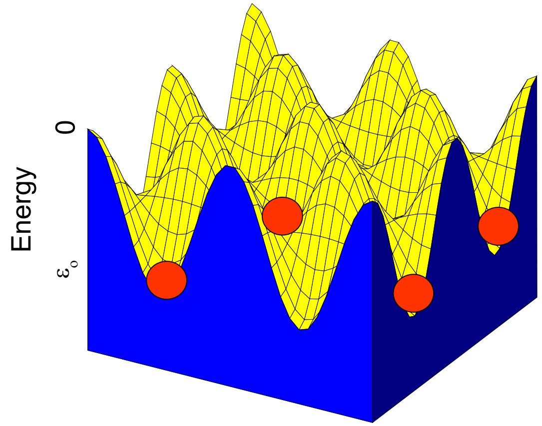
Forced diffusion

$$J = -L\left(\frac{\partial \mu}{\partial x} - eZE\right)$$

$$= -L\left(\frac{\partial \mu}{\partial c}\frac{\partial c}{\partial x} - eZE\right)$$

$$= -D\frac{\partial c}{\partial x} - eZE\left(\frac{D}{\partial \mu / \partial c}\right)$$

Particles in a lattice gas



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

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

$$\mu = kT \ln\left(\frac{c}{1-c}\right) + \varepsilon_o$$

$$\frac{\partial \mu}{\partial c} = \frac{kT}{c(1-c)}$$

Usual diffusion

$$J = -D\frac{\partial c}{\partial x}$$

$$\frac{\partial \mu}{\partial c} = \frac{kT}{c(1-c)} \cong \frac{kT}{c}$$

Forced diffusion

$$J = -L\left(\frac{\partial \mu}{\partial x} - eZE\right)$$

$$= -L\left(\frac{\partial \mu}{\partial c}\frac{\partial c}{\partial x} - eZE\right)$$

$$= -D\frac{\partial c}{\partial x} - eZE\left(\frac{D}{\partial \mu / \partial c}\right)$$

$$J = -D\frac{\partial c}{\partial x} - eZE\left(\frac{cD}{kT}\right)$$

Usual diffusion

$$J = -D\frac{\partial c}{\partial x}$$

Forced diffusion

$$J = -D\frac{\partial c}{\partial x} - eZE\left(\frac{cD}{kT}\right)$$

$$\frac{\partial c}{\partial t} + divJ = 0$$

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - B\frac{\partial c}{\partial x}$$

