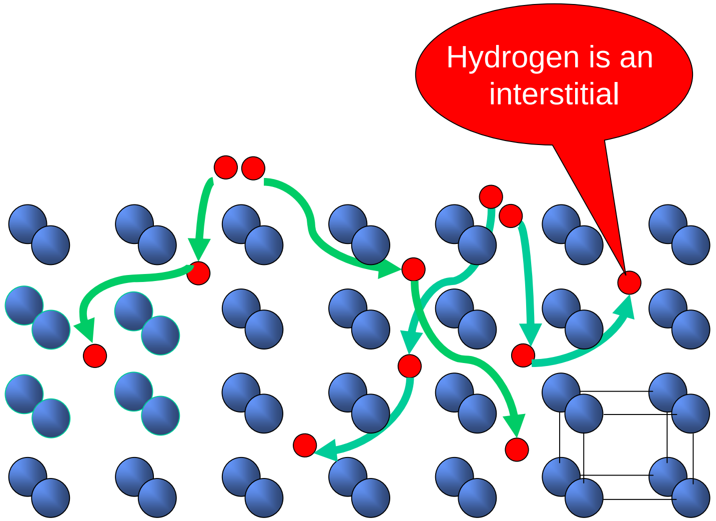
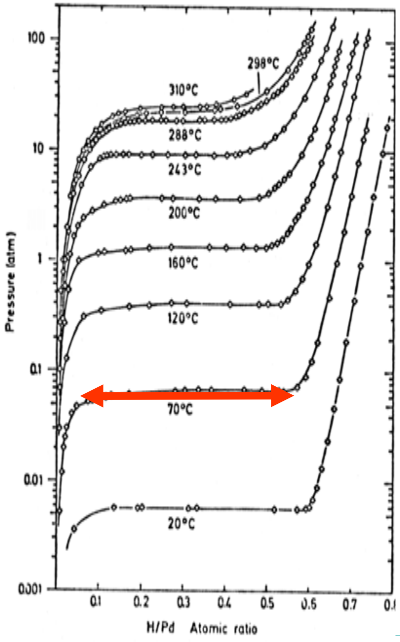
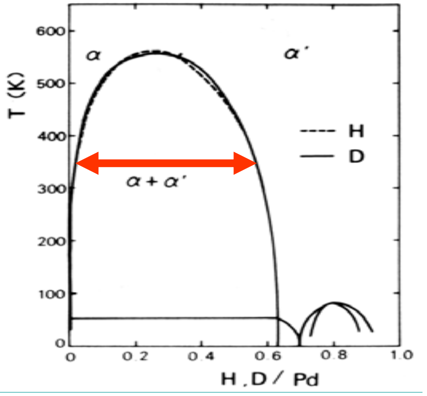
Reminder

Interstitial alloy

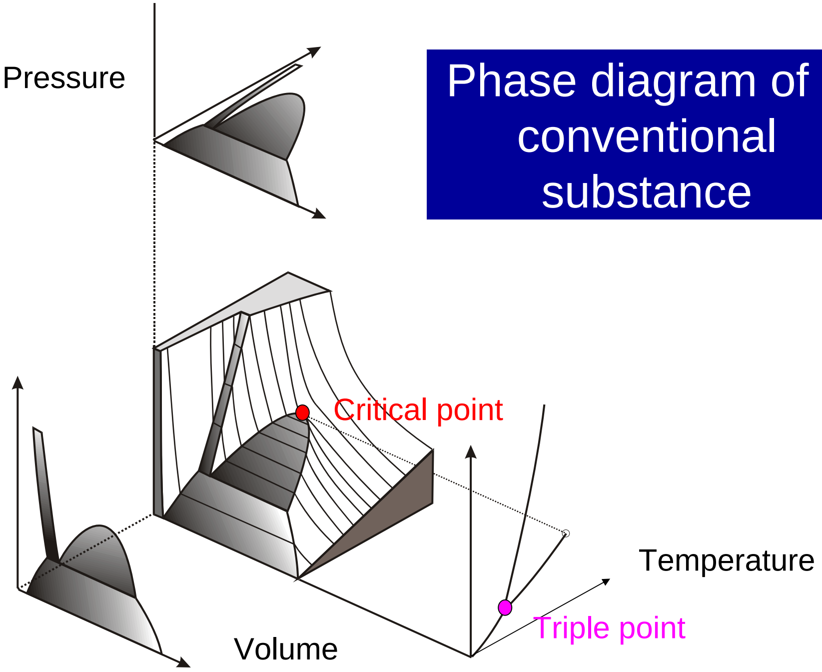


P-c isotherms and phase diagram





Phase diagram of a conventional substance



Solubility isotherms

$$\mu_{H_2} = \varepsilon_b + kT\ln\left[\frac{p}{p_0(T)}\right]$$

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

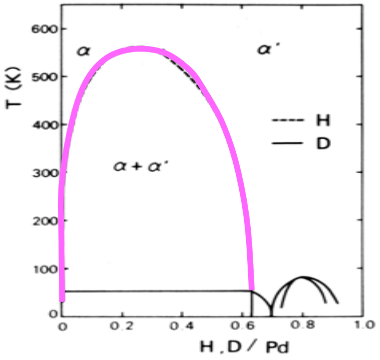
$$p_0(T) = \left(\frac{(kT)^{7/2}\,\Theta_{H_2}\, m_{H_2}^{3/2}}{\hbar^5 (2\pi)^{3/2}}\right)$$

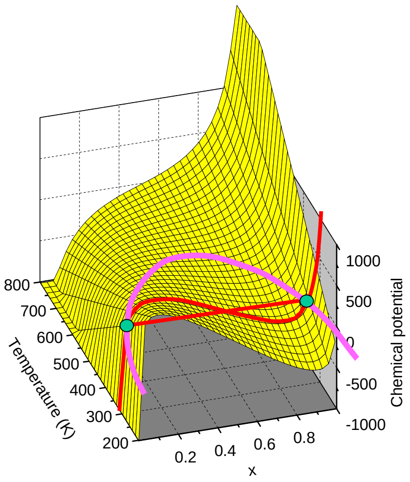
$$p_0(T) = \left(\frac{T}{9.13}\right)^{7/2}$$

with p_o
expressed in bar
and T in Kelvin.

