Modeling excess heat in the Fleischmann-Pons experiment

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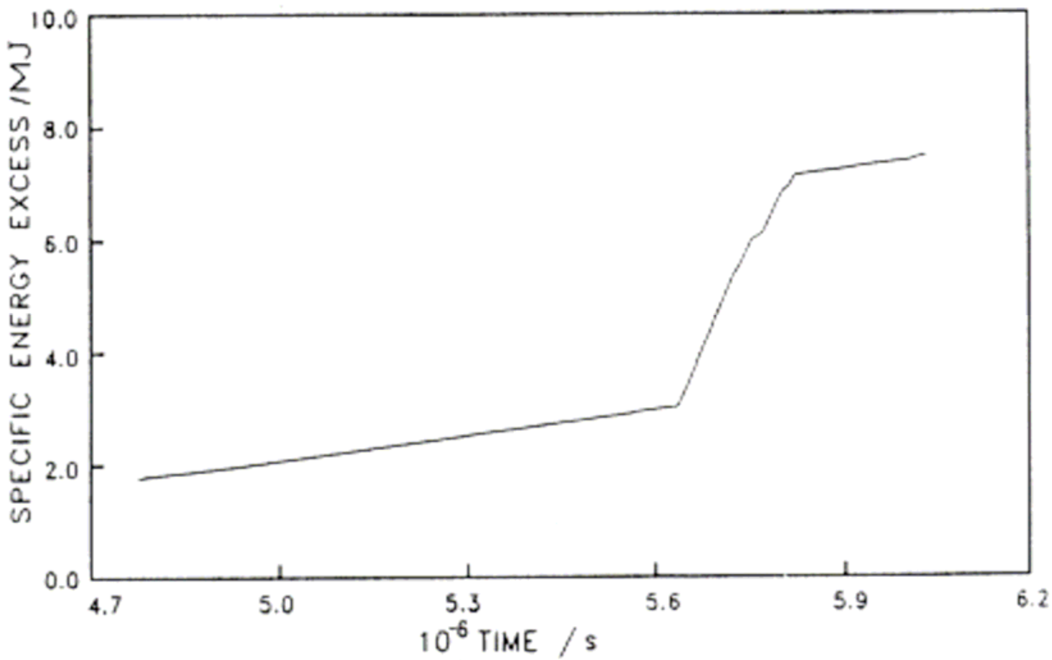
Outline

- Energy without energetic particles
- Converting a big quantum into small ones
- Excitation transfer
- Simulating
- Conclusions

Excess energy

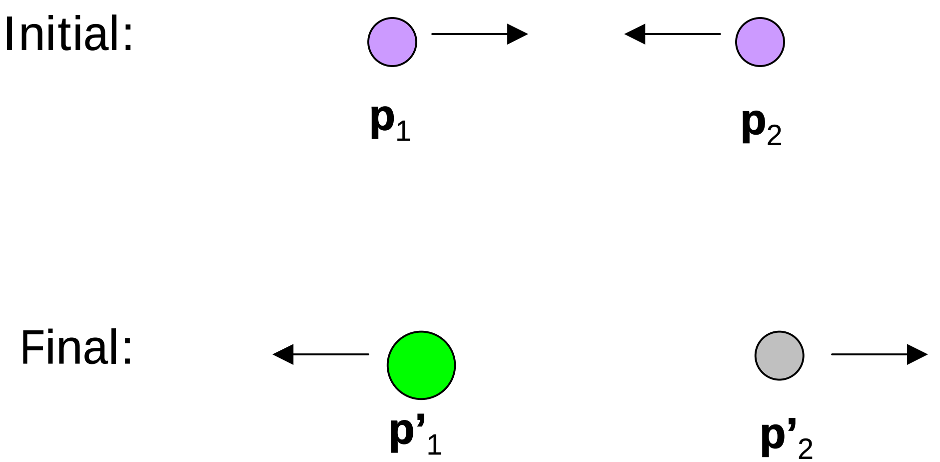


4 MJ observed during 80 hours

Would get 1.2 kJ for detonation of equivalent cathode volume (0.157 cc) of TNT

M Fleischmann et al, J Electroanalytical Chem **287** 293 (1990)

Energy and momentum conserved in nuclear reactions

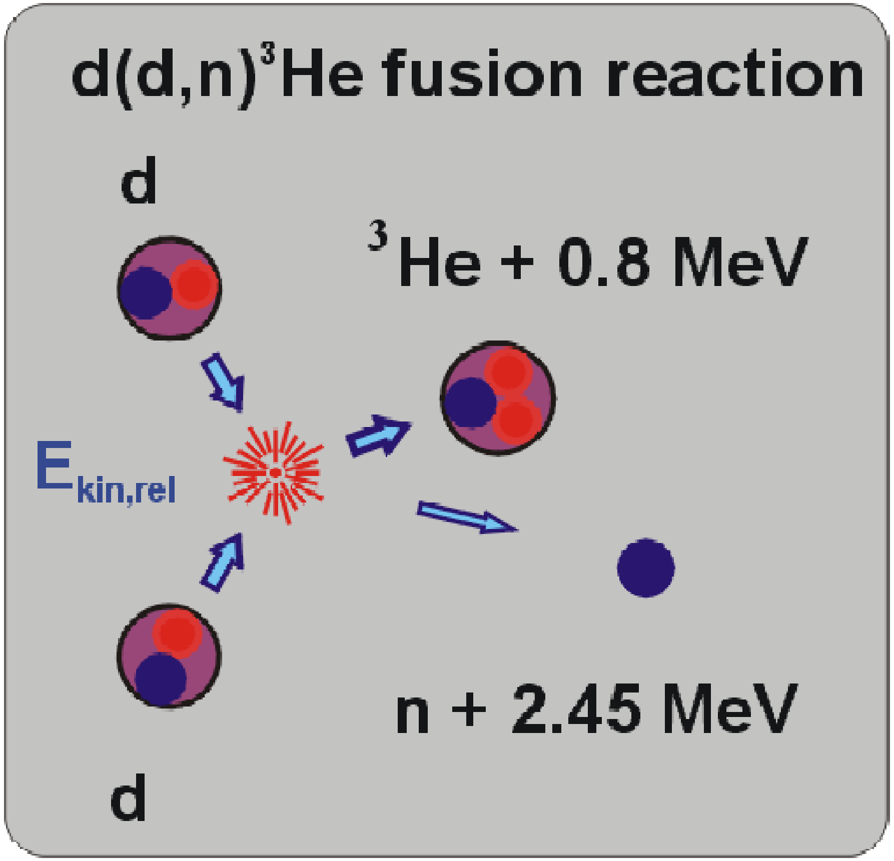


E. Rutherford

$$\mathbf{p}_1 + \mathbf{p}_2 = \mathbf{p}'_1 + \mathbf{p}'_2$$

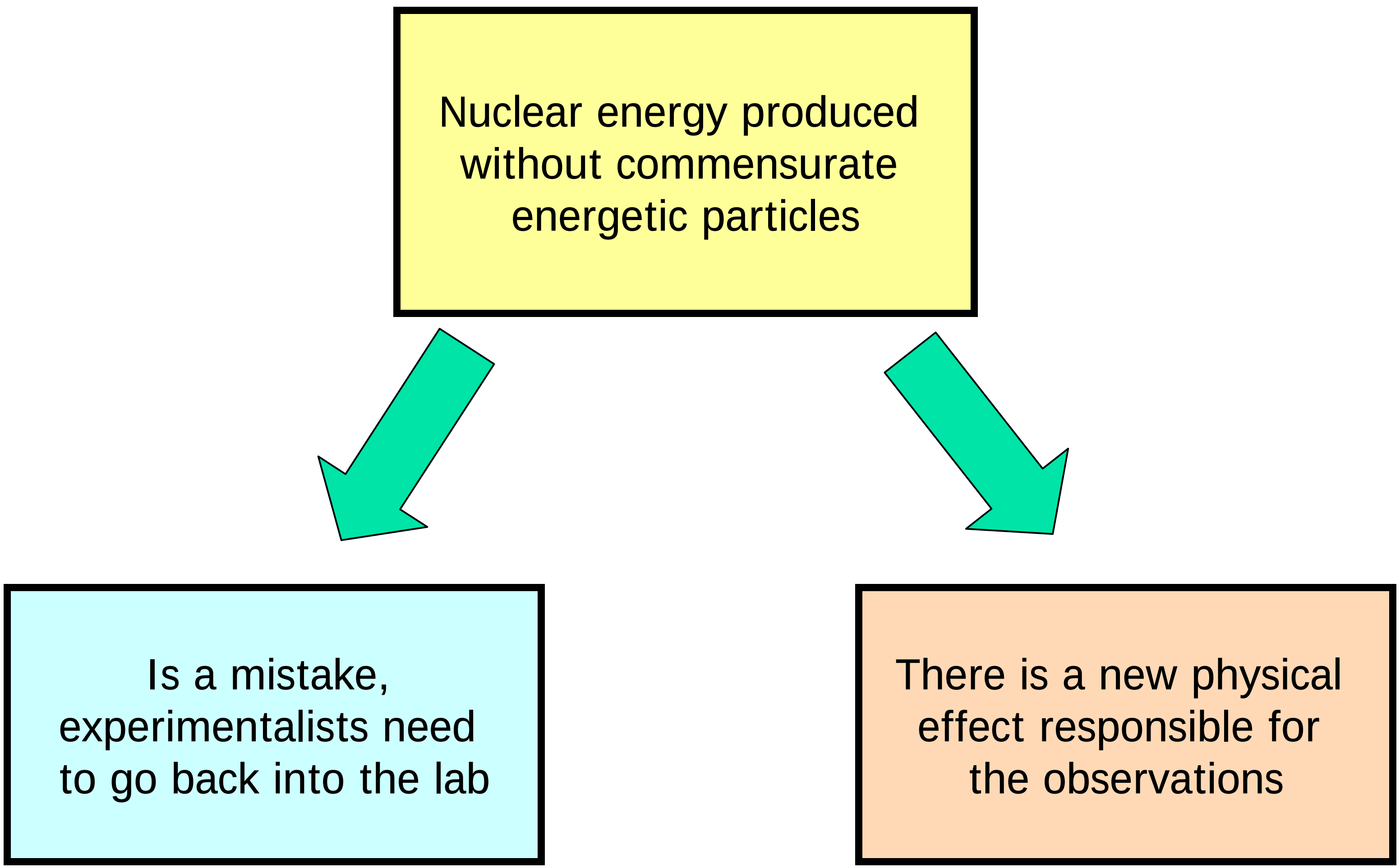
$$M_1 v^2_1/2 + M_2 v^2_2/2 + \Delta M c^2 = M_1'(v'_1)^2/2 + M_2'(v'_2)^2/2$$

Excess energy expressed as product kinetic energy



No energetic particles commensurate with energy

Only two possibilities



Helium

^{4}He is observed in the gas correlated with the energy produced

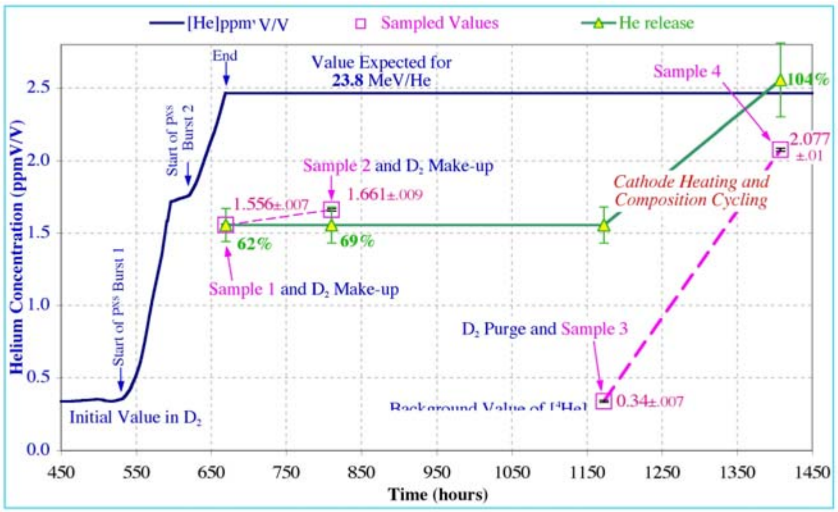
•No evidence that helium is energetic

•Positive evidence (lack of large amounts of Pd Kα x-rays) that helium is born with less than 20 keV