with $B = \left(\frac{eZED}{kT}\right)$

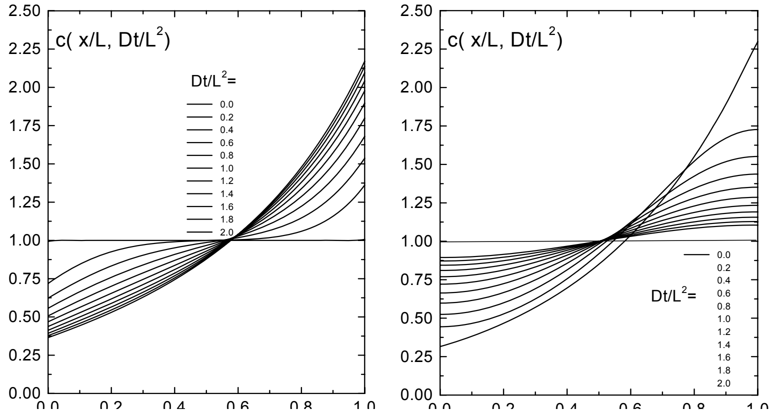
Electromigration

$$\mathbf{J} = L_{HH}\left(eZ^*\mathbf{E} - grad\,\mu_H\right)$$

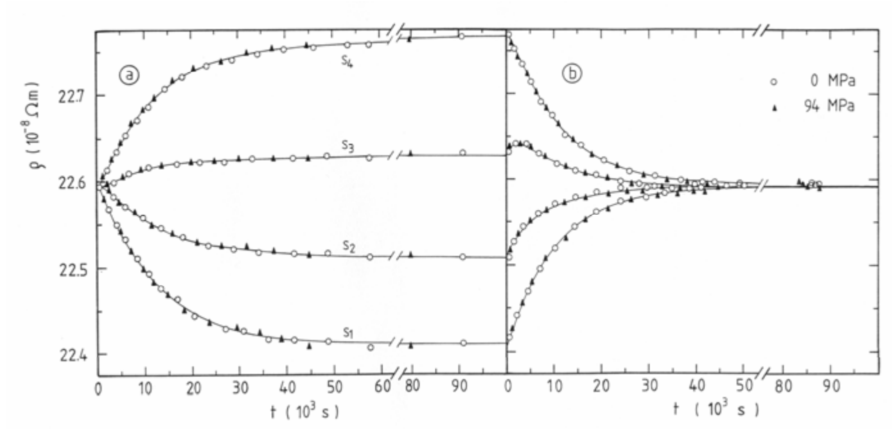
$$\frac{\partial c}{\partial t} + div\mathbf{J} = 0$$

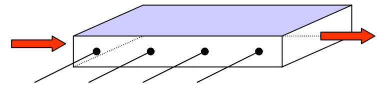
$$L_{HH} = D\left(\frac{\partial \mu_H}{\partial c}\right)^{-1} \cong D\left(\frac{kT}{c}\right)^{-1}$$

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - MeZ^*\mathbf{E}\frac{\partial c}{\partial x}$$



Electromigration of H in V

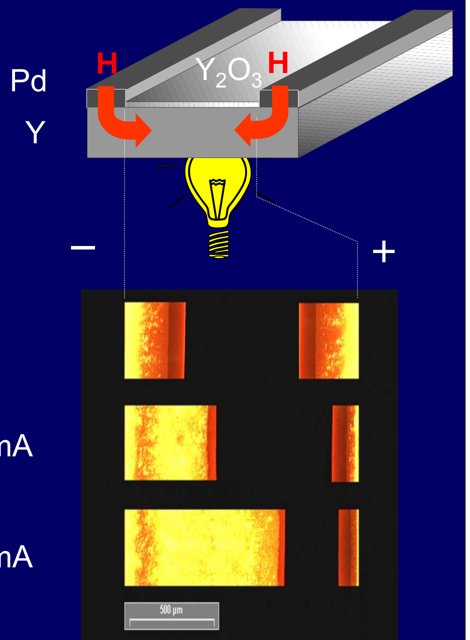




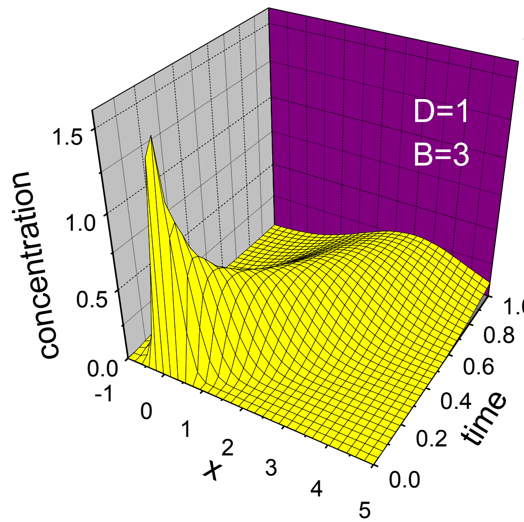
Electro-diffusion of hydrogen in yttrium

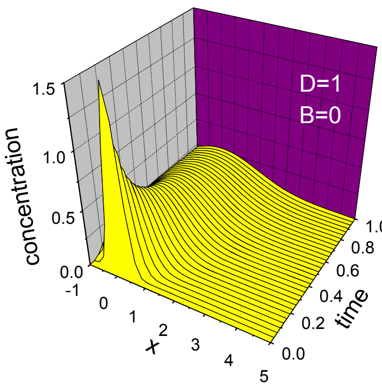
Den Broeder, van der Molen et al. Nature 394 (1998) 656