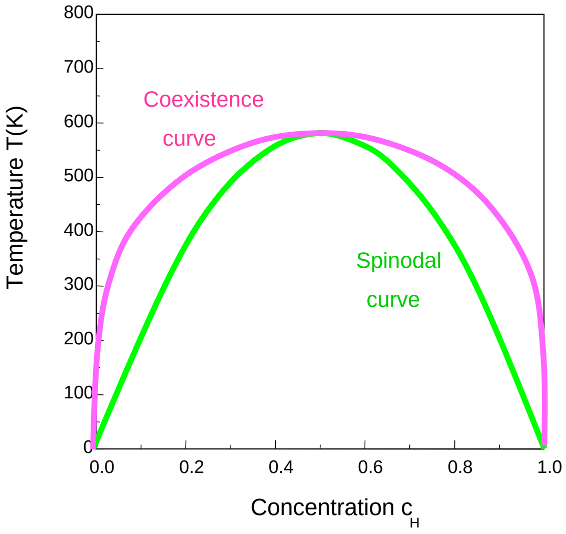
$$\frac{1}{2}\left(\varepsilon_b + kT\ln\frac{p}{p_0(T)}\right) = kT\ln\frac{c_H}{1-c_H} + \varepsilon_0 + \varepsilon n c_H$$

P-c isotherms and phase diagram





Coexistence and spinodal curves



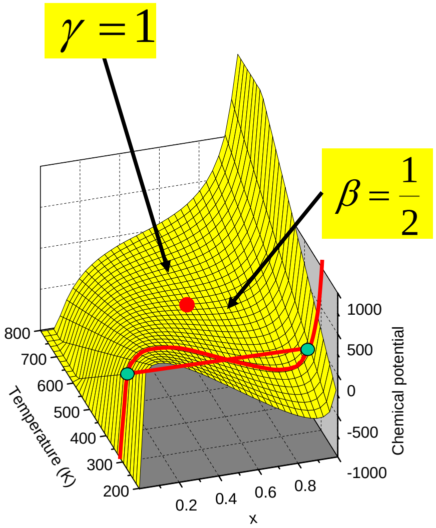
Critical behaviour and H-H interaction

Ronald Griessen
Vrije Universiteit, Amsterdam
Feb. 2008

Coexistence curve
Critical point
Critical exponents

$$T_c = -\frac{\varepsilon n}{4k}$$

For PdH$_x$
T$_c$= 566 K
εn= -0.20 eV
T$_c$=566 K



$\gamma = 1$

$\beta = \frac{1}{2}$

Critical exponents for various systems

System	Experiment	β Mean field theory	3-dim Ising model	Experiment	γ Mean field theory	3-dim Ising model
CO$_2$	0.35	1/2	5/16	1.26	1	5/4
Xe	0.35			1.26		
^{4}He	0.359			1.24		
^{3}He	0.361			1.18		
O$_2$	0.353			1.25		
n-pentane	0.35			1.25		
CrBr$_3$	0.368			1.21		
Gd	0.37	1/2	5/16	1.25	1	5/4
Ni	0.37			1.28		
YIG ≡ Y$_3$Fe$_5$O$_{12}$	0.38			1.31		
Pd-H [(a)]	0.55	1/2	5/16	1.01 ± 0.1	1	5/4
Pd$_{0.9}$Ag$_{0.1}$H[(b)]				1.02 ± 0.04		
EuO	0.368			1.29		

a) From de Ribaupierre and Manchester (1974a, 1974b and 1975)
b) Buck and Alefeld (1971)
*)Table in part out Capocaccia et al. (1971). See also Stanley (1971)

What is this telling us ?

The range of the H-H interaction

Fluctuations in the number of H in a sphere of radius b containing n$_H$ H atoms

$$\left(\Delta n_H\right)^2 = \frac{kT}{\left(\dfrac{\partial \mu_H}{\partial n_H}\right)_{p,T}}$$

$$\frac{\left(\Delta n_H\right)^2}{n_H^2} = \frac{kT}{n_H^2\left(\dfrac{\partial \mu_H}{\partial n_H}\right)_{p,T}} = \frac{kT}{c_H^2 \rho_{mi} V_b \dfrac{\partial \mu_H}{\partial c_H}} << 1$$