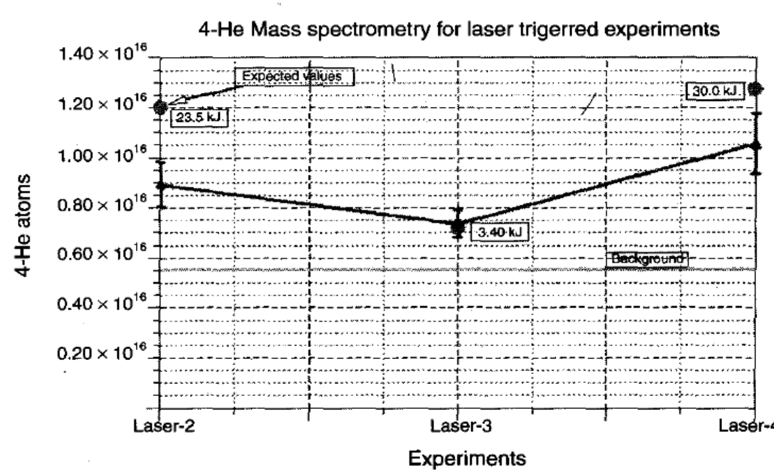
•Some helium retained in cathode

•Hinders accurate Q-value measurements

Two observations so far with stripping of ^{4}He from cathode



M4 cell at SRI



Laser-3 experiment at ENEA Frascati

Results in both cases consistent with Q = 24 MeV

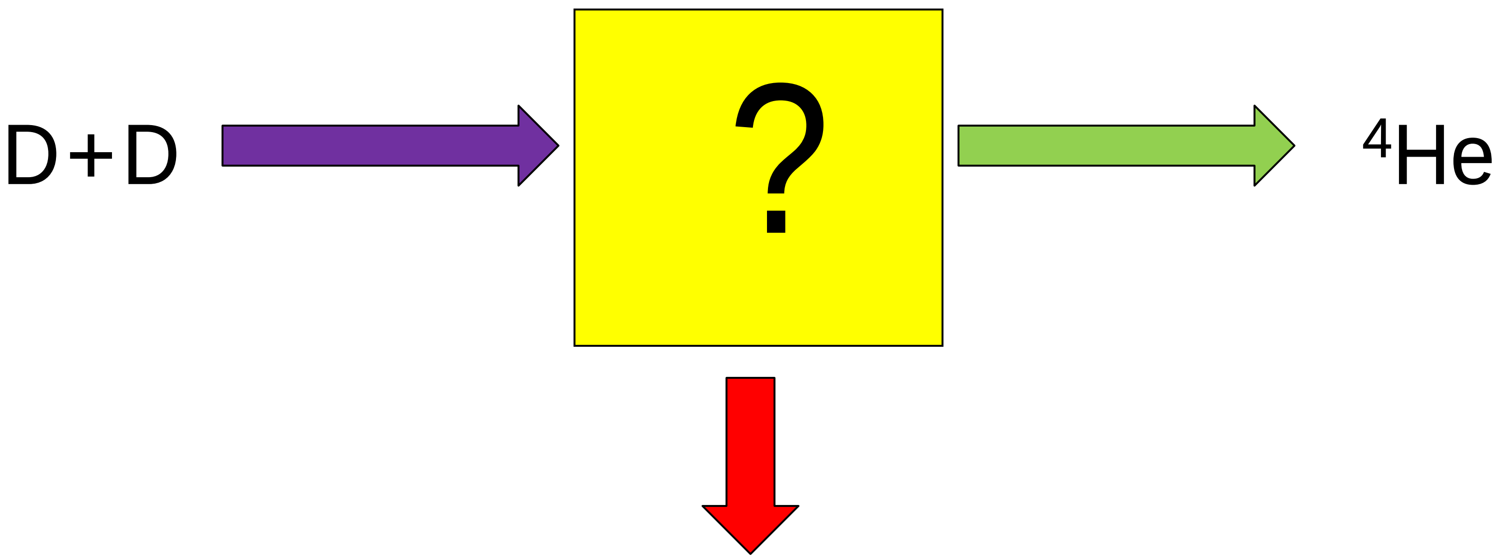
^{4}He as ash with Q=24 MeV

Mass difference between two deuterons and ^{4}He:

$$M_D c^2 + M_D c^2 = M_{4He} c^2 + 23.86 \text{ MeV}$$

Q-value consistent with deuterons reacting in new process to make ^{4}He

Experimental input for new process



Q = 23.86 MeV
no energetic particles

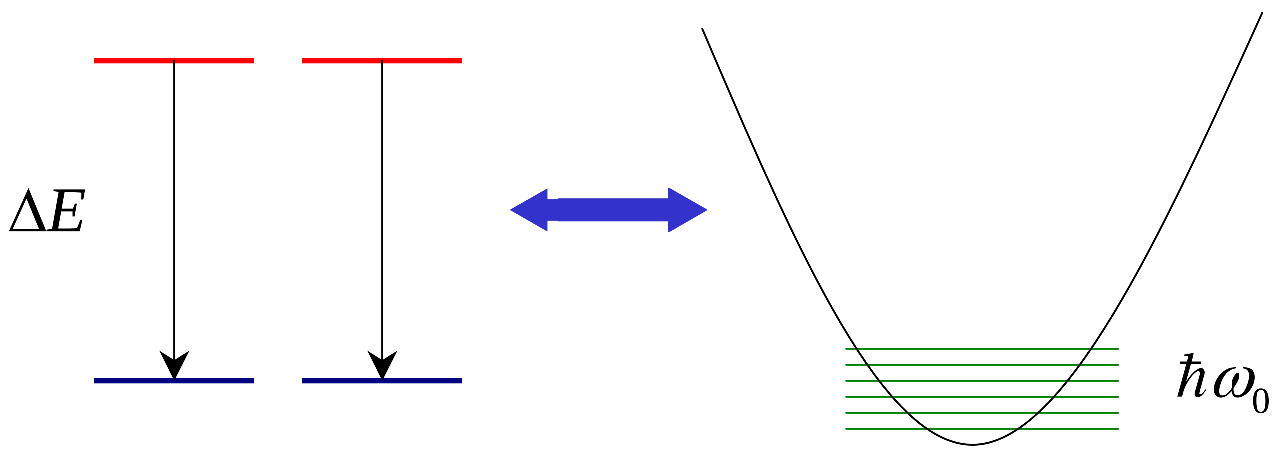
Theoretical problem

Although many more results available from experiment, we have enough so far to pose the key theory problem:

How to split up a large ΔE quantum into lots of small quanta?

The major implication of the Fleischmann-Pons experiment is that this is possible and occurs in energy production

Basic toy model



Two-level systems

Macroscopic
excited mode

$$\Delta E \; >> \; \hbar\omega_0$$

Many-spin spin-boson model

C. Cohen-Tannoudji

$$\hat{H} = \Delta E \frac{\hat{S}_z}{\hbar} + \hbar\omega_0 \hat{a}\hat{a}^\dagger + V \frac{2S_x}{\hbar}\left(\hat{a} + \hat{a}^\dagger\right)$$

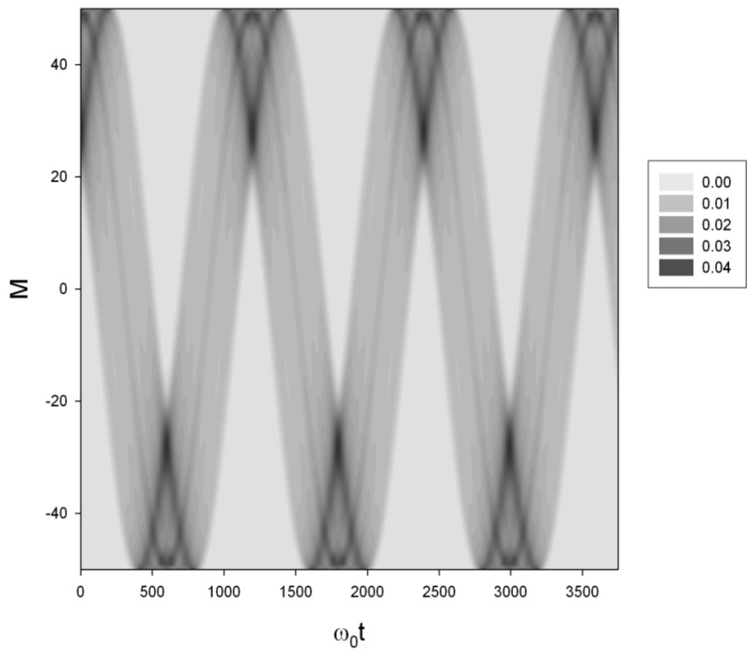
Two-level systems energy

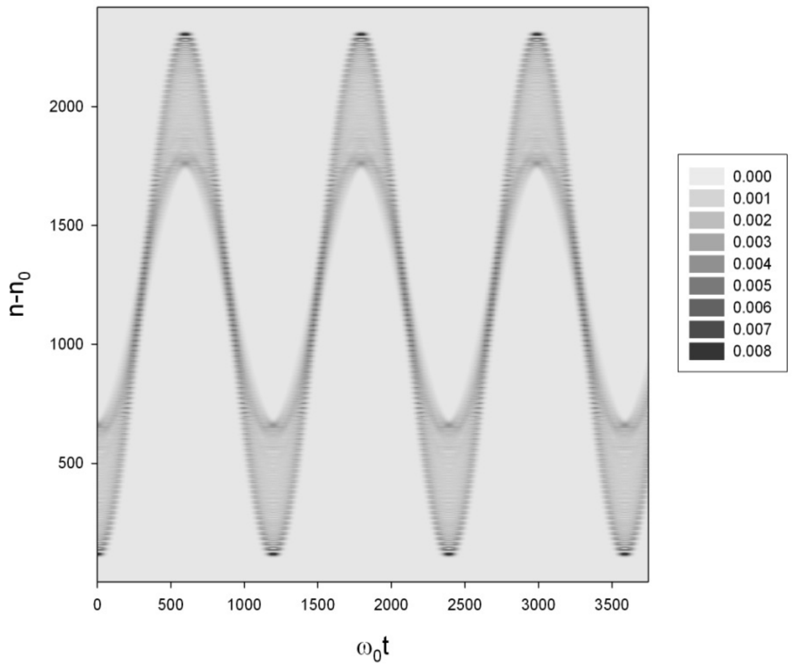
Harmonic oscillator energy

Linear coupling between two-level systems and oscillator

Earlier versions of the model due to Bloch and Siegert (1940)

Coherent energy exchange





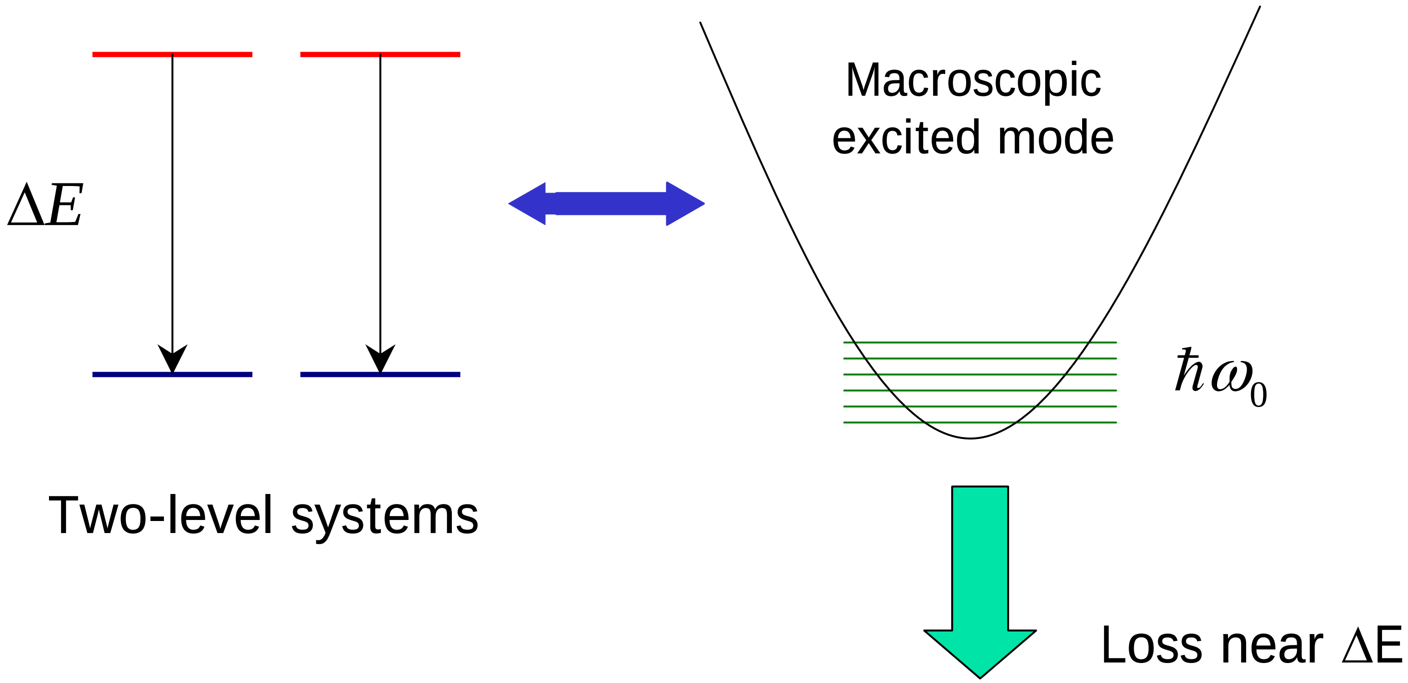
Numerical results for exchanging energy between 1700 oscillator quanta and 100 two-level systems

Thinking about toy model

Coherent multi-quantum energy exchange predicted by toy model

- Effect is weak
- Stringent resonance requirements
- Can exchange up to about 100 quanta coherently
- Exactly kind of model needed, except energy exchange effect is too weak

