Some Computational Studies of Hydrogen in Palladium

Viva Presentation

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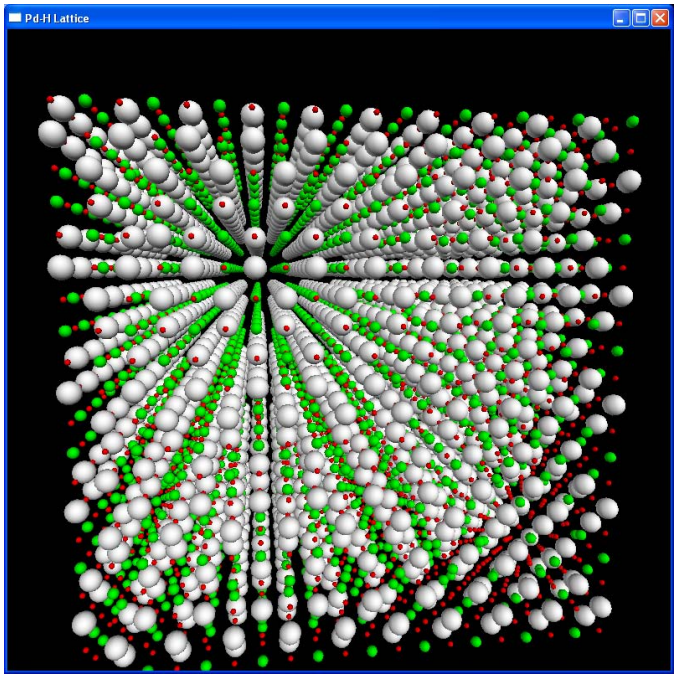
Broad Detail 1



Aim was to build a simple, robust computational model of H in Pd with a minimum number of 'tweaks' utilising a common code base for all studies.

Runs typically performed with a 40x40x40 cube.

Over 2000 runs on various models were performed with 'anneal' times typically between 1 and 30 hrs per run.

Secondary programs written to aid visualisation of the resulting lattice, analysis of results and generate virtual diffractograms.

Broad Detail 2

Runtime variants included

- Kawasaki vs. Glauber dynamics
- Canonical vs. grand-canonical assembly
- Site potential model inc. long-range and short-range effects
- Attempts to model surface blocking
- Zero-point energies in gas and solid phases

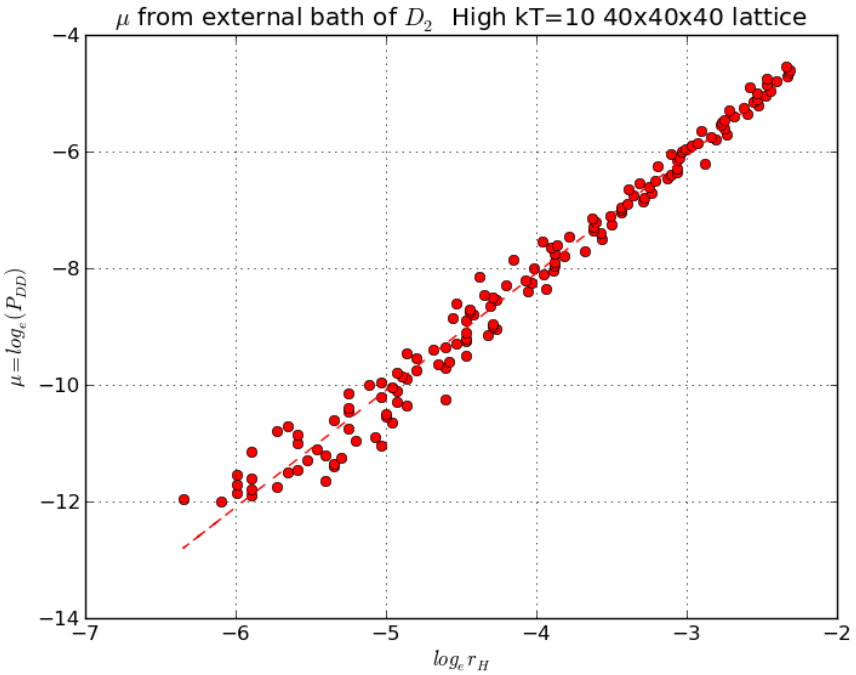
Output included:-

- Lattice concentration by isotope
- Various measures of local ordering
- Chemical potential variation by Ghost Particle method
- Tracer and bulk diffusion coefficients
- Enthalphy
- 'Snapshots' of the lattice