For PdH$_x$, $\rho_{mi}V_b=(16\pi/3)(b/a)^3$ and in the BW approximation

$$\frac{T-T_c}{T_c} >> \frac{3}{16\pi}\left(\frac{a}{b}\right)^3$$

As $(T-T_c)/T_c>10^{-3}$ ⇒ $b >> 4a$

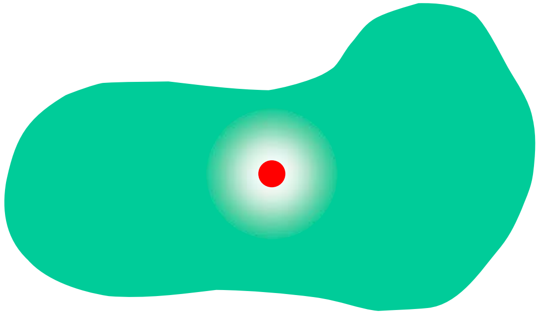
The interaction cannot be electronic

Potential of charge Ze
in vacuum

$$V_0(r) = \frac{Ze^2}{r}$$

Potential of charge Ze
in a metal

$$V_0(r) = \frac{Ze^2 e^{-\frac{r}{r_{TF}}}}{r}$$



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

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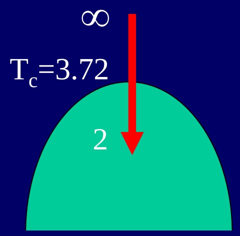
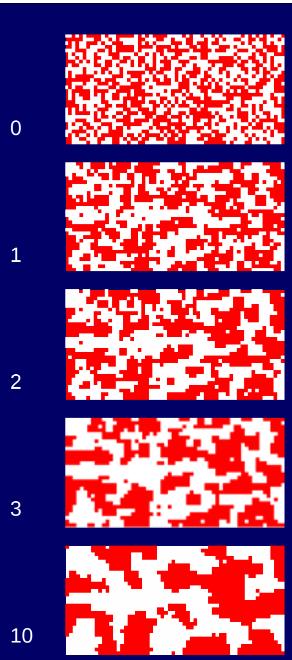
Short range interaction only nearest-neighbours



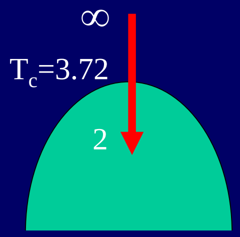
$$H = -\frac{J}{2}\sum \mathbf{S}_i\mathbf{S}_j + \frac{D}{2}\sum \frac{a^2}{R_{ij}^2}\mathbf{S}_i\mathbf{S}_j$$

J=1.64 D=0

Steps: 0, 1, 2, 3, 10



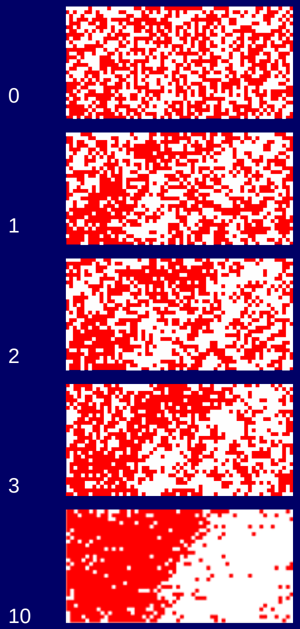
Long-range interaction $\propto$ 1/r2



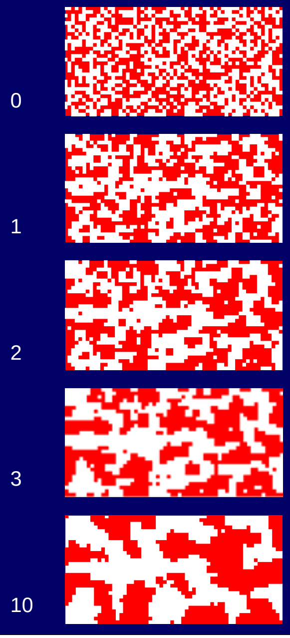
$$H = -\frac{J}{2}\sum \mathbf{S}_i\mathbf{S}_j + \frac{D}{2}\sum \frac{a^2}{R_{ij}^2}\mathbf{S}_i\mathbf{S}_j$$

J=0 D=-0.2

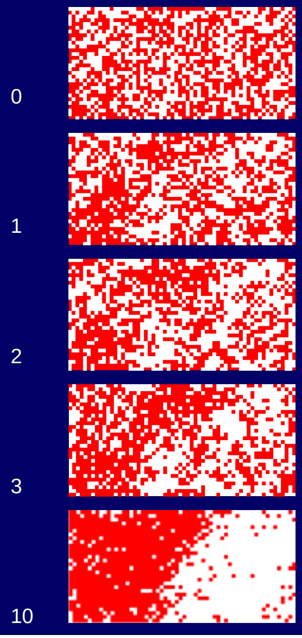
Steps: 0, 1, 2, 3, 10



Short-range



Long-range



MC

Spinodal decomposition

Gibbs free energy

$$G = \int dx \left(g(c_H) + g_{elastic}(c_H) + \alpha \left(\frac{dc_H}{dx} \right)^2 \right)$$

with

$$g(c_H) = \frac{kTN}{V} [c_H \ln c_H + (1 - c_H) \ln(1 - c_H)] + N[\varepsilon_o c_H + \varepsilon \frac{n}{2} c_H{}^2]$$

and an eleastic deformation energy

$$g_{elastic}(c_H) = \frac{E}{1-\nu} \left(\frac{d \ln a}{dc} \right)^2 (c_H - c_{H0})^2 = \eta (c_H - c_{H0})^2$$

Conservation of number of particles $\int (c_H - c_{H0}) dx = 0$

Spinodal decomposition

Define a new function M

$$M = g(c_H) + g_{elastic}(c_H) + \alpha \left(\frac{dc_H}{dx} \right)^2 - \tilde{\mu}(c_H - c_{H0})$$

with

$$\delta \int dx \left(g(c_H) + g_{elastic}(c_H) + \alpha \left(\frac{dc_H}{dx} \right)^2 - \tilde{\mu}(c_H - c_{H0}) \right) = 0$$