Improved toy model



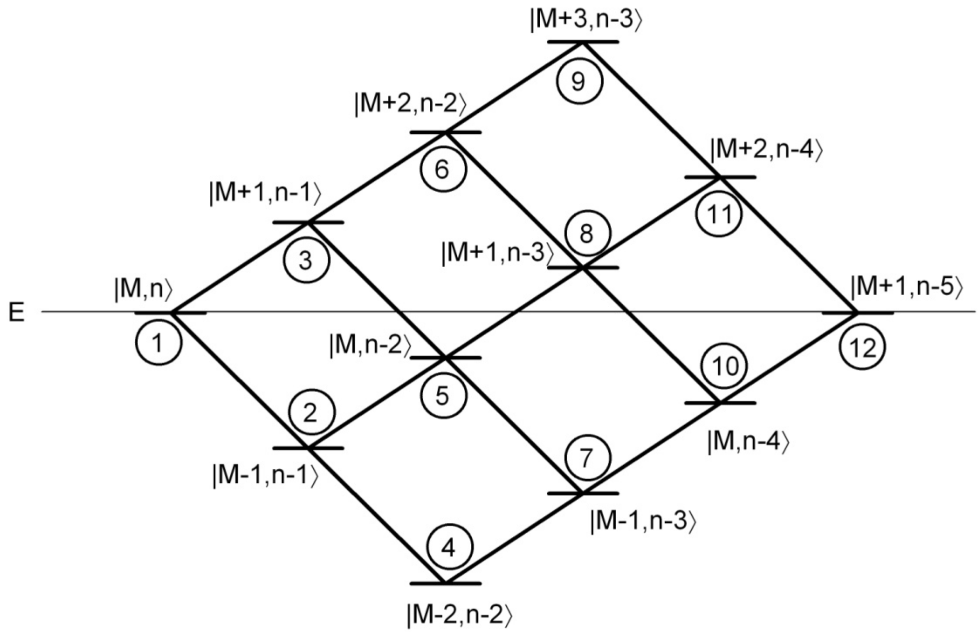
$$\Delta E \;>>\; \hbar\omega_0$$

Lossy version of model

$$\hat{H} = \Delta E \frac{\hat{S}_z}{\hbar} + \hbar\omega_0 \hat{a}\hat{a}^\dagger + V \frac{2S_x}{\hbar}\left(\hat{a} + \hat{a}^\dagger\right) - i\frac{\hbar}{2}\Gamma\left(E\right)$$

Loss term, which allows the system to decay when a large energy quantum is available

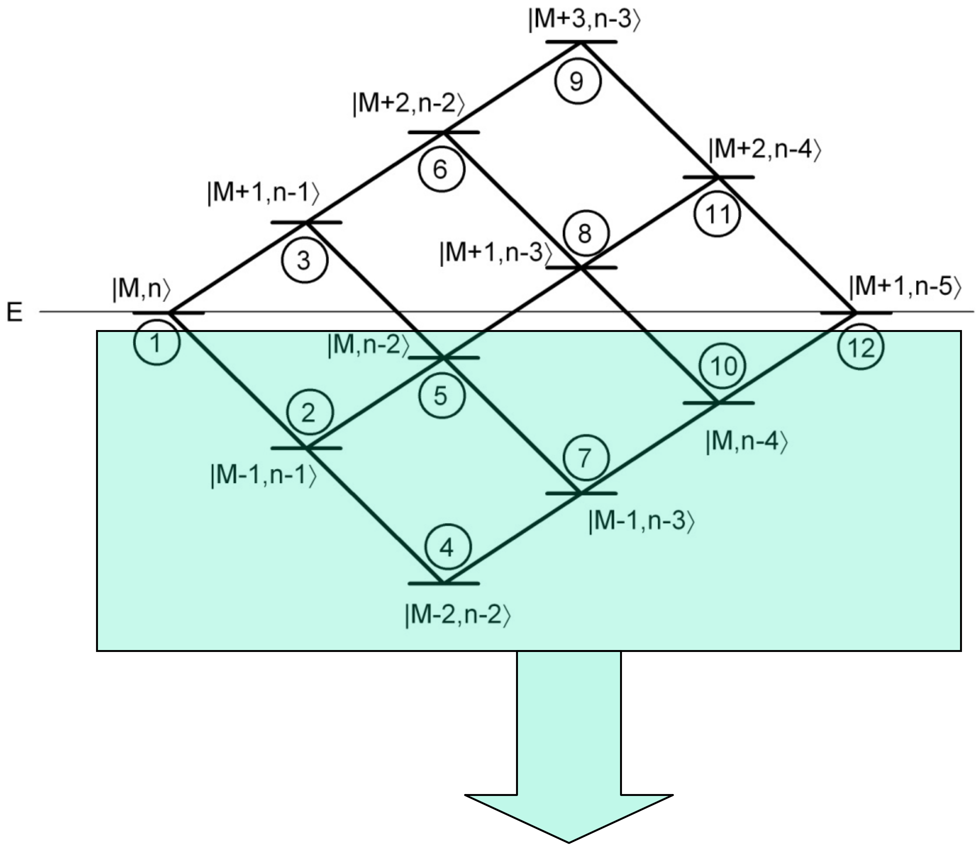
Perturbation theory



Many paths from initial to final state, with interference between upper and lower paths

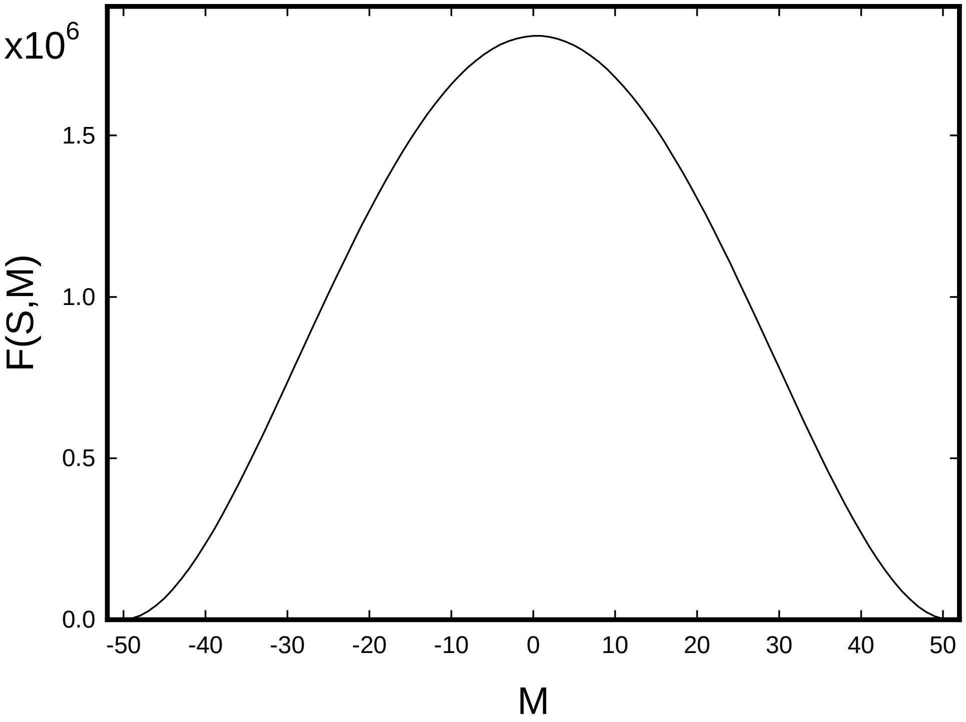
Finite basis approximation for $|n\rangle \otimes |M\rangle \rightarrow |n-5\rangle \otimes |M+1\rangle$

Perturbation theory



Loss channels available for off-resonant states with energy excess, which spoils the destructive interference

Enhancement due to loss

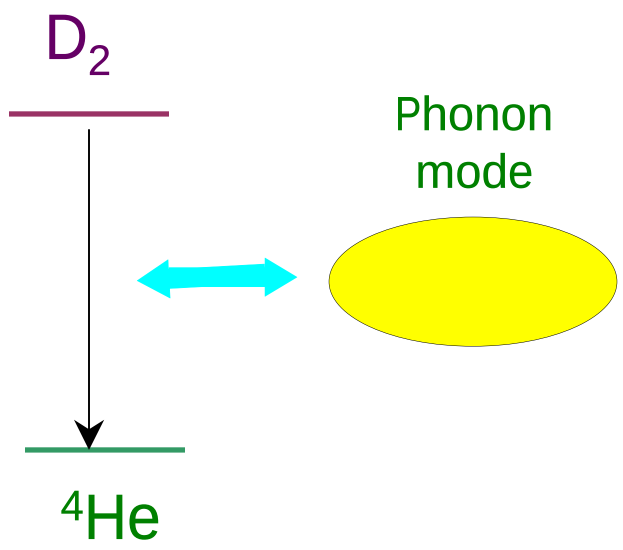


$$\left[V_{1,12}(E)\right]_{\Gamma=\infty} = \left[V_{1,12}(E)\right]_{\Gamma=0} F(S,M)$$

Lossy version of model

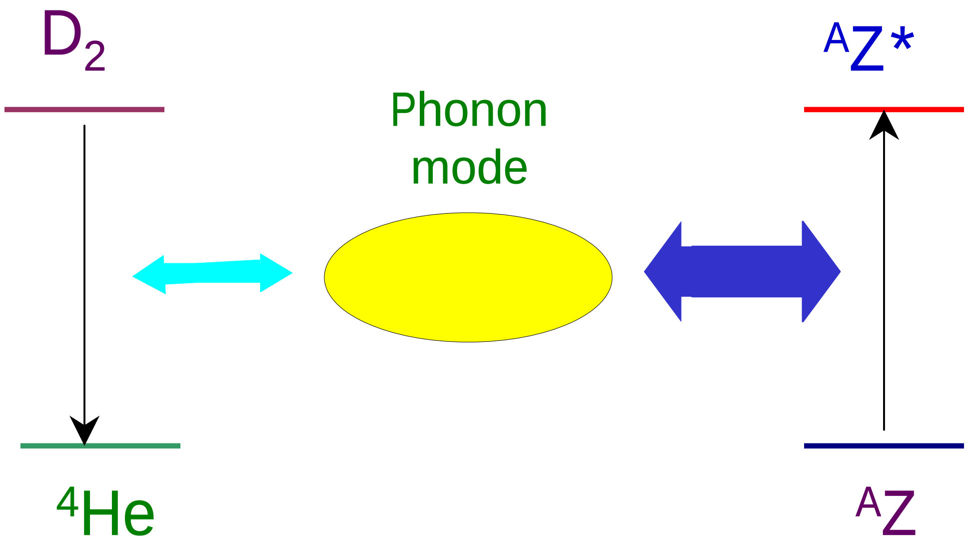
- Loss spoils the destructive interference
- Coherent energy exchange rates increased by orders of magnitude
- Much stronger effect
- Model capable of converting 24 MeV to atomic scale quanta

Thinking about PdD



Unfortunately, coupling is too weak because of Coulomb repulsion

Excitation transfer



Indirect evidence from experiment implicates ^{A}Z = ^{4}He, and theory and experiment suggest that $^{A}Z^{*}$ is a localized two-deuteron state

Basic model

$$\hat{H} = \Delta E_1 \frac{\hat{S}_z^{(1)}}{\hbar} + \Delta E_2 \frac{\hat{S}_z^{(2)}}{\hbar} + \hbar\omega_0 \hat{a}\hat{a}^\dagger - i\frac{\hbar}{2}\Gamma(E)$$

$$+ V_1 e^{-G} \frac{2S_x^{(1)}}{\hbar}\left(\hat{a} + \hat{a}^\dagger\right) + V_2 \frac{2S_x^{(2)}}{\hbar}\left(\hat{a} + \hat{a}^\dagger\right)$$

This kind of model is first one relevant to experiment

Strong-coupling limit

When the coupling between the receiver-side two-level systems and oscillator is strong, then the problem simplifies

$$\Gamma \rightarrow \frac{\hbar\omega_0}{\Delta E(g)} \left| \frac{\langle S, M, n+\Delta n | \hat{H} | S, M+1, n \rangle}{\hbar} \right|$$

When the excitation transfer step is the bottleneck, then

$$\Gamma = \frac{V_1\sqrt{n}}{\hbar}\left(\frac{\hbar\omega_0}{\Delta E}\right)e^{-G}\sqrt{(S+M)(S-M)}$$

Coupling between nuclei and phonons

Strong force interaction matrix element expressed in terms of phonon coordinates and internal nuclear coordinates

$$M_{fi} = \iint\iint \Psi_f^*\left(\{\boldsymbol{\xi}_f\},\{\sigma_\beta\},\{\tau_\beta\},\mathbf{q}_f\right) V_n \, \Psi_i\left(\{\boldsymbol{\xi}_i\},\{\sigma_\alpha\},\{\tau_\alpha\},\mathbf{q}_i\right)$$
$$\times \Delta\left(\mathbf{q}_i,\mathbf{q}_f\right)\Delta\left(\boldsymbol{\xi}_i,\boldsymbol{\xi}_f\right) d\mathbf{q}_i d\mathbf{q}_f d\boldsymbol{\xi}_i d\boldsymbol{\xi}_f$$

$$\Delta\left(\boldsymbol{\xi}_i,\boldsymbol{\xi}_f\right) = \prod_\alpha \delta\left(\mathbf{r}_\alpha^f - \mathbf{r}_\alpha^i\right)$$

$$\Delta\left(\mathbf{q}_i,\mathbf{q}_f\right) = \delta\left(\mathbf{q}_i - \mathbf{A}\cdot\mathbf{q}_f - \mathbf{b}\right) \qquad \mathbf{q}_f = \mathbf{A}\cdot\mathbf{q}_i + \mathbf{b}$$

P. L. Hagelstein et al, *Proc. ICCF14*

Can we calculate it for real?