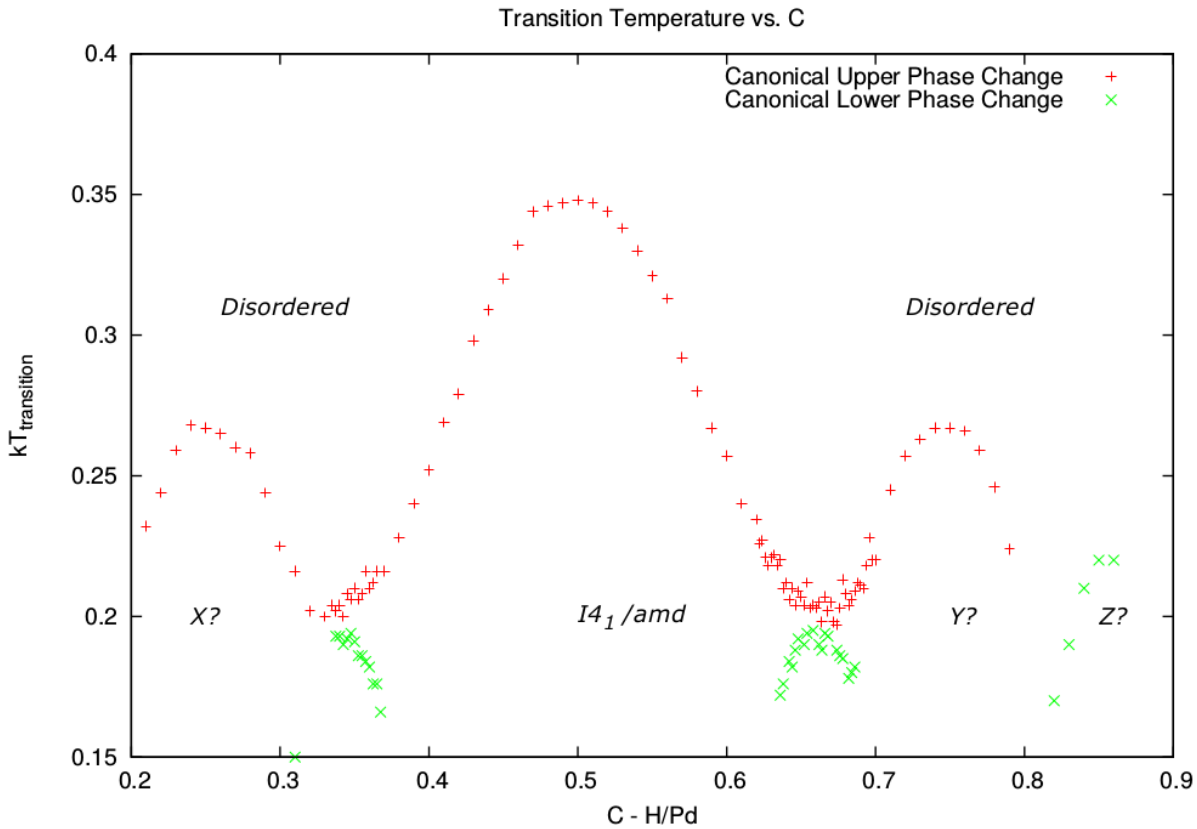
Sieverts' Law

Model correctly reproduces Sieverts' Law when ordering is suppressed due to low concentration or high temperatures.

Runs gave $C \propto P^{0.498\mu}$ *to 1:1000*.