This leads to

$$\tilde{\mu} = \frac{dg}{dc_H} + 2\eta(c_H - c_{H0}) - 2\alpha \frac{d^2 c_H}{dx^2}$$

which plays the role of chemical potential

Spinodal decomposition

$$j_H = -L \frac{\partial \tilde{\mu}}{\partial x}$$

$$\frac{\partial c_H}{\partial t} + \frac{\partial j_H}{\partial x} = 0$$

$$\frac{\partial c_H}{\partial t} = L \left[\frac{d^2 g}{dc_H{}^2} \frac{\partial^2 c_H}{\partial x^2} + \frac{d^3 g}{dc_H{}^3} \left(\frac{\partial c_H}{\partial x} \right)^2 + 2\eta \frac{\partial^2 c_H}{\partial x^2} - 2\alpha \frac{\partial^4 c_H}{\partial x^4} \right]$$

To lowest order this diffusion equation is solved with

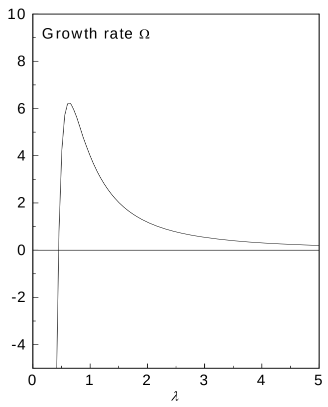
$c_H = Ce^{i\frac{x}{\lambda}} e^{\Omega t}$ where $\Omega = -L \left[\left(\frac{d^2 g}{dc_H{}^2} + 2\eta \right) \left(\frac{1}{\lambda^2} \right) + 2\alpha \left(\frac{1}{\lambda^4} \right) \right]$

Spinodal decomposition

$$c_H = Ce^{i\frac{x}{\lambda}} e^{\Omega t}$$

Maximum at wavelength

$$\lambda = 2 \frac{\alpha}{\left| \frac{d^2 g}{dc_H{}^2} + 2\eta \right|}$$



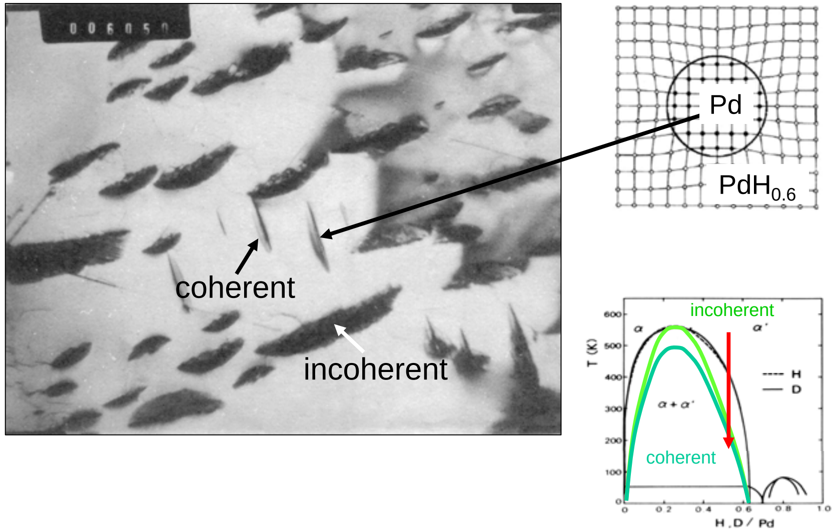
Coherent spinodal

$$kT = (-\varepsilon n - 2\eta) c_H (1 - c_H)$$

Incoherent spinodal

$$kT_{spinodal} = -\varepsilon n c_H (1 - c_H)$$

Coherent and incoherent grains



All we did so far is independent of the boundary of a sample.

There are in fact also macroscopic density modes that are both size and shape dependent

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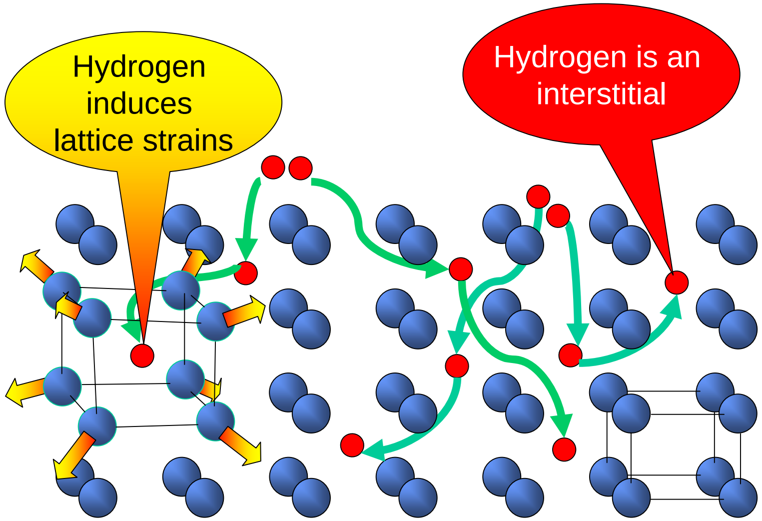
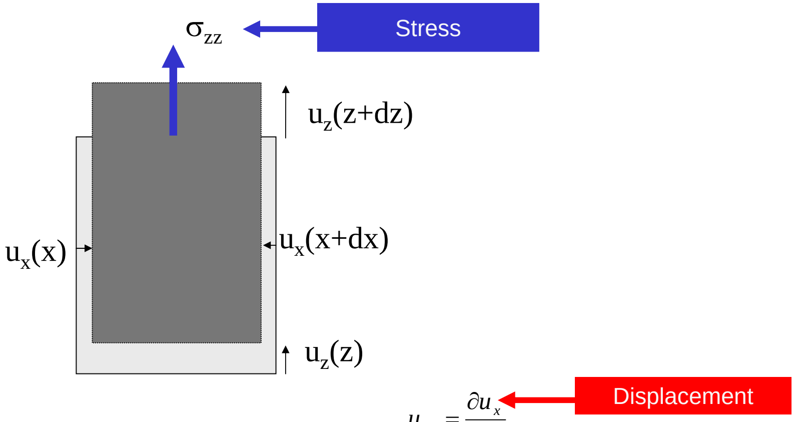
Elastic H-H interaction