Recent work focuses on computation of phonon nuclear coupling for the simpler 3-body version of the problem p+d → ^{3}He + Q

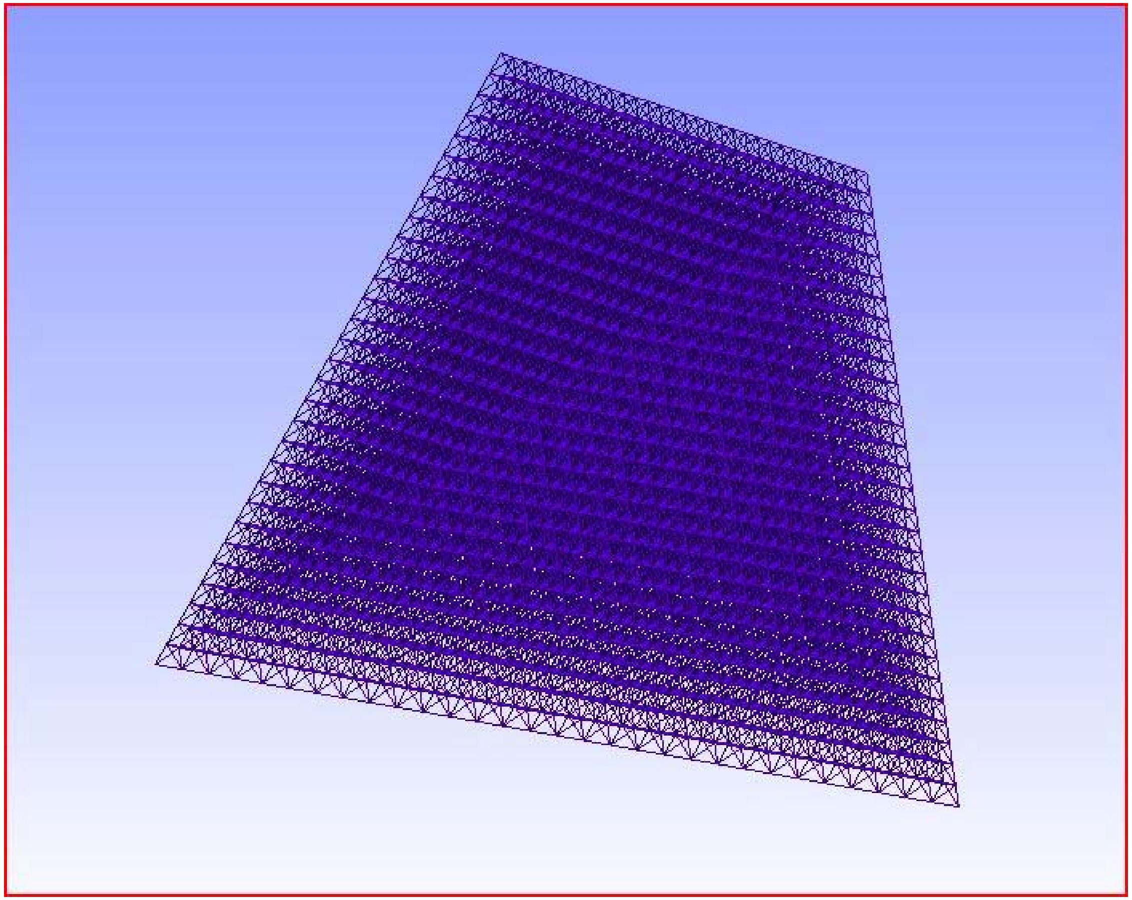
First need wavefunctions and nuclear force model

$$E\Psi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = -\frac{\hbar^2}{2M}\left(\nabla_1^2+\nabla_2^2+\nabla_3^2\right)\Psi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)+V_n\Psi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$$

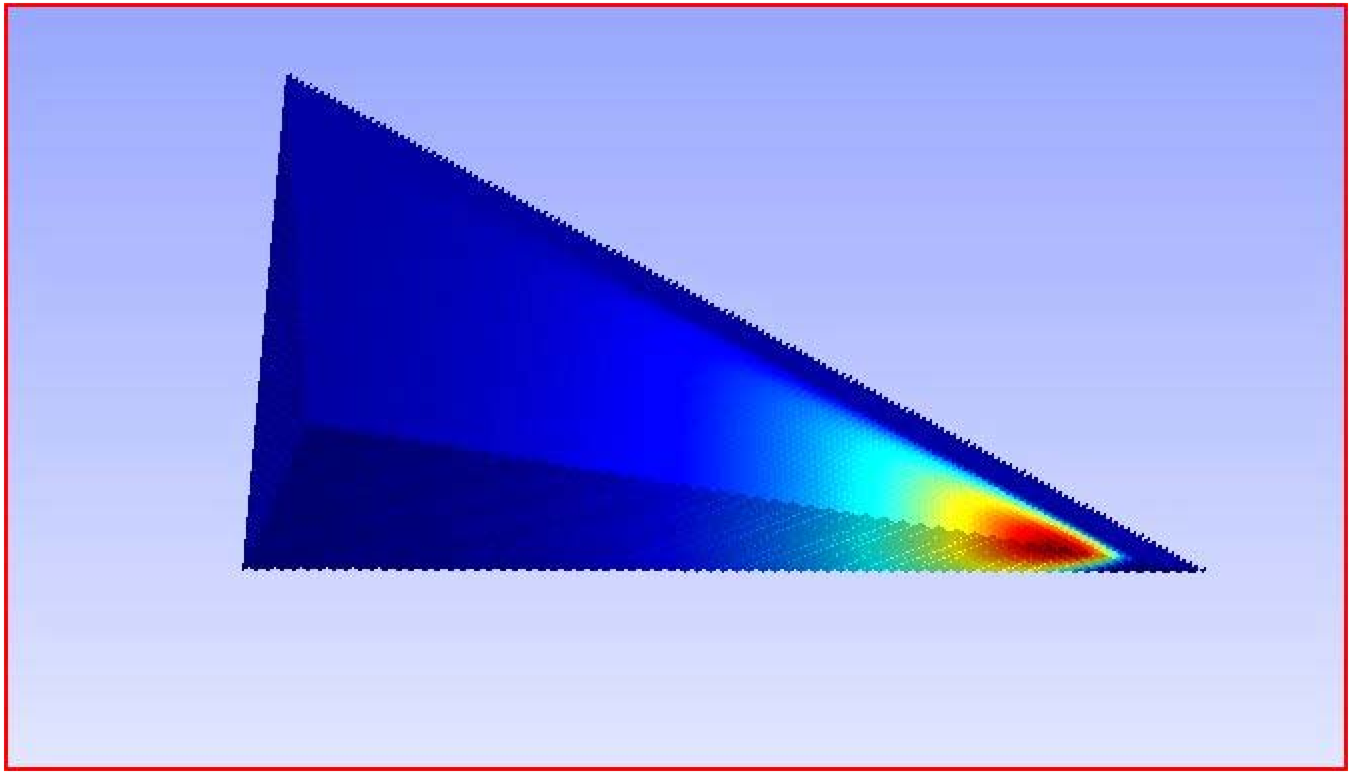
Simplest reasonable approximation for wavefunction

$$\Psi = \Phi_S+\Phi_{D1}+\Phi_{D2}+\Phi_{D3}$$

Full computational mesh



Example S channel wavefunction using the Hamada-Johnston potential



Simplest model for dynamics

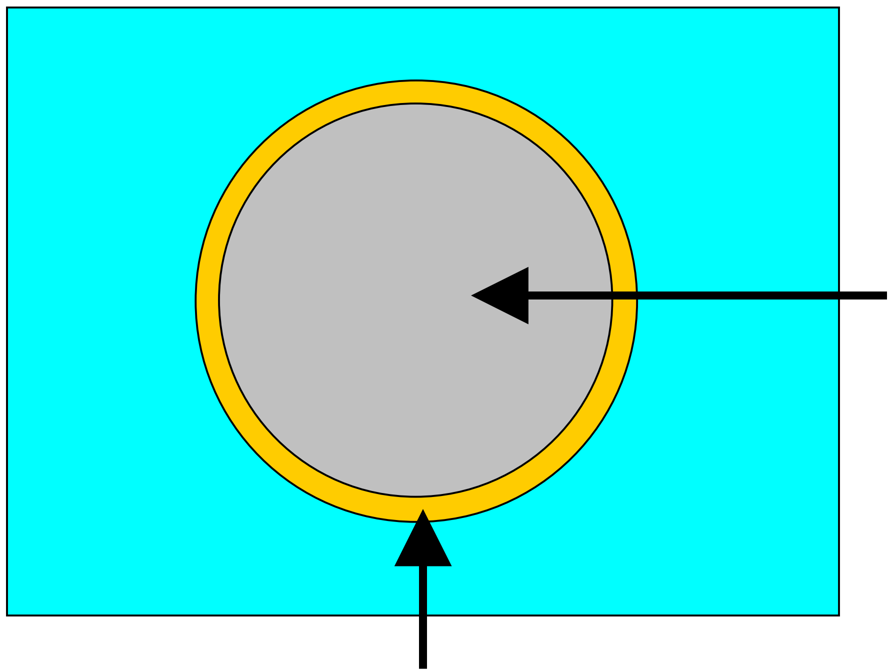
$$\frac{d}{dt}N_{D2} + \frac{N_{D2} - N_{D2}^{0}}{\tau_{D2}} = -\Gamma_0\sqrt{N_{D2}N_{He}}\,\Theta\left(n - n_{thresh}\right)$$

$$\frac{d}{dt}N_{He} + \frac{N_{He} - N_{He}^{0}}{\tau_{He}} = \Gamma_0\sqrt{N_{D2}N_{He}}\,\Theta\left(n - n_{thresh}\right)$$

$$\frac{d}{dt}n + \frac{n - n_0}{\tau_p} = \gamma_J + \frac{\Delta E}{\hbar\omega_0}\Gamma_0\sqrt{N_{D2}N_{He}}\,\Theta\left(n - n_{thresh}\right)$$

Molecular D_2 in lattice lost in reaction, replaced by diffusion
^{4}He created in reaction, removed by diffusion
Phonons produced by reaction and by deuterium flux, lost to thermalization

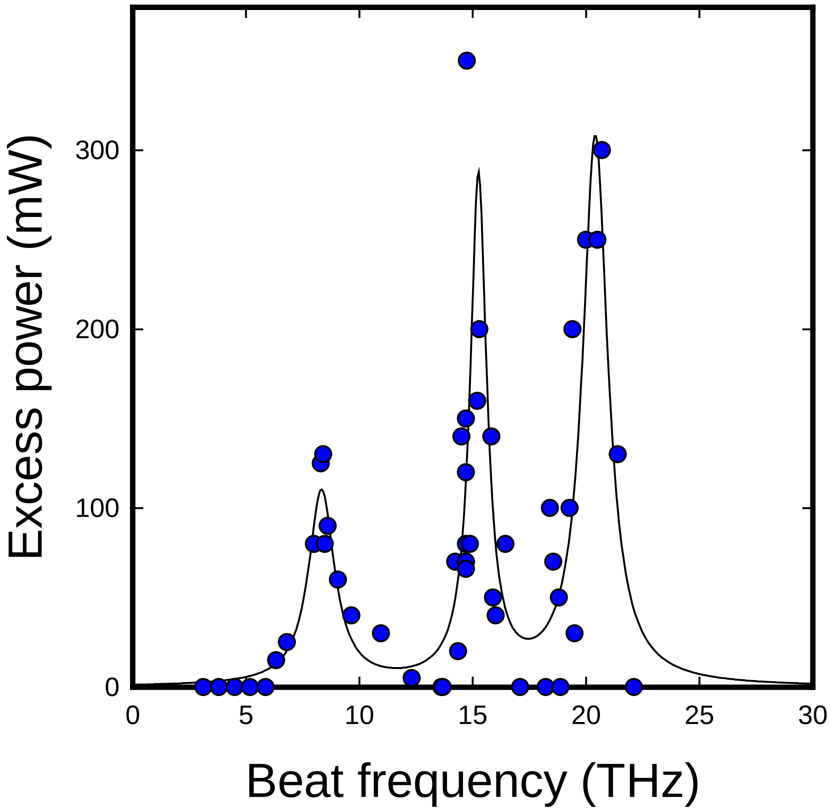
Where is the D_2?