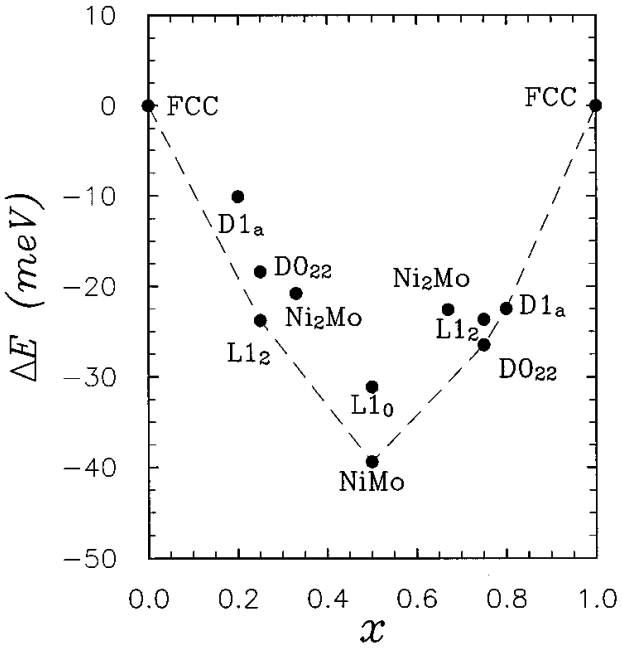


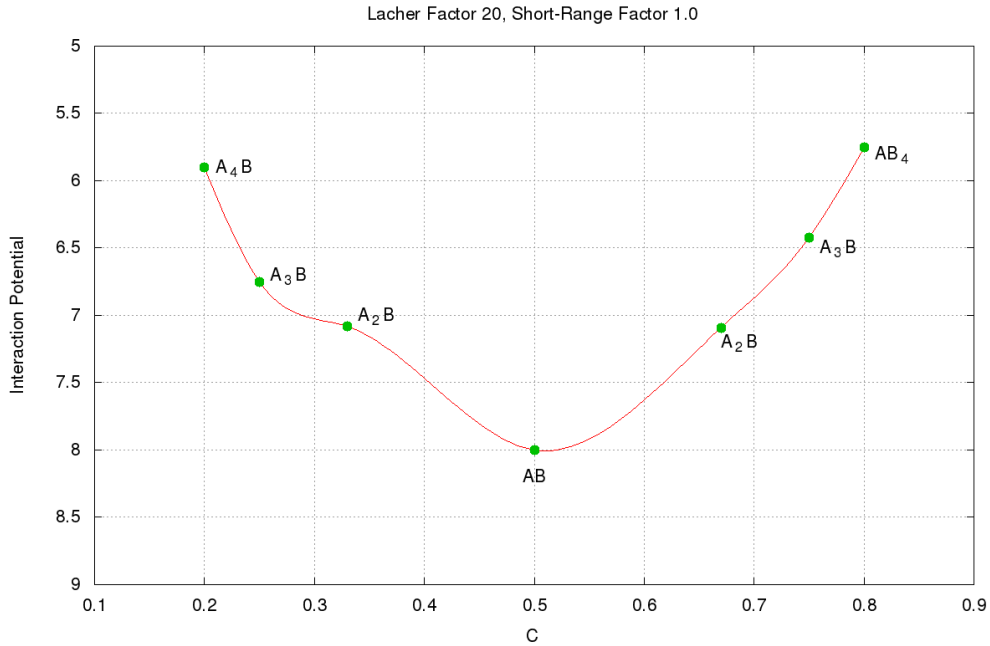
Extended Phase Diagram



Previous phase diagrams were extended to higher and lower concentrations.

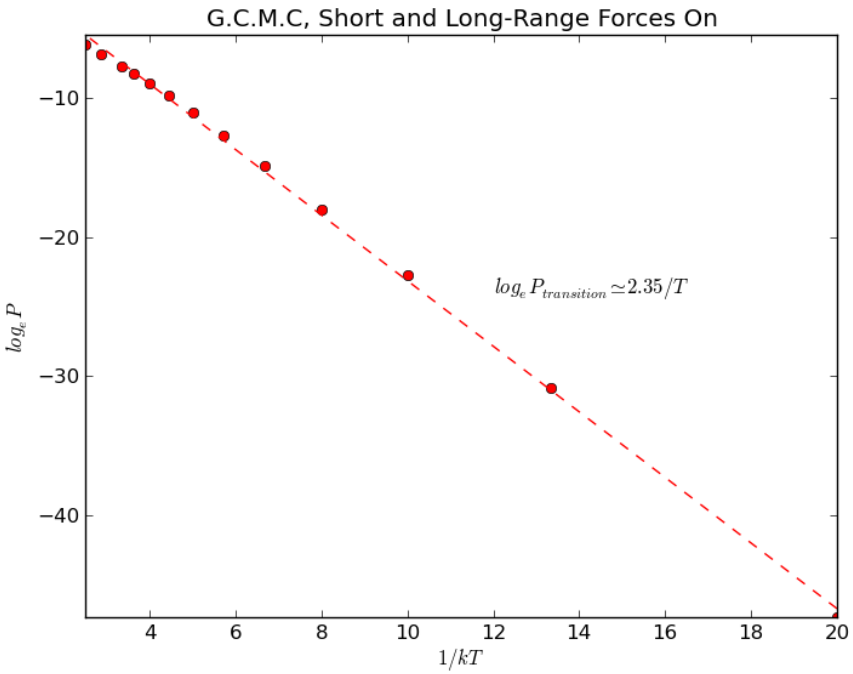
Formation Energies





Formation energies for various Pd-H structures - C.M.C. simulations employing both long and short-range forces.

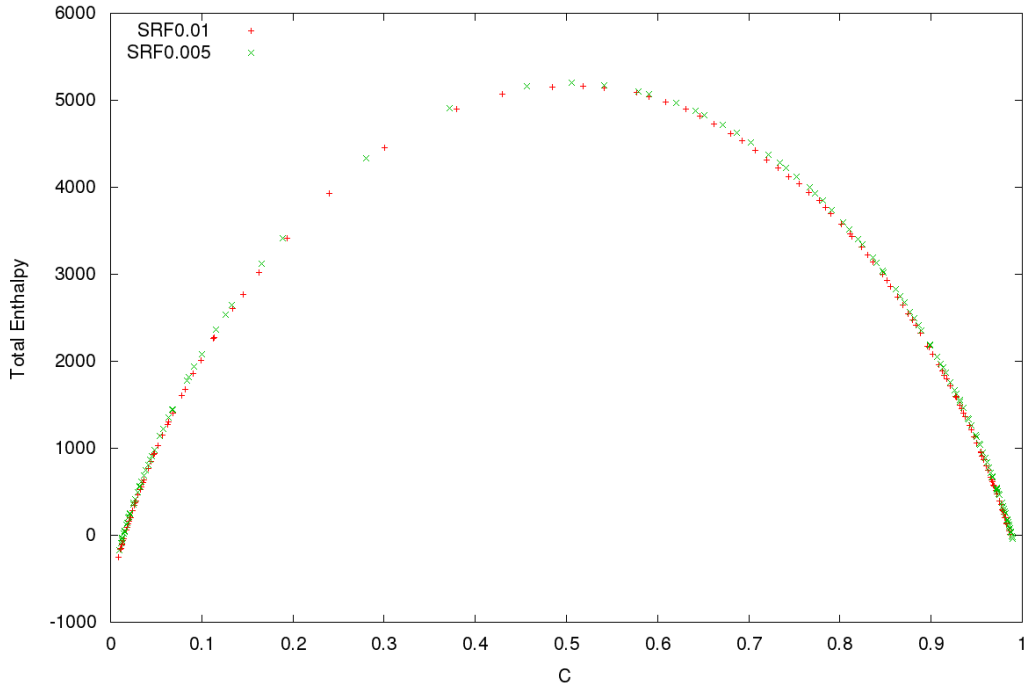
Arrhenius Relationship



Model correctly exhibits an Arrhenius relationship between transition temperature and chemical potential of gas phase ($log_e P$)

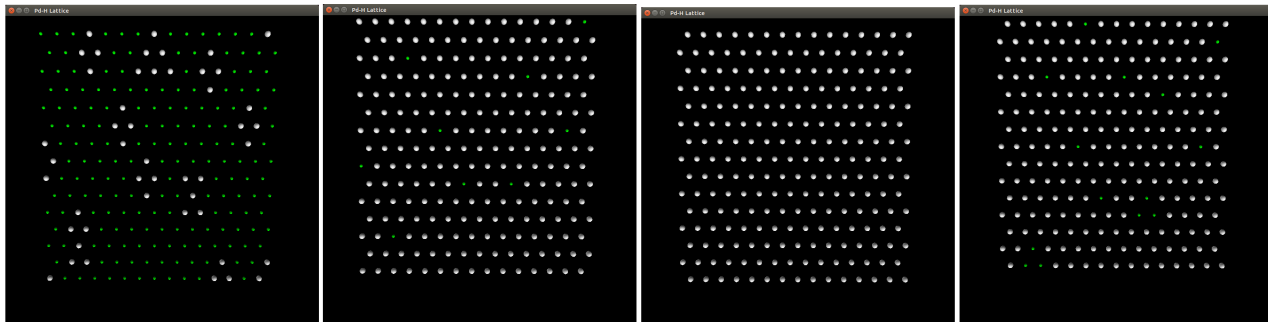
Enthalpy

Enthalpy minimised at C=0.5 H/Pd



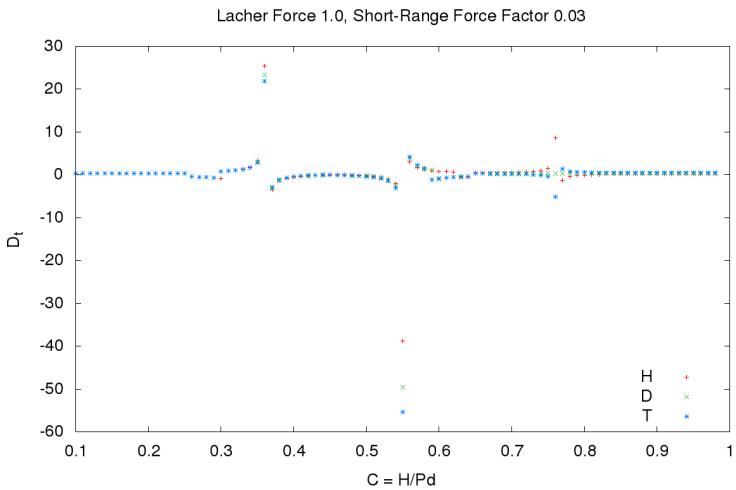
High Concentration Phases — C ∼ 75-80%

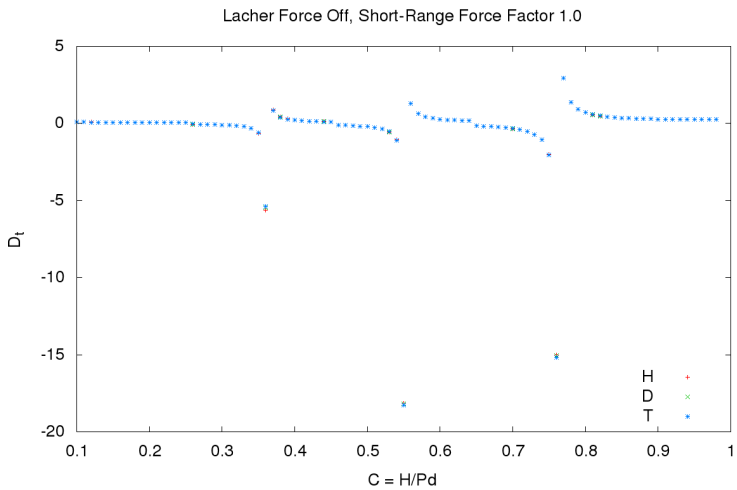
In range C ∼ 75-80% complex reordering and meta-stable structures appeared



C=0.76, progressive filling of fourth plane (left) in (420) partly due to vacancies (green) appearing in adjacent planes

Tracer Diffusion During Ordering





Monitoring the tracer diffusion rate often gave clearer and more reproducable indication of reordering processes than mean site potential particularly when the site potential included large long-range forces.