H behaves like a negative ion

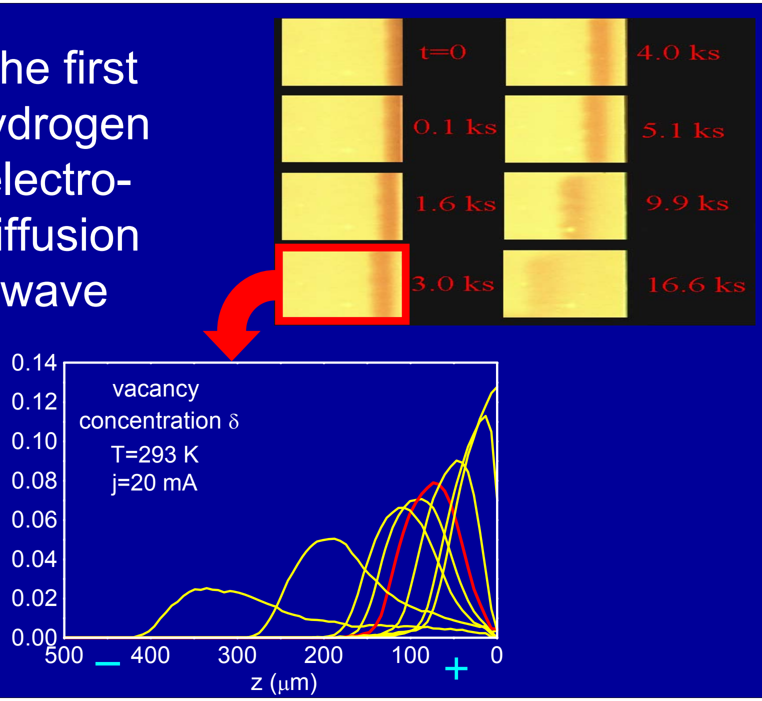


Time decay of a driven delta function





The first hydrogen electro-diffusion wave



Diffusion waves

Diffusion waves

- Diffusion equation

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

- Diffusion equation with a source

$$D\frac{\partial^2 c}{\partial x^2} - \frac{\partial c}{\partial t} = 0 \quad \text{for x} > 0 \text{ and t} > 0$$

$$\text{c(x, 0)} = 0 \quad \text{and} \quad \text{c(0, t)} = \sin \omega t$$

Separation of variables

$$D\frac{\partial^2 c}{\partial x^2} - \frac{\partial c}{\partial t} = 0 \text{ with } \quad c(x=0,t) = \sin \omega t$$

We seek a solution in the form of

$$c(x,t) = \exp(kx)\exp(\pm i\omega t) \quad \text{and obtain}$$

$$Dk^2 \mp i\omega = 0 \qquad k^2 = \pm\frac{i\omega}{D} \qquad k = \pm\sqrt{\frac{\omega}{2D}}(1+i)$$

$$c(x,t) = e^{-\sqrt{\frac{\omega}{2D}}x}\sin\left(\sqrt{\frac{\omega}{2D}}x - \omega t\right)$$

Characteristic quantities

$$c(x,t) = e^{-\sqrt{\frac{\omega}{2D}}x} \sin\left(\sqrt{\frac{\omega}{2D}}x - \omega t\right) = e^{-\frac{x}{L}} \sin(qx - \omega t)$$