No D_2 in the bulk due to occupation of antibonding sites

Conjecture that D_2 forms at vacancy sites in codeposition region near cathode surface

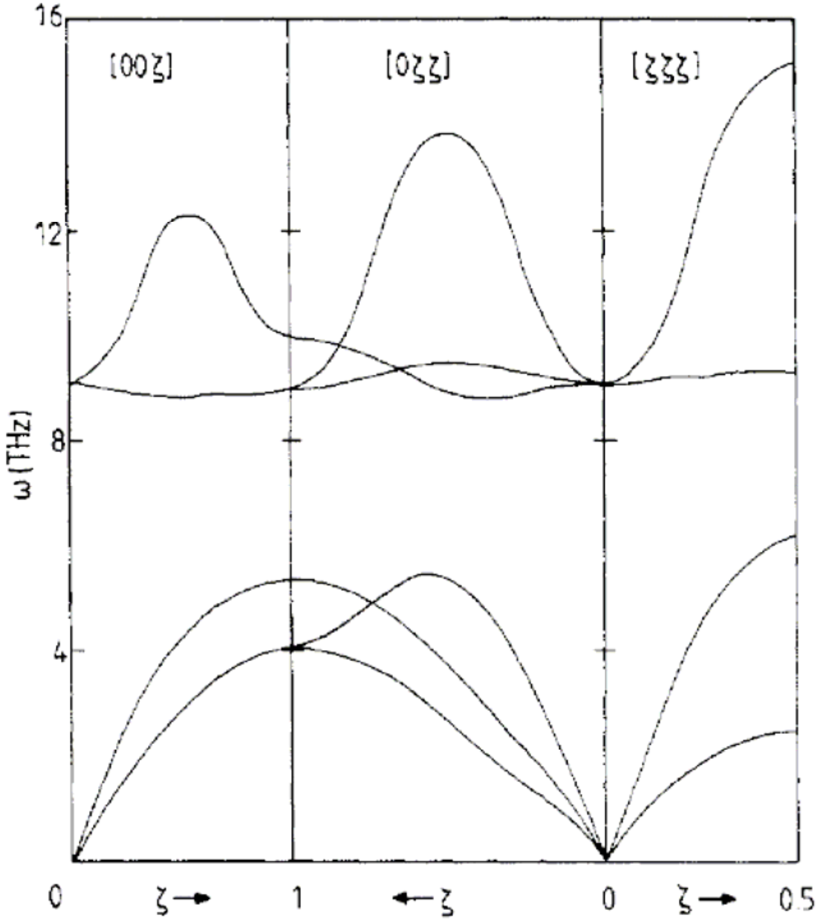
What oscillator modes?



Frequency (THz)	width (THz)
8.3	0.70
15.3	0.44
20.4	0.68

Results from dual laser experiments of Letts, *Proc. ICCF14* and *ACS Sourcebook* vol 2

Dispersion curve for PdD



L E Sansores et al
J Phys C **15** 6907 (1982)

Trying out the model

$$\frac{d}{dt}N_{D2} + \frac{N_{D2} - N_{D2}^{0}}{\tau_{D2}} = -\Gamma_0\sqrt{N_{D2}N_{He}}\,\Theta\left(n - n_{thresh}\right)$$

$$\frac{d}{dt}N_{He} + \frac{N_{He} - N_{He}^{0}}{\tau_{He}} = \Gamma_0\sqrt{N_{D2}N_{He}}\,\Theta\left(n - n_{thresh}\right)$$

$$\frac{d}{dt}n + \frac{n - n_0}{\tau_p} = \gamma_J + \frac{\Delta E}{\hbar\omega_0}\Gamma_0\sqrt{N_{D2}N_{He}}\,\Theta\left(n - n_{thresh}\right)$$

Example: fast He diffusion

Active region:
$A = 1\ cm^2$
$\Delta r = 100\ nm$

D_2 parameters:
$f[vacancy] = 0.25$
$f[D_2] = 0.005$
$N[D_2] = 1.8 \times 10^{15}$
$\tau_{D2} = 2 \times 10^{-8}$ sec

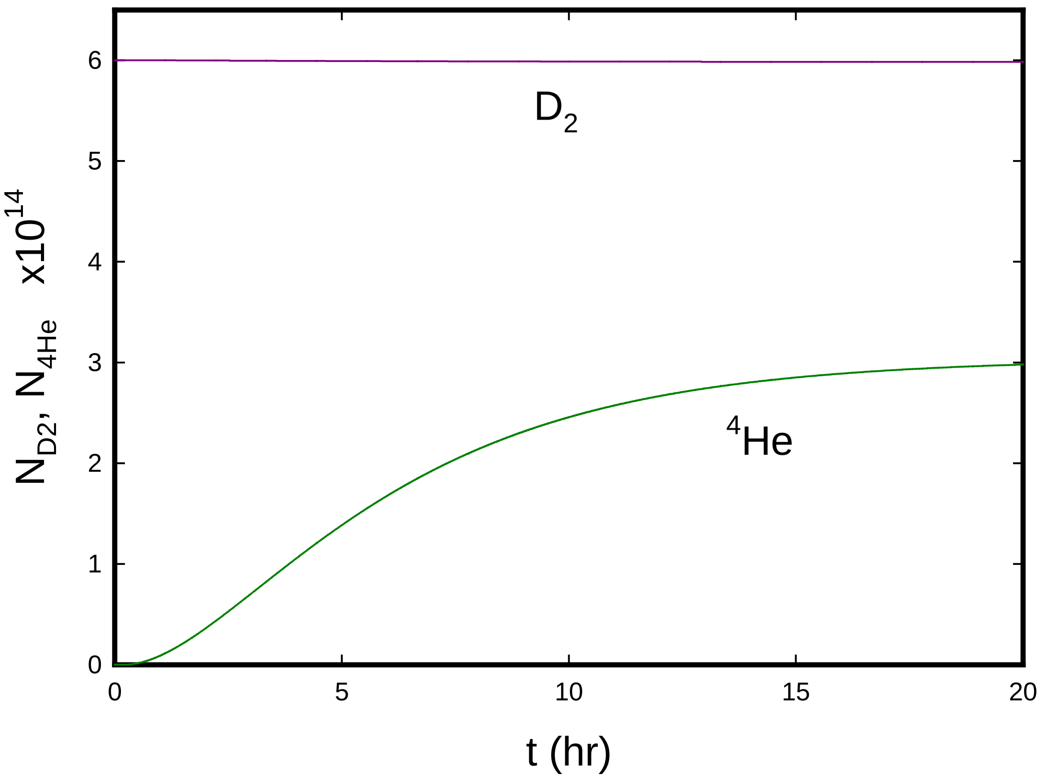
^4He parameters:
$D_{He} = 1.3 \times 10^{-14}\ cm^2/sec$
$\tau_{He} = \Delta r^2/D_{He} = 2.1$ hr

Phonon mode:
$f_0 = 8.3$ THz
$Q = 20$

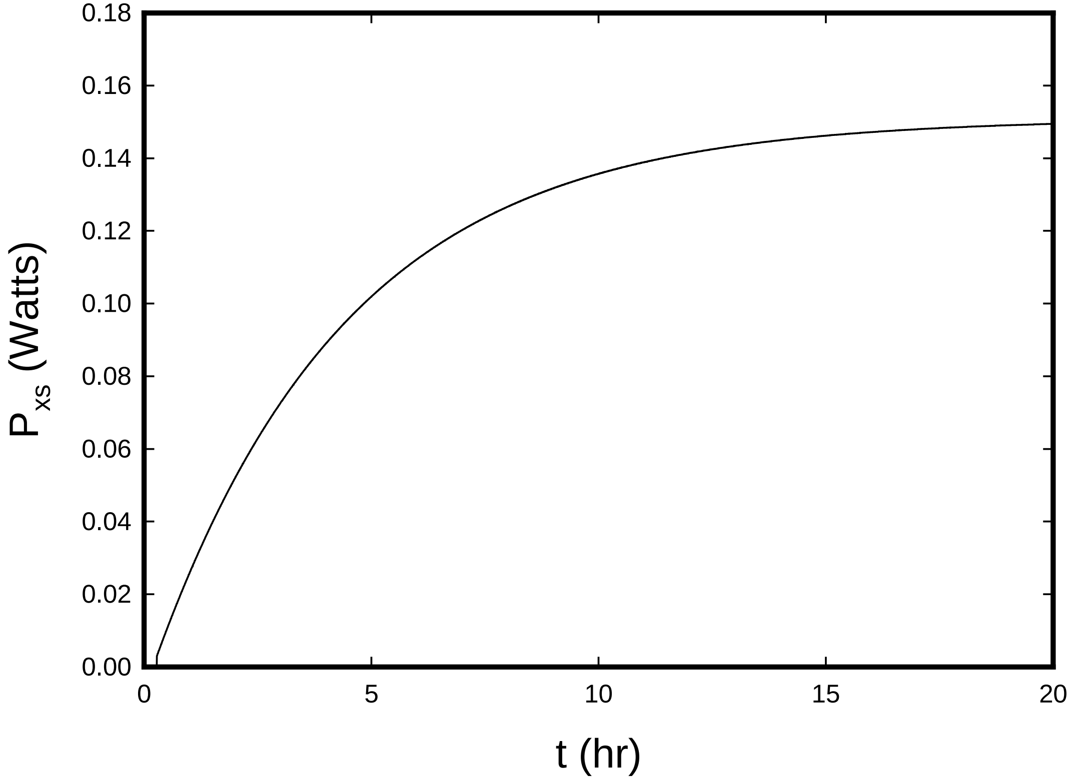
Deuterium flux:
$P_{flux} = 1\ Watt/cm^3$
$n_{thresh} = 100$

Basic reaction rate:
$\Gamma_0 = 1/(3\ hr)$

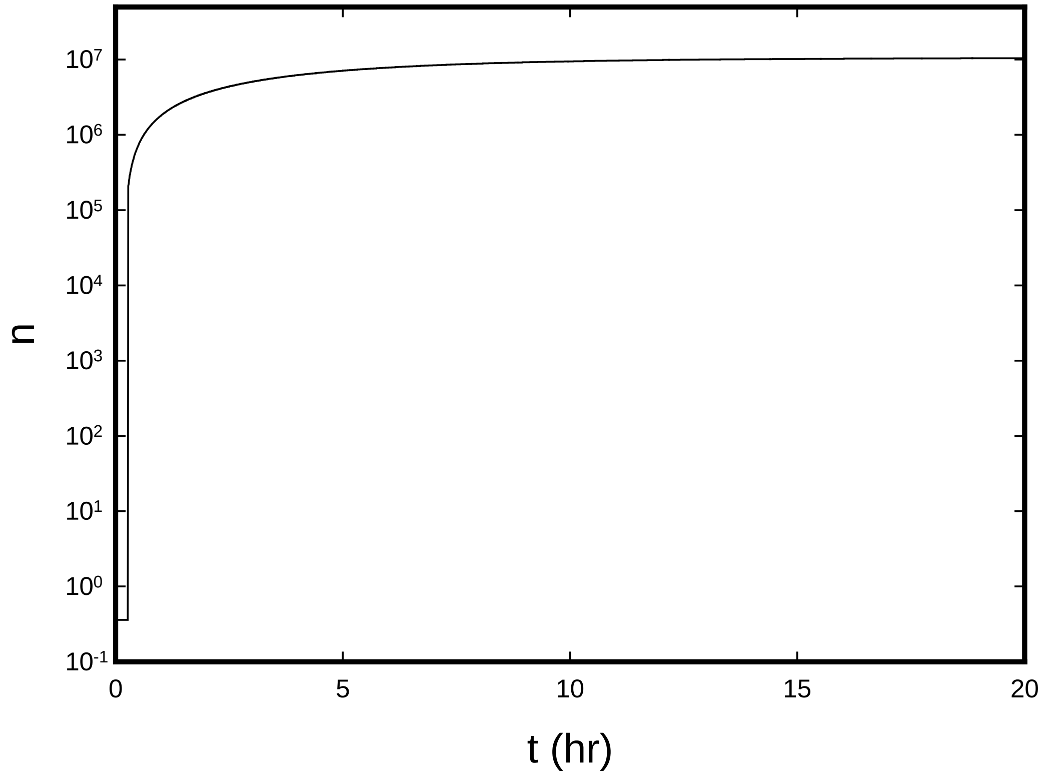
Evolution of dideuterium, ^{4}He



Excess power



Number of phonons



Thermal: 0.36 Flux generated (1 W/cm^3): 700 P_{xs} generated: 10^7

Example: slow He diffusion

Active region:
$A = 0.1\ cm^2$
$\Delta r = 500\ nm$

D_2 parameters:
$f[vacancy] = 0.25$
$f[D_2] = 0.005$
$N[D_2] = 3.0 \times 10^{14}$
$\tau_{D2} = 2 \times 10^{-8}$ sec

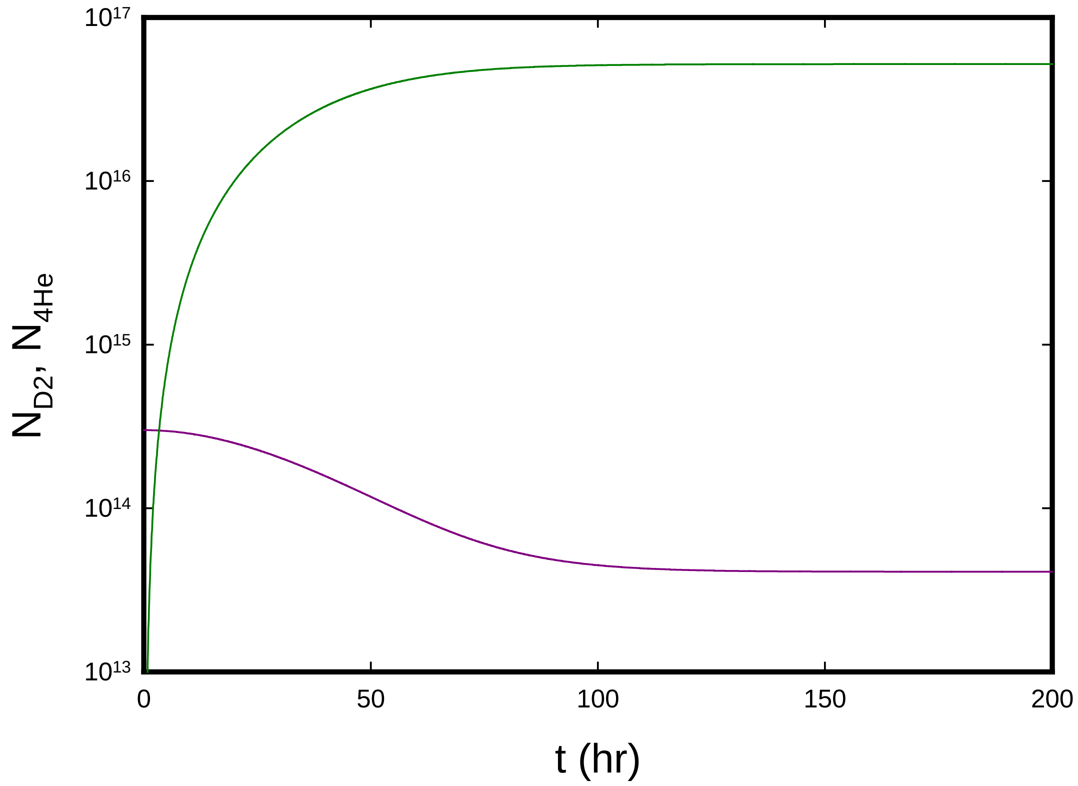
^4He parameters:
$D_{He} = 1.3 \times 10^{-14}\ cm^2/sec$
$\tau_{He} = \Delta r^2/D_{He} = 53.4$ hr