Displacements, strains and stresses



$$u_{xx} = \frac{\partial u_x}{\partial x}$$

Strain

$$u_{zz} = \frac{\partial u_z}{\partial z}$$

Hookes's law

$$u_{xx} = \frac{1}{E}\left[\sigma_{xx} - \nu\left(\sigma_{yy} + \sigma_{zz}\right)\right]$$

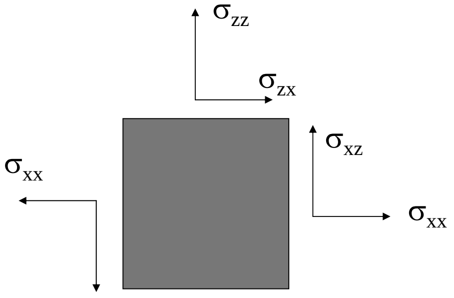
$$u_{yy} = \frac{1}{E}\left[\sigma_{yy} - \nu\left(\sigma_{xx} + \sigma_{zz}\right)\right]$$

$$u_{zz} = \frac{1}{E}\left[\sigma_{zz} - \nu\left(\sigma_{xx} + \sigma_{yy}\right)\right]$$

$$u_{zy} = \frac{(1+\nu)}{E}\sigma_{zy}$$

$$u_{zx} = \frac{(1+\nu)}{E}\sigma_{zx}$$

$$u_{xy} = \frac{(1+\nu)}{E}\sigma_{xy}$$



Hookes's law: stress and strains

$$u_{xx} = \frac{1}{E}\left[\sigma_{xx} - \nu\left(\sigma_{yy} + \sigma_{zz}\right)\right]$$

$$u_{yy} = \frac{1}{E}\left[\sigma_{yy} - \nu\left(\sigma_{xx} + \sigma_{zz}\right)\right]$$

$$u_{zz} = \frac{1}{E}\left[\sigma_{zz} - \nu\left(\sigma_{xx} + \sigma_{yy}\right)\right]$$

$$u_{zy} = \frac{(1+\nu)}{E}\sigma_{zy}$$

$$u_{zx} = \frac{(1+\nu)}{E}\sigma_{zx}$$

$$u_{xy} = \frac{(1+\nu)}{E}\sigma_{xy}$$

$$\Leftrightarrow$$

$$\sigma_{xx} = \frac{E}{(1+\nu)(1-2\nu)}\left[(1-\nu)u_{xx} + \nu\left(u_{yy} + u_{zz}\right)\right]$$

$$\sigma_{yy} = \frac{E}{(1+\nu)(1-2\nu)}\left[(1-\nu)u_{yy} + \nu\left(u_{xx} + u_{zz}\right)\right]$$

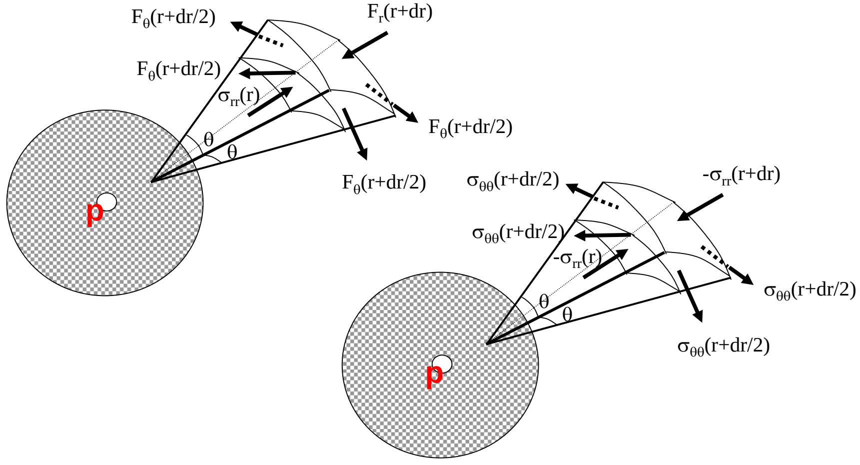
$$\sigma_{zz} = \frac{E}{(1+\nu)(1-2\nu)}\left[(1-\nu)u_{zz} + \nu\left(u_{xx} + u_{yy}\right)\right]$$

$$\sigma_{zy} = \frac{E}{(1+\nu)}u_{zy}$$

$$\sigma_{zx} = \frac{E}{(1+\nu)}u_{zx}$$

$$\sigma_{xy} = \frac{E}{(1+\nu)}u_{xy}$$

Equilibrium of forces



$$-\sigma_{rr}\left[r+dr\right]\times\theta^2\left(r+dr\right)^2 + 4\sigma_{\theta\theta}\left[r+{}^{dr}\!/_{2}\right]\times\theta\times r\times\frac{\theta}{2}dr + \sigma_{rr}\left[r\right]\times\theta^2\times r^2 = 0$$

Equation for displacements *u(r)*

$$-\sigma_{rr}\left[r+dr\right]\times\theta^2\left(r+dr\right)^2 + 4\sigma_{\theta\theta}\left[r+{}^{dr}\!/_{2}\right]\times\theta\times r\times\frac{\theta}{2}dr + \sigma_{rr}\left[r\right]\times\theta^2\times r^2 = 0$$