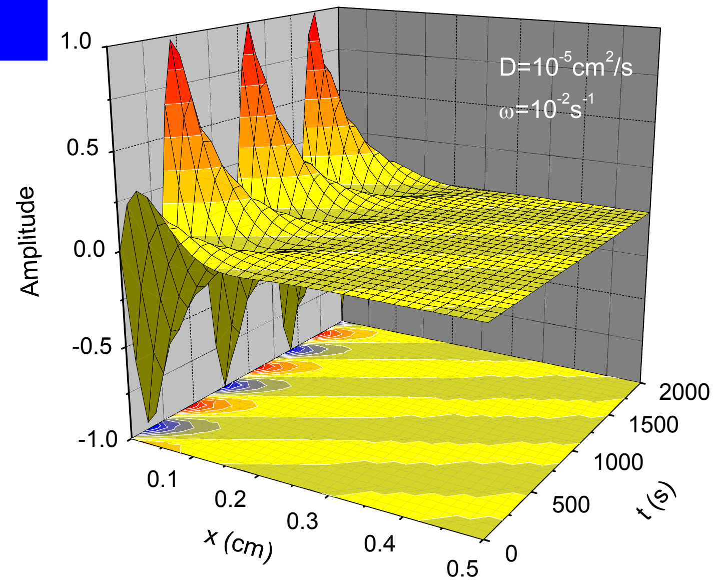
Damping length $L(\omega) = \sqrt{\frac{2D}{\omega}}$

Wave vector $q = \sqrt{\frac{\omega}{2D}}$

Wave length $\lambda \equiv \frac{2\pi}{q} = 2\pi\sqrt{\frac{2D}{\omega}}$

Phase velocity $v_{phase} \equiv \frac{x}{t} = \sqrt{2D\omega}$

A diffusion wave



Electro-diffusion waves

- Diffusion equation in presence of a force

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - B\frac{\partial c}{\partial x}$$

- Diffusion equation with a source

$$\frac{\partial c}{\partial t} - D\frac{\partial^2 c}{\partial x^2} - B\frac{\partial c}{\partial x} = \delta(x=0)\sin\omega t$$

Separation of variables

$$D\frac{\partial^2 c}{\partial x^2} + B\frac{\partial c}{\partial x} - \frac{\partial c}{\partial t} = 0 \text{ with } c(x=0,t) = \sin\omega t$$