Phonon mode:
$f_0 = 8.3$ THz
$Q = 20$

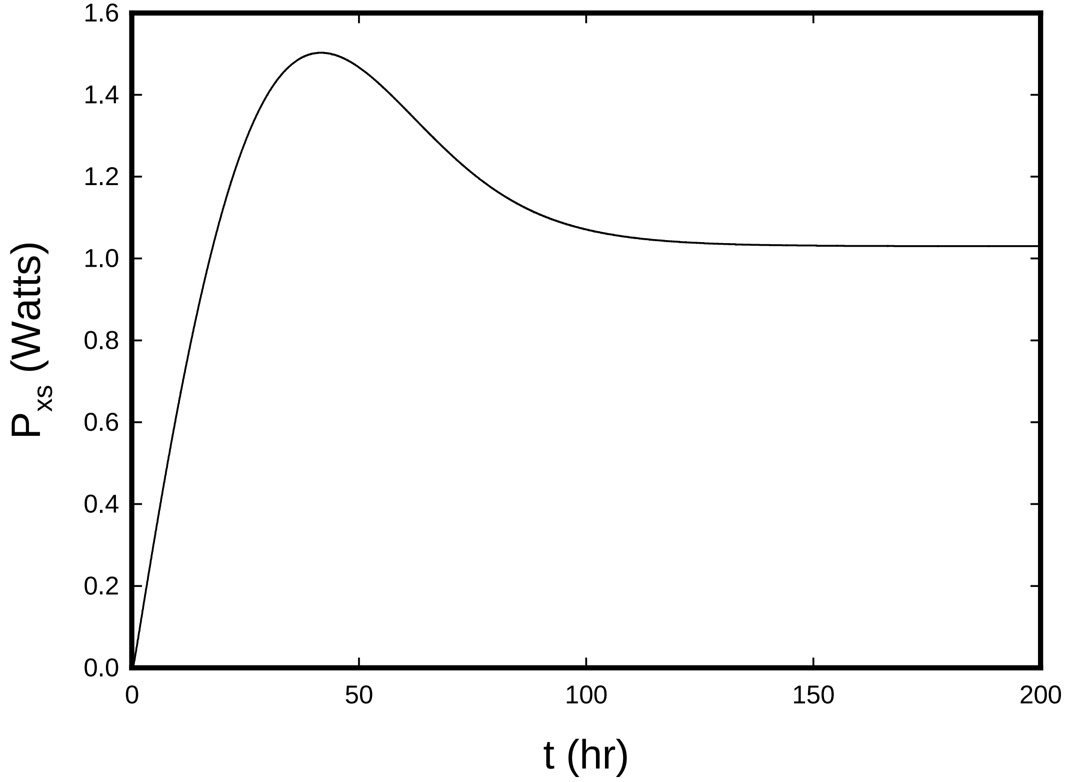
Deuterium flux:
$P_{flux} = 1\ Watt/cm^3$
$n_{thresh} = 100$

Basic reaction rate:
$\Gamma_0 = 1/(1.5\ hr)$

Evolution of dideuterium, ^4He



Excess power

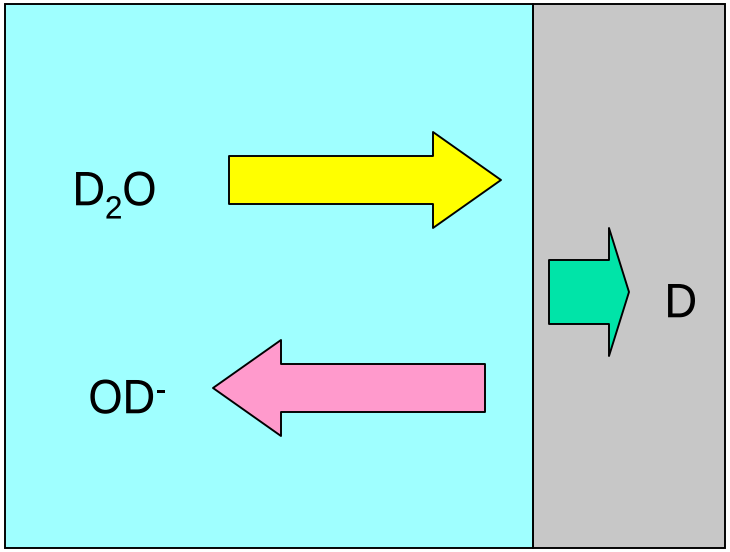


Thinking about simulations

There are several other parts to the problem:

- Loading
- Codeposition
- Dideuterium
- Deuterium flux

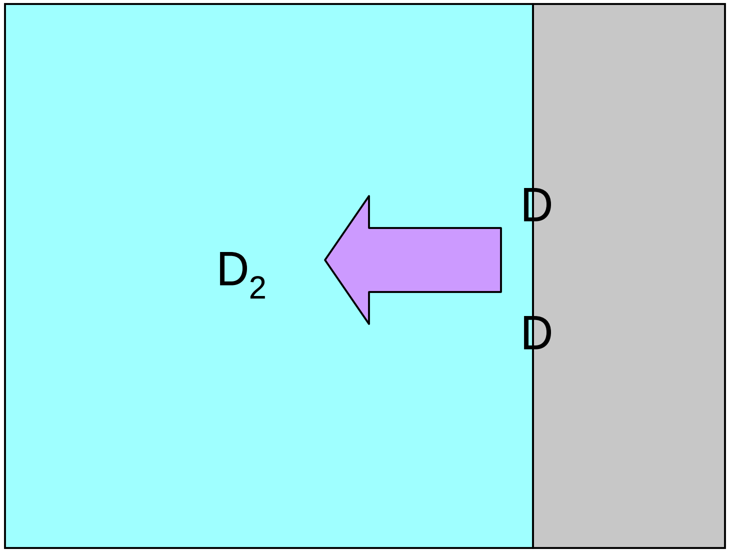
Loading deuterium into Pd



M. Volmer

Electrochemical current density J loads 1 D per charge.

Deuterium loss from PdD



J Tafel

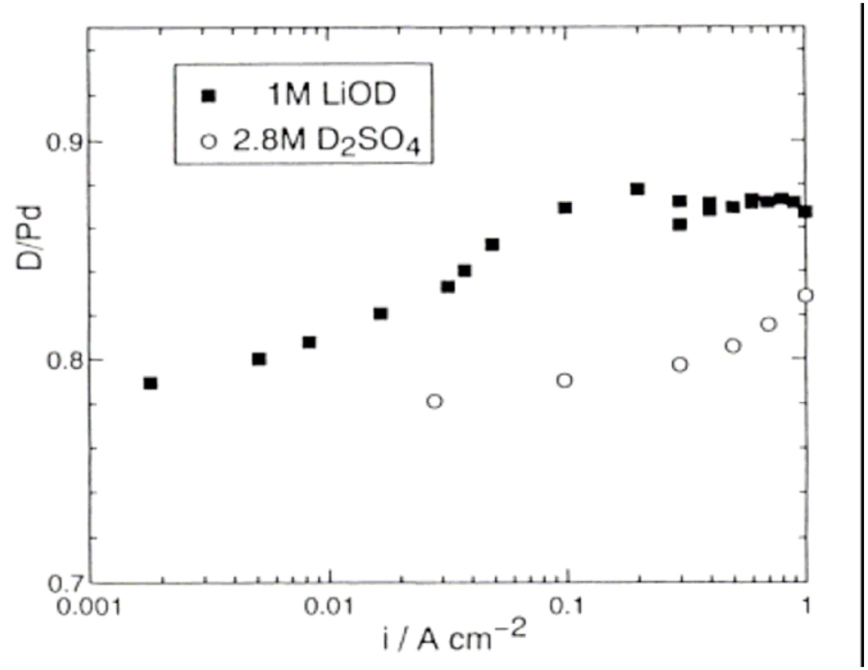
Deuterium on the surface combines to make D_2 gas. Rate depends on deuterium potential and the surface blocking.

Simple loading model

Electrochemical current density J determines surface loading x = D/Pd given surface coverage

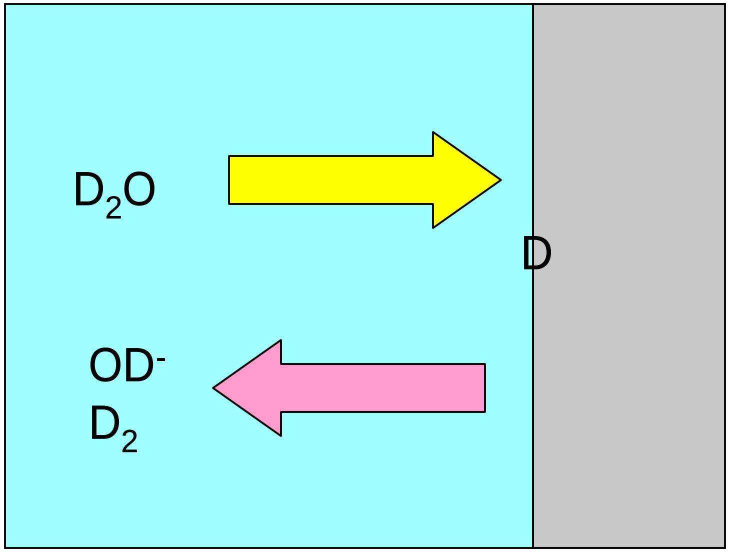
$$x(R) = x[J]$$

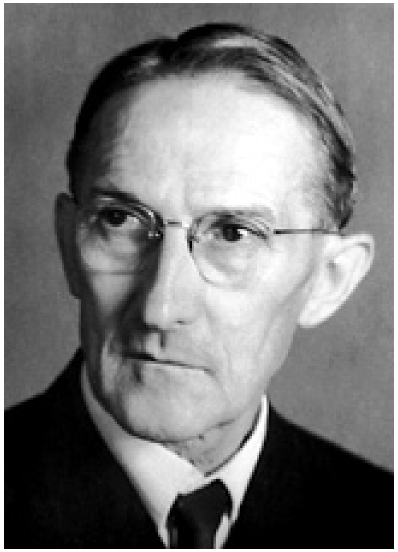
Surface loading determined by balance between deuterium input from J, and D_2 gas release



Kunimatsu et al Proc. ICCF3 (1992)

An additional pathway

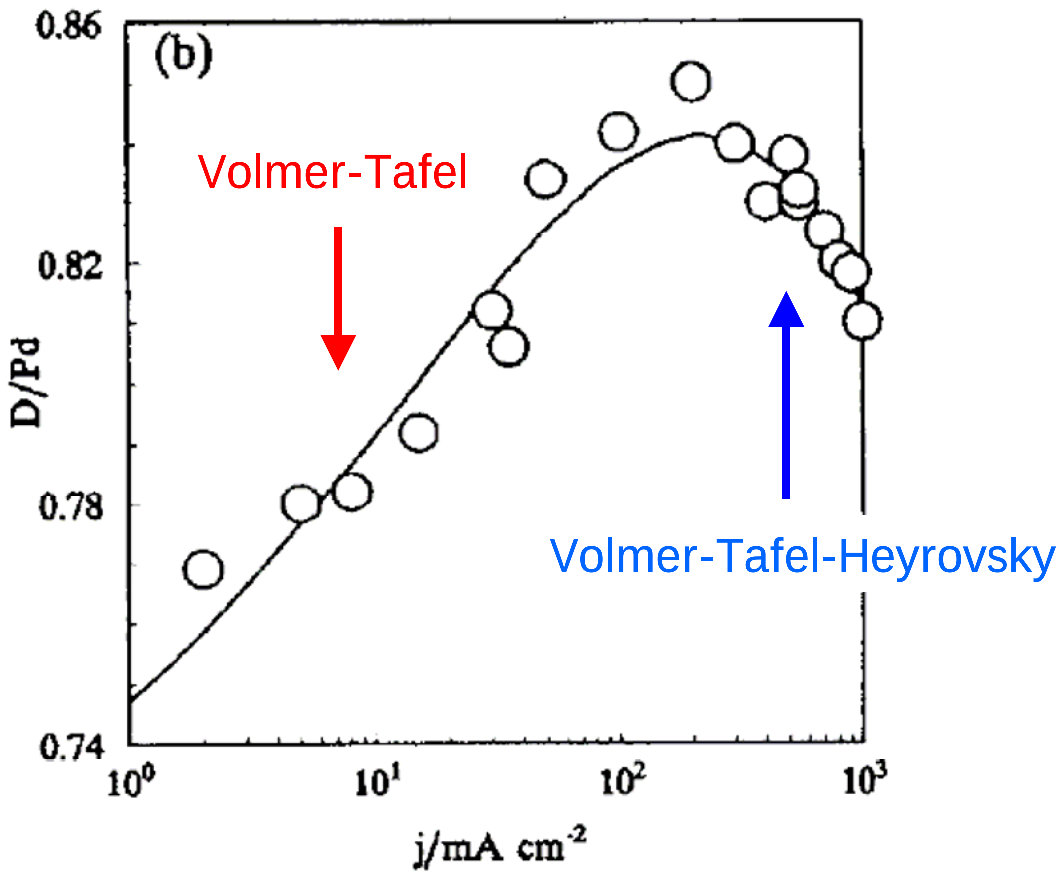




J Heyrovsky

If the chemical potential of deuterium is high, then the electrochemical current density J contains a part that deloads deuterium

Reduction of loading at high J



Data of Akita et al, ICCF4 (1994)

Model of Zhang et al, J Electronal. Chem. (1997).

Electrochemical models

- S. Szpak, C. J. Gabriel, J. J. Smith, R. J. Nowak, *J. Electroanalyt. Chem.* **309** 273 (1991)

- T. Green and D. Britz, *J. Electroanalyt. Chem.* **412** 59 (1996)

- W-S Zhang, X-W Zhang, H-Q Li, *J. Electroanalyt. Chem.* **434** 31 (1997)

- W-X Chen, *Int. J. Hydrogen Energy*, **26** 603 (2001)

...and many others

Deuterium diffusion model

Diffusion model in α-β region with flat chemical potential:

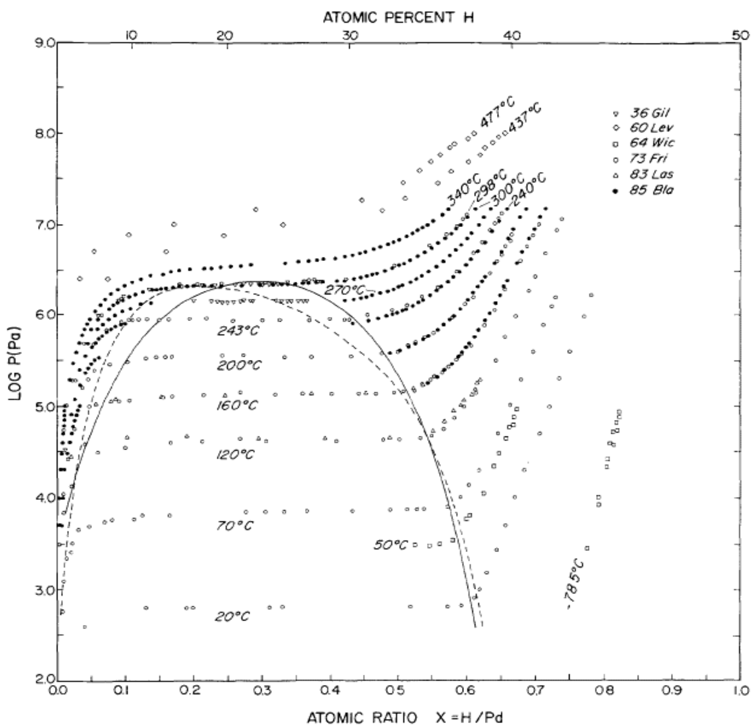
$$\frac{\partial}{\partial t} n_D = \nabla \cdot \left(D \nabla n_D \right)$$

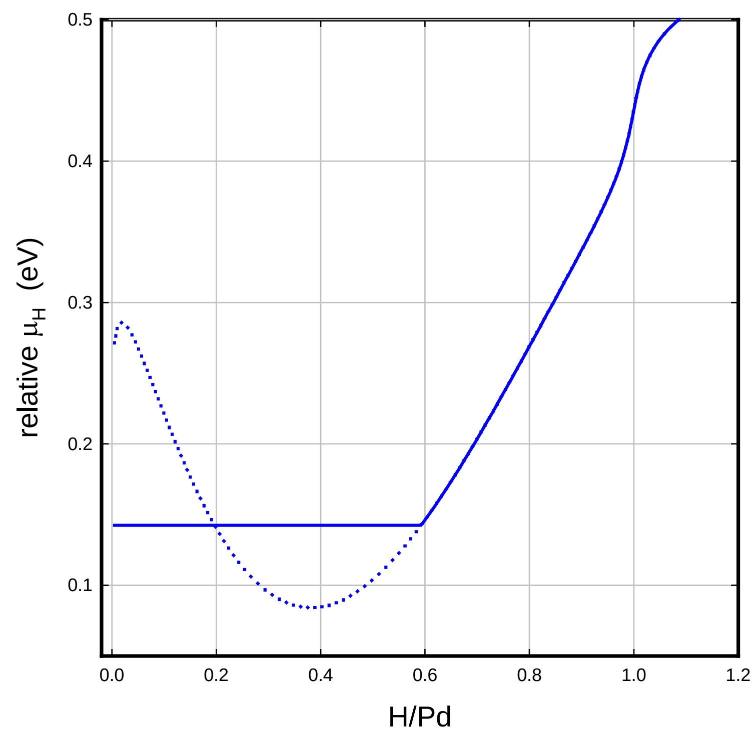
Onsager-type diffusion model for higher loading:

$$\frac{\partial n_D}{\partial t} = \nabla \cdot \left(B n_D \nabla \mu_D \right)$$

Data available for low concentration, but little available for high loading

Chemical potential model

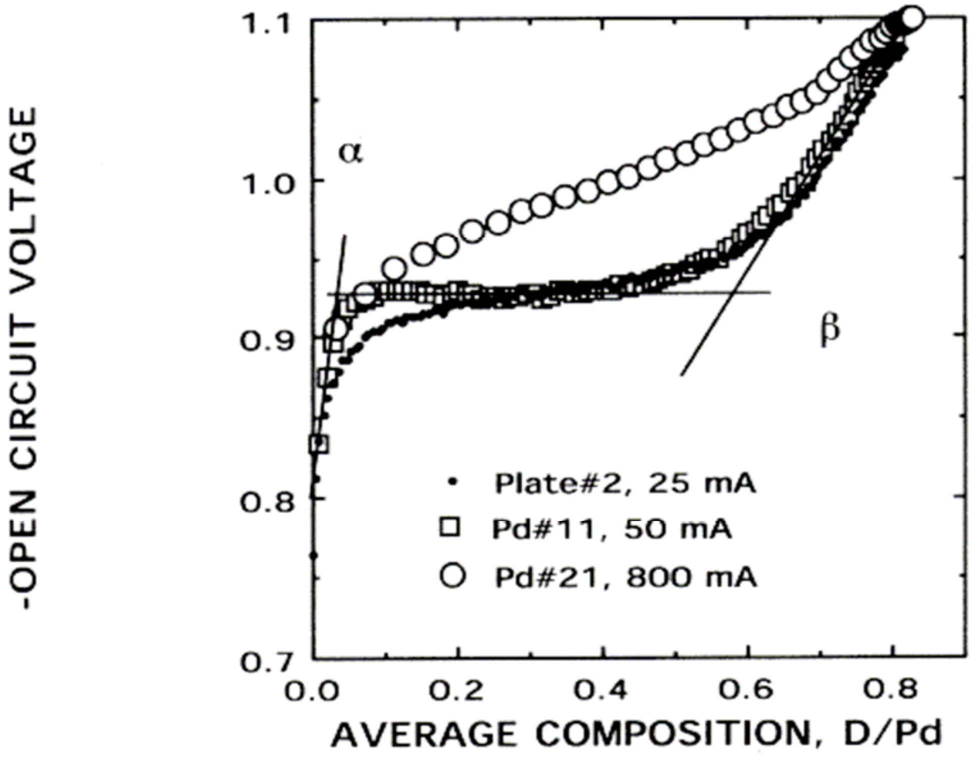




$$Q = \sum_{M_O}\sum_{M_T} \frac{N_O!}{M_O!\left(N_O - M_O\right)!}\frac{N_T!}{M_T!\left(N_T - M_T\right)!} e^{-\left(M_O E_O + M_T E_T\right)}$$

$$M = M_O + M_T$$

Relation to V_{oc}



E. Storms, Proc. ICCF7 p. 356 (1998)

Connection with electrochemical models

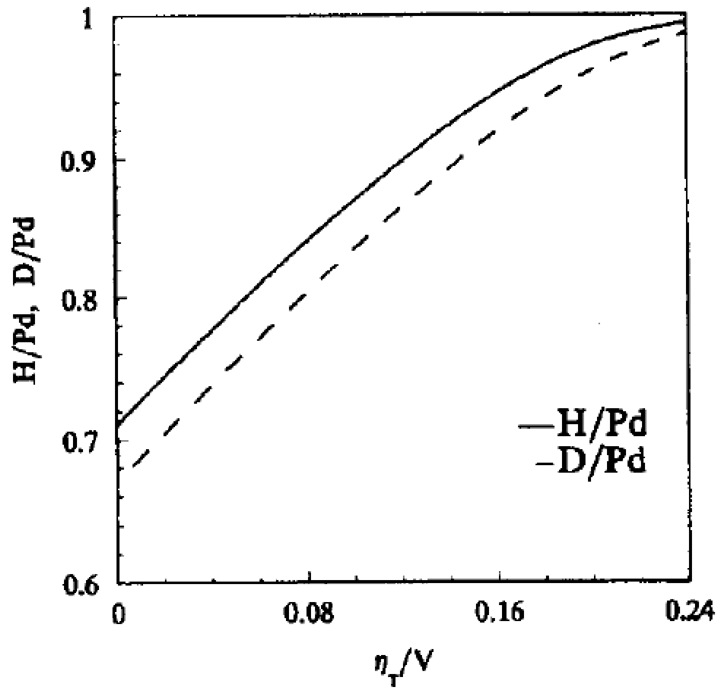
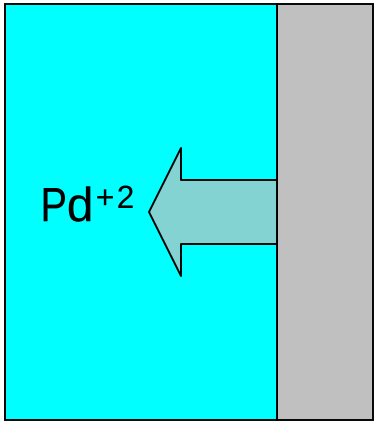


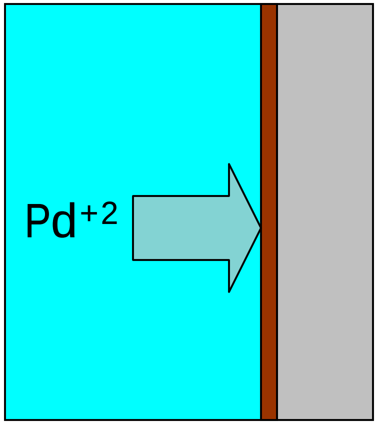
Fig. 1. Dependence of the loading ratio, $x = H/Pd$ (D/Pd), on η_T, the overpotential of the Tafel step. $f_{H_2,0} = f_{D_2,0} = 1$ atm, $T = 298$ K.

W-S Zhang et al (1997)

Codeposition



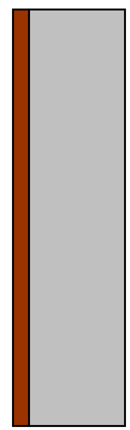
Anodic current



Cathodic current

Conjecture that a small amount of Pd is stripped off during anodic current cycles, and then codeposited during subsequent cathodic loading [most of the Pd in solution is $Pd(OH)_4^{-2}$, Mountain and Wood (1988)]

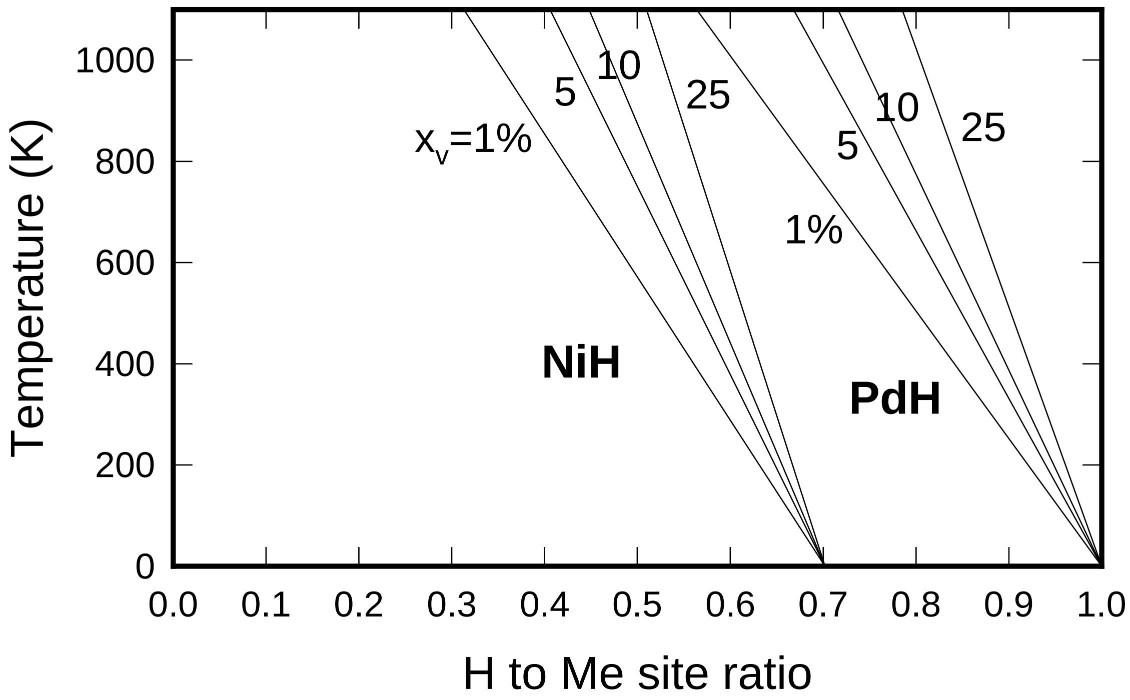
Argument for codeposition



The elemental analysis of the surface of Pd cathodes used in Fleischmann-Pons experiments show Pt, Cu and other impurities at depths > 100 nm [Hagans, Dominguez, and Imam ICCF6 p. 249 (1996)]

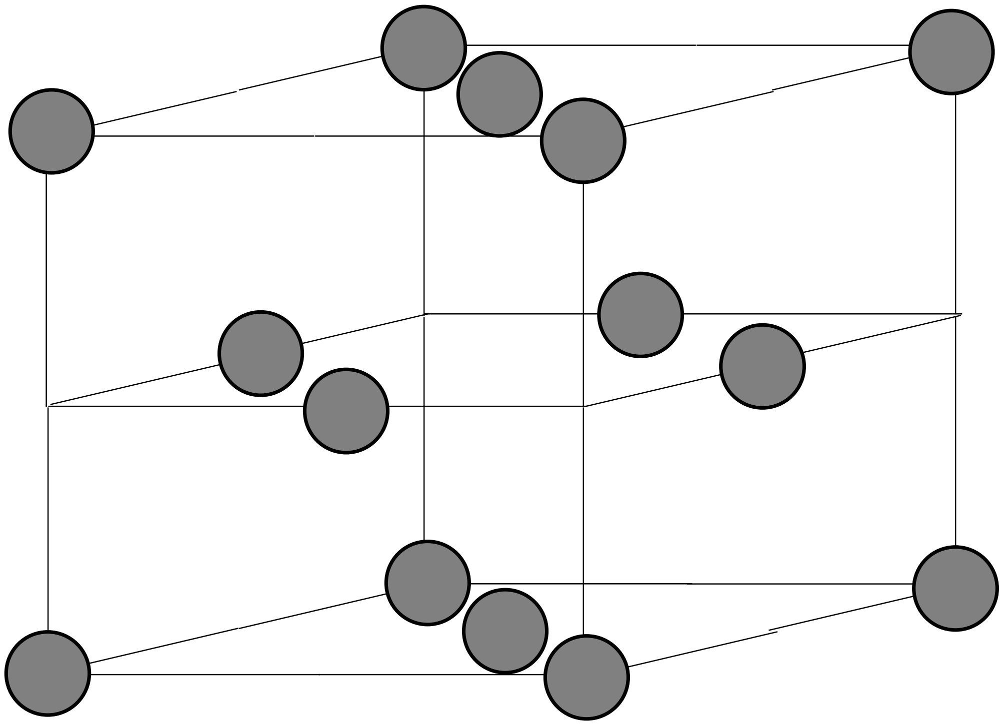
Szpak experiment gives similar results with codeposition on Cu

Vacancies in host lattice

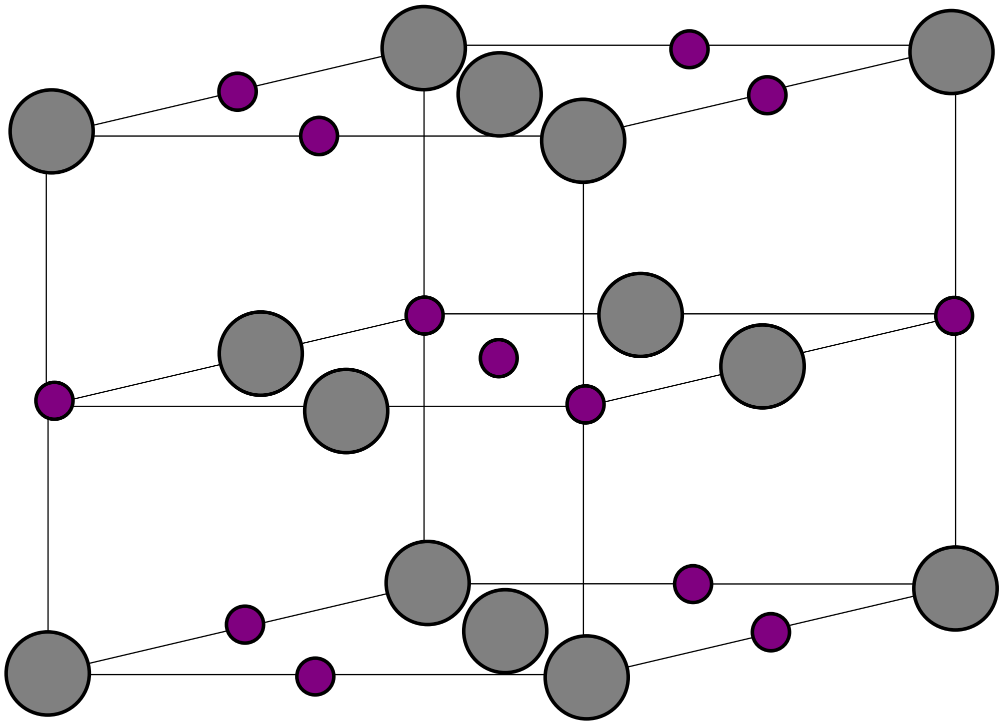


Vacancies in host metal lattice are thermodynamically favored at high loading

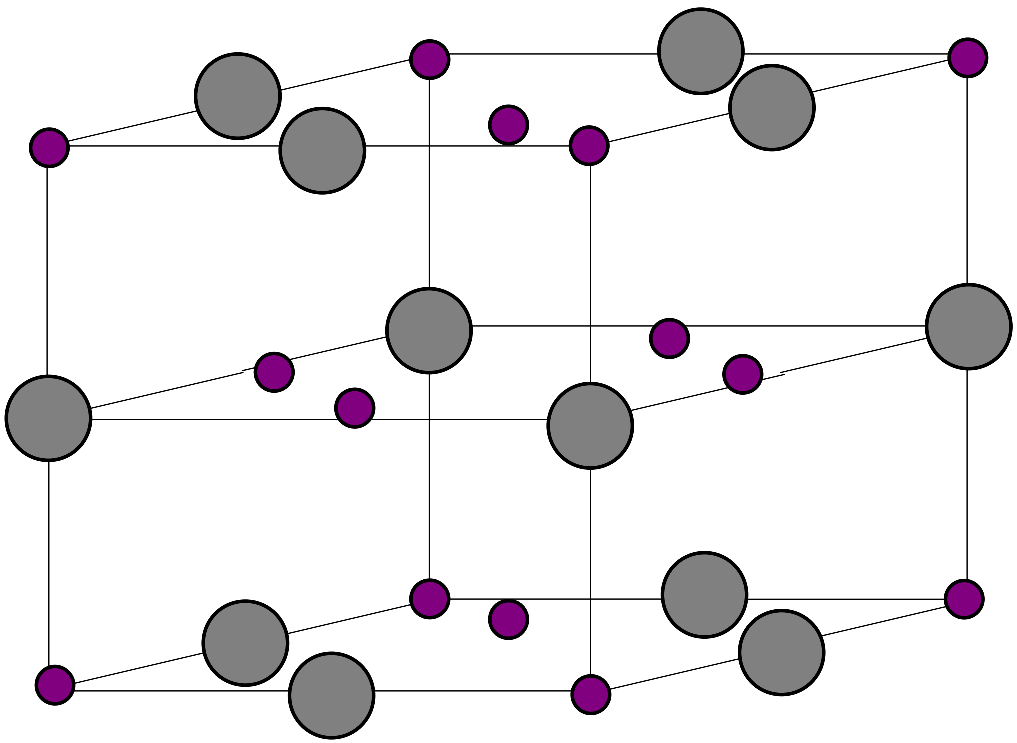
Pd lattice structure (fcc)



PdD lattice structure (fcc)



PdD Host lattice vacancy



Deuterium atoms relax toward host vacancy

D_2 near vacancy

Propose that molecular D_2 can occur near vacancy

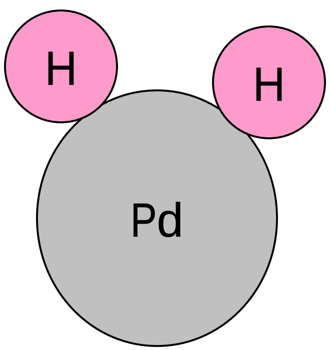
- Little in the way of discussion in literature
- Possible to test with NMR experiments
- Precedent in dihydrogen molecules
- First QM computation of Me-H_2 done for Pd-H_2

Pd-H_2: d_{PdH} = 1.67-2.05 Angstroms
d_{HH} < 0.81 Angstroms

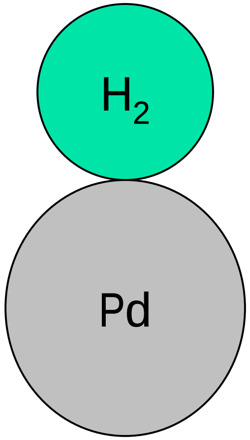
Experimental verification of Pd-H_2 in low temperature experiments (1986)

G J Kubas, Metal dihydrogen and σ-bond complexes, (2001)

Dihydrogen complex



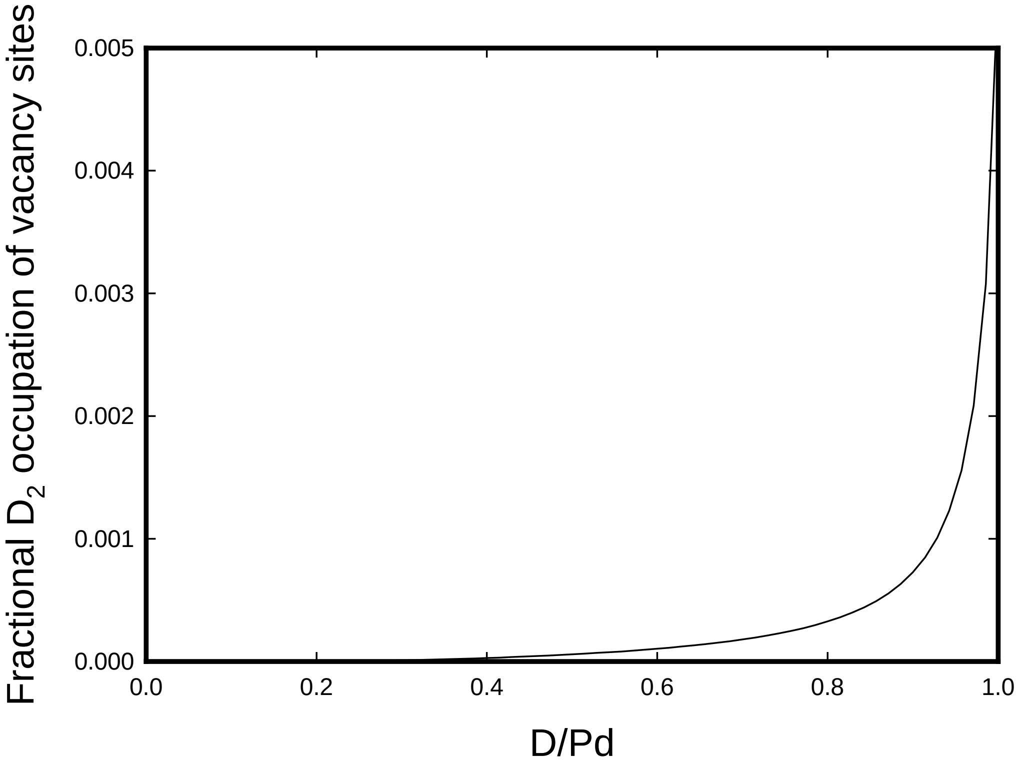
PdH_2



$Pd\text{-}H_2$

Palladium sigma-bonded dihydrogen

Molecular D_2 fraction



Need high loading to make vacancies during codeposition, then need high Loading for D_2 to form near the vacancies

Flux heating

The deuterium flux produces local heating

$$\Delta P_J = J_D \Delta \mu_D$$

In an Osager formulation the current is related to the chemical potential

$$\mathbf{J} = -B n_D \nabla \mu_D$$

The resistive power per unit volume is

$$\frac{\Delta P_J}{\Delta V} = \frac{|\mathbf{J}|^2}{n_D B}$$

Important as mechanism to stimulate optical phonon modes

Conclusions

- Biggest theory issue is splitting big quantum into many small ones
- Donor-receiver type spin-boson model augmented with loss proposed
- Coupling matrix (with U_e=115 eV) estimated to be about right size
- Detailed computation in progress
- Basic model proposed for dynamics
- Dideuterium formation in vacancies in outer codeposited layer
- Deuterium flux stimulates optical phonons