Keeping terms to first order only we obtain $r^2\frac{d\sigma_{rr}}{dr} + 2r\sigma_{rr} - 2r\sigma_{\theta\theta} = 0$

$$\sigma_{rr} = \frac{E}{(1+\nu)(1-2\nu)}\left[(1-\nu)u_{rr} + \nu\left(u_{\theta\theta} + u_{\theta\theta}\right)\right]$$

$$\sigma_{\theta\theta} = \frac{E}{(1+\nu)(1-2\nu)}\left[(1-\nu)u_{\theta\theta} + \nu\left(u_{rr} + u_{\theta\theta}\right)\right]$$

$$u_{rr} = \frac{du}{dr}$$

$$u_{\theta\theta} = \frac{u}{r}$$

$$r^2\frac{d^2u}{dr^2} + 2r\frac{du}{dr} - 2u = 0$$

Solution for displacements *u(r)*

The general solution of

$$r^2\frac{d^2u}{dr^2} + 2r\frac{du}{dr} - 2u = 0$$

The displacement is of the form

$$u(r) = ar + \frac{b}{r^2}$$

and the strains

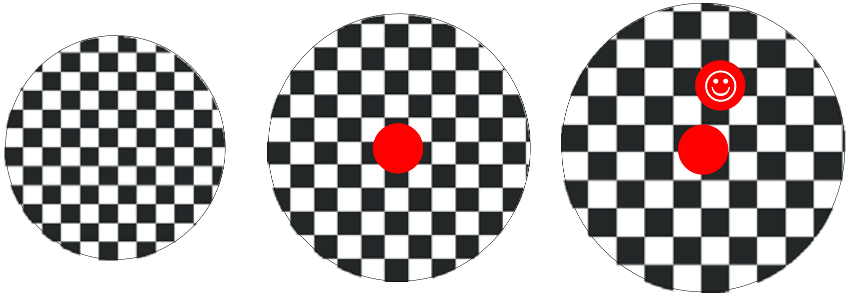
$$u_{rr} = \frac{du}{dr} = a - \frac{2b}{r^3}$$

$$u_{\theta\theta} = \frac{u}{r} = a + \frac{b}{r^3}$$

and the local volume dilation

$$\left.\frac{\Delta V}{V}\right|_{matrixl} = u_{rr} + 2u_{\theta\theta} = 3a = P\frac{2(1-2\nu)^2}{E(1-\nu)}$$

Long range attractive elastic interaction



$$\left.\frac{\partial(\mu/T)}{\partial(1/T)}\right|_{p,n} = \left.\frac{\partial H}{\partial n}\right|_{p,T} \equiv \overline{H}$$

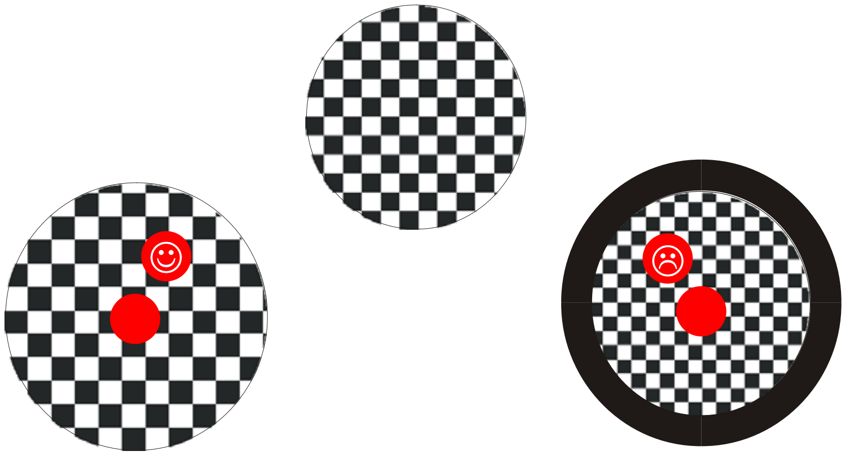
$$\frac{\partial}{\partial p}\left(\left.\frac{\partial(\mu/T)}{\partial(1/T)}\right|_{p,n}\right) = \frac{\partial}{\partial(1/T)}\left(\left.\frac{\partial(\mu/T)}{\partial p}\right|_{T,n}\right) = \overline{V} = \left.\frac{\partial\overline{H}}{\partial p}\right|_{n,T}$$

$$\left(-\frac{\partial\overline{H}}{\partial \ln V}\right) = B\overline{V}$$

For PdH_x:

$$\delta\left(\Delta\overline{H}\right) = -324\frac{\text{kJ}}{\text{molH}}\left(\frac{\delta V}{V}\right)$$

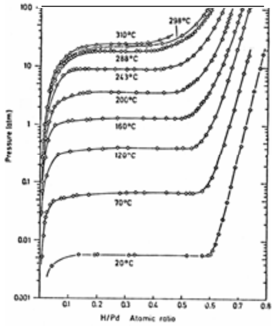
Effect of boundary conditions on H-H interaction

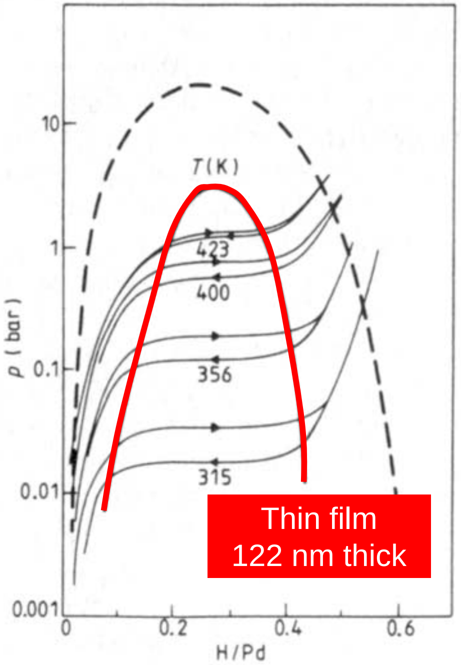


attractive

repulsive

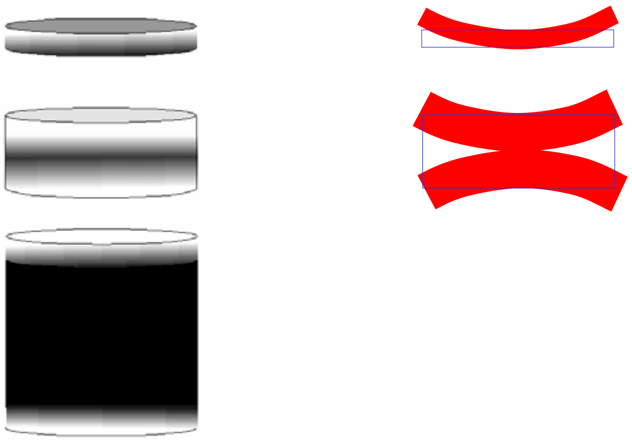
T_c lowering in PdHx films



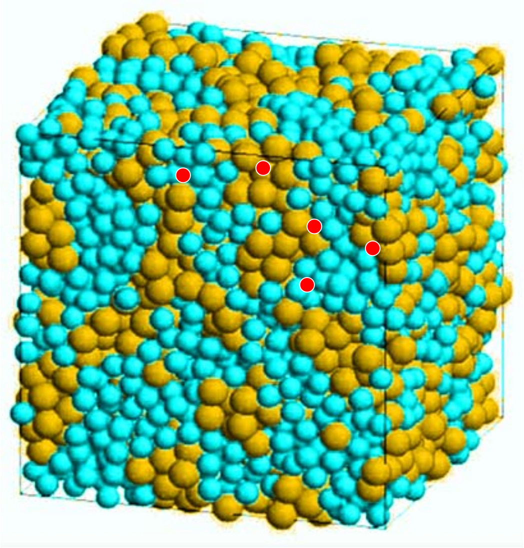


Thin film
122 nm thick

Macroscopic density modes

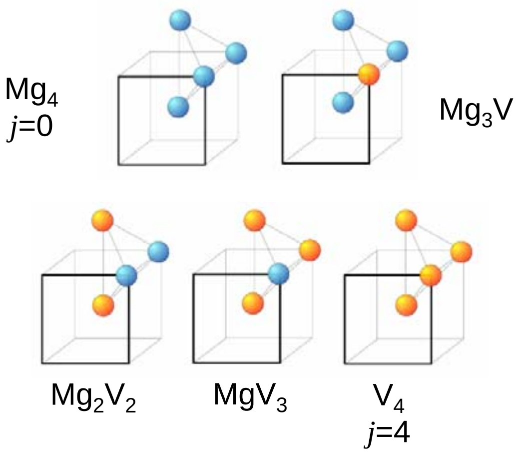


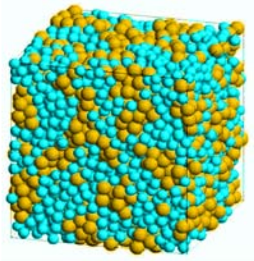
Hydrogen in an alloy



Multi-site lattice-gas model

H occupies tetrahedral sites formed of (*4-j*)-Mg and *j*-V atoms.
There are 5 clusters $1 \leq j \leq 5$





Multi-site lattice-gas model

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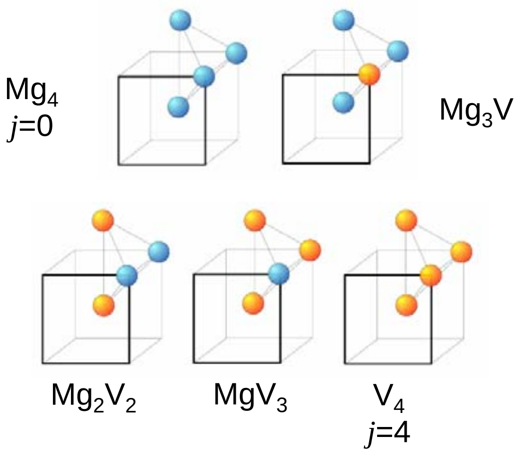
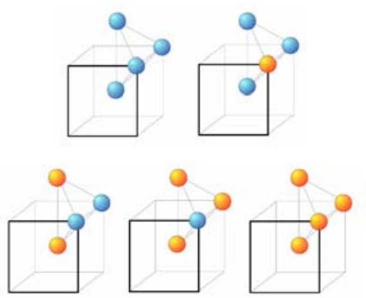


$$c = \sum g_j x_j$$

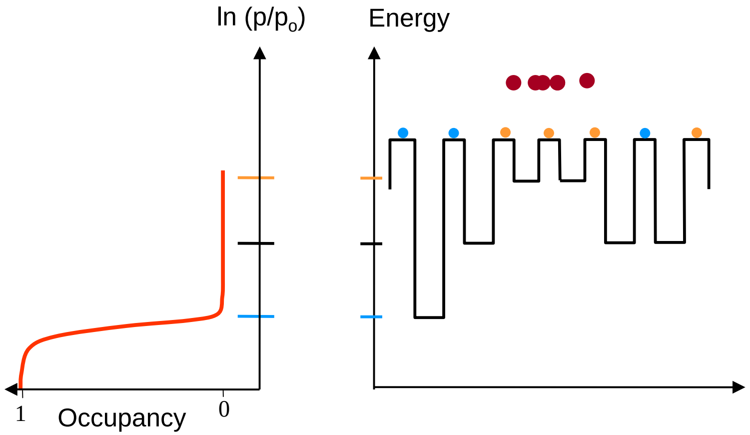
$$x_j = \frac{N_j^H}{N_j}$$

Pair probabilities in a Mg_yV_{1-y} alloy



$$P_{V\text{-}V} = (1-y)$$
$$P_{V\text{-}Mg} = y$$
$$P_{Mg\text{-}V} = (1-y)$$
$$P_{Mg\text{-}Mg} = y$$

Gradual filling of sites



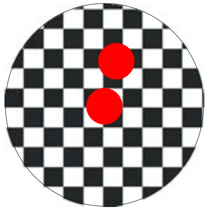
H in alloys and compounds II

$$\mu_H = kT\ln\left(\frac{c_H}{1-c_H}\right) + \varepsilon_0 + \varepsilon n c_H$$

leads to Fermi statistics for
H in M

$$c_H = \frac{1}{e^{\frac{\varepsilon_0 + \varepsilon n c_H - \mu_H}{kT}} + 1}$$

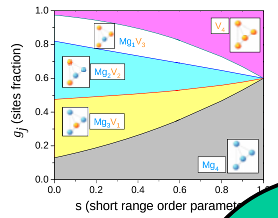
$$c = \sum g_j x_j$$

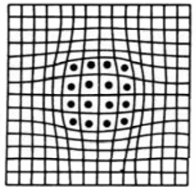


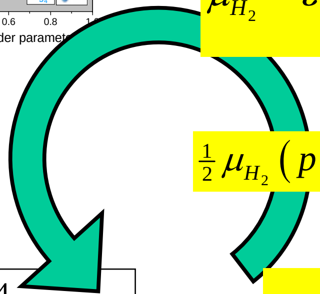
Elastic interaction not site dependent ⇒ depends only on **total** concentration c

$$x_j = \frac{1}{e^{\frac{\varepsilon_j + f(c,T) - \mu_H}{kT}} + 1}$$

H in alloys







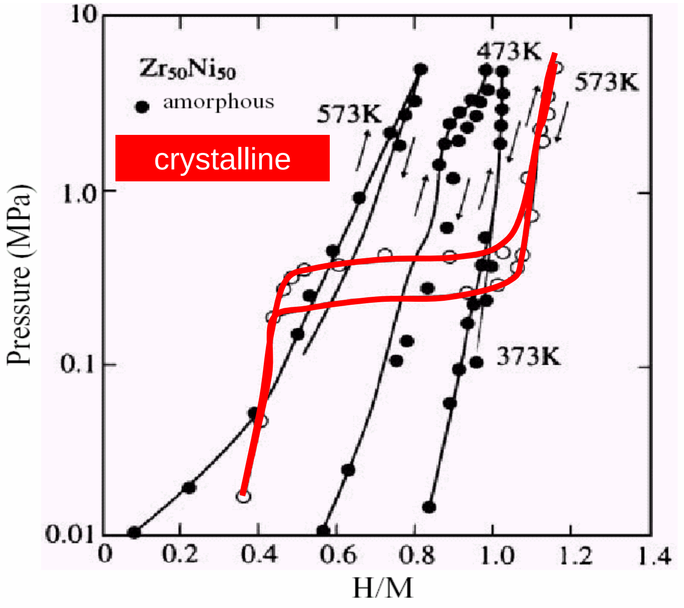
$$\mu_{H_2} = \varepsilon_b + kT\ln\left[\frac{p}{p_0(T)}\right]$$

$$\tfrac{1}{2}\mu_{H_2}(p,T) = \mu_H^j(p,T,c_H)$$

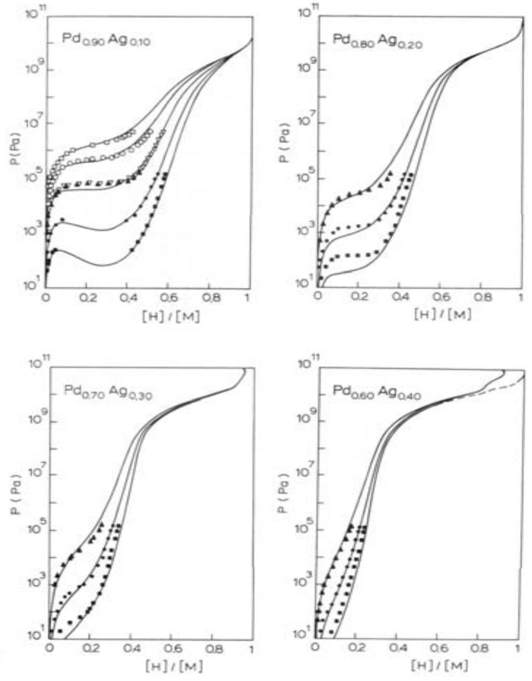
$$x_j = \frac{1}{e^{\frac{\varepsilon_j + f(c,T) - \mu_H^j}{kT}} + 1}$$

$$c = \sum_{j=0}^{4} g_j x_j$$

No plateau in amorphous films



Pressure-composition isotherms of Pd-Ag alloys



Influence of only 5% U impurities in Pd