We seek a solution in the form of

$c(x,t) = \exp(kx)\exp(\pm i\omega t)$ and obtain

$$Dk^2 + Bk \mp i\omega = 0$$

$$c(x,t) = e^{-\frac{x}{L}} \sin(qx - \omega t)$$

Characteristic quantities

$$c(x,t) = e^{-\frac{x}{L}} \sin\left(qx - \omega t\right)$$

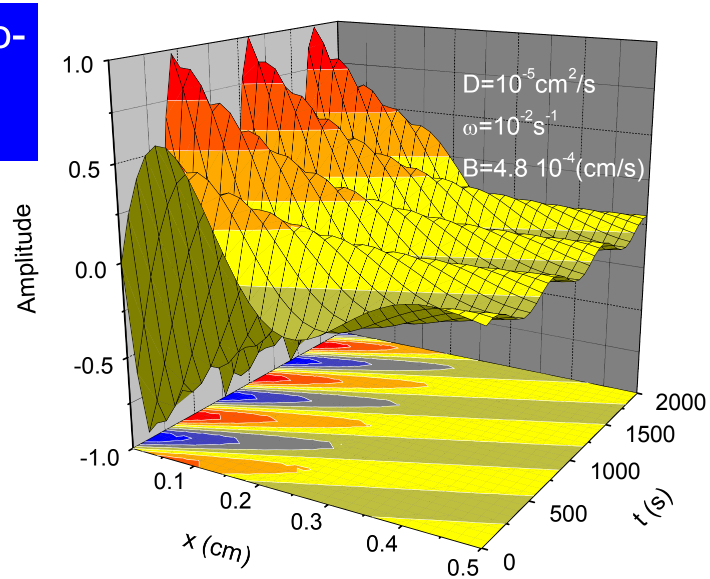
Damping length

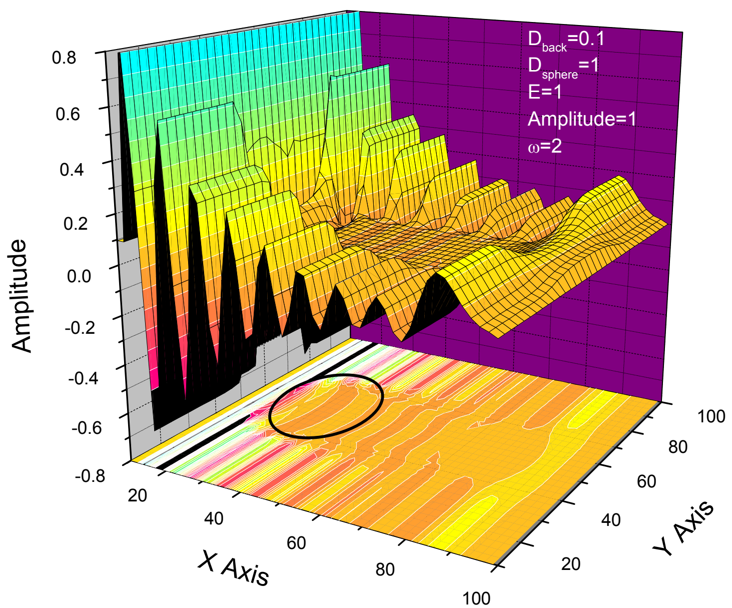
$$L = \frac{1}{\frac{B}{2D}\left[\frac{1}{\sqrt{2}}\left(\sqrt{\sqrt{1+\frac{16\omega^2 D^2}{B^4}}-1}\right)-1\right]}$$

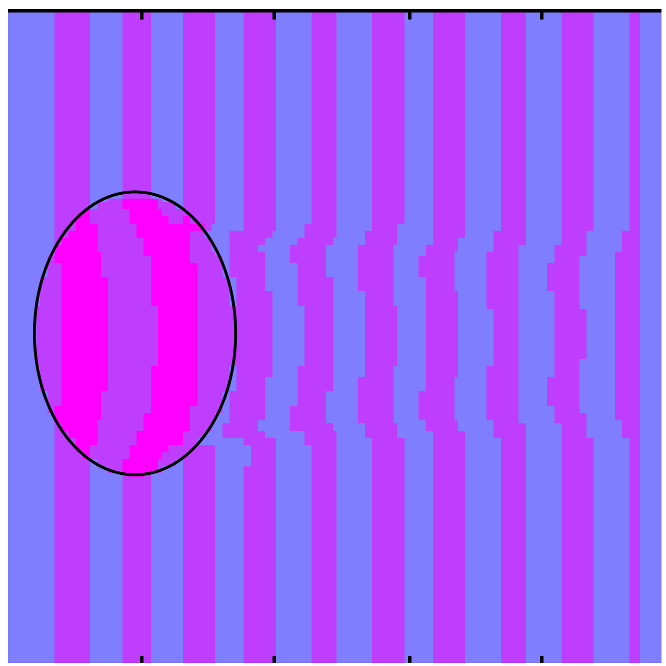
Wave vector

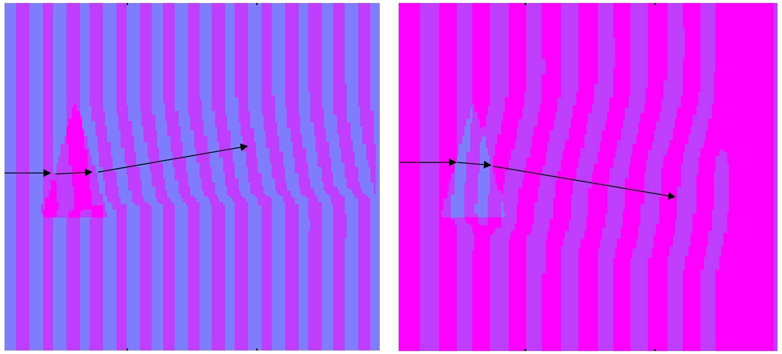
$$q = \frac{B}{2D}\left[\frac{1}{\sqrt{2}}\left(\sqrt{\sqrt{1+\frac{16\omega^2 D^2}{B^4}}-1}\right)\right]$$

An electro-diffusion wave









$D_{prism}=1$ $D_{back}=0.1$

$D_{prism}=0.1$ $D_{back}=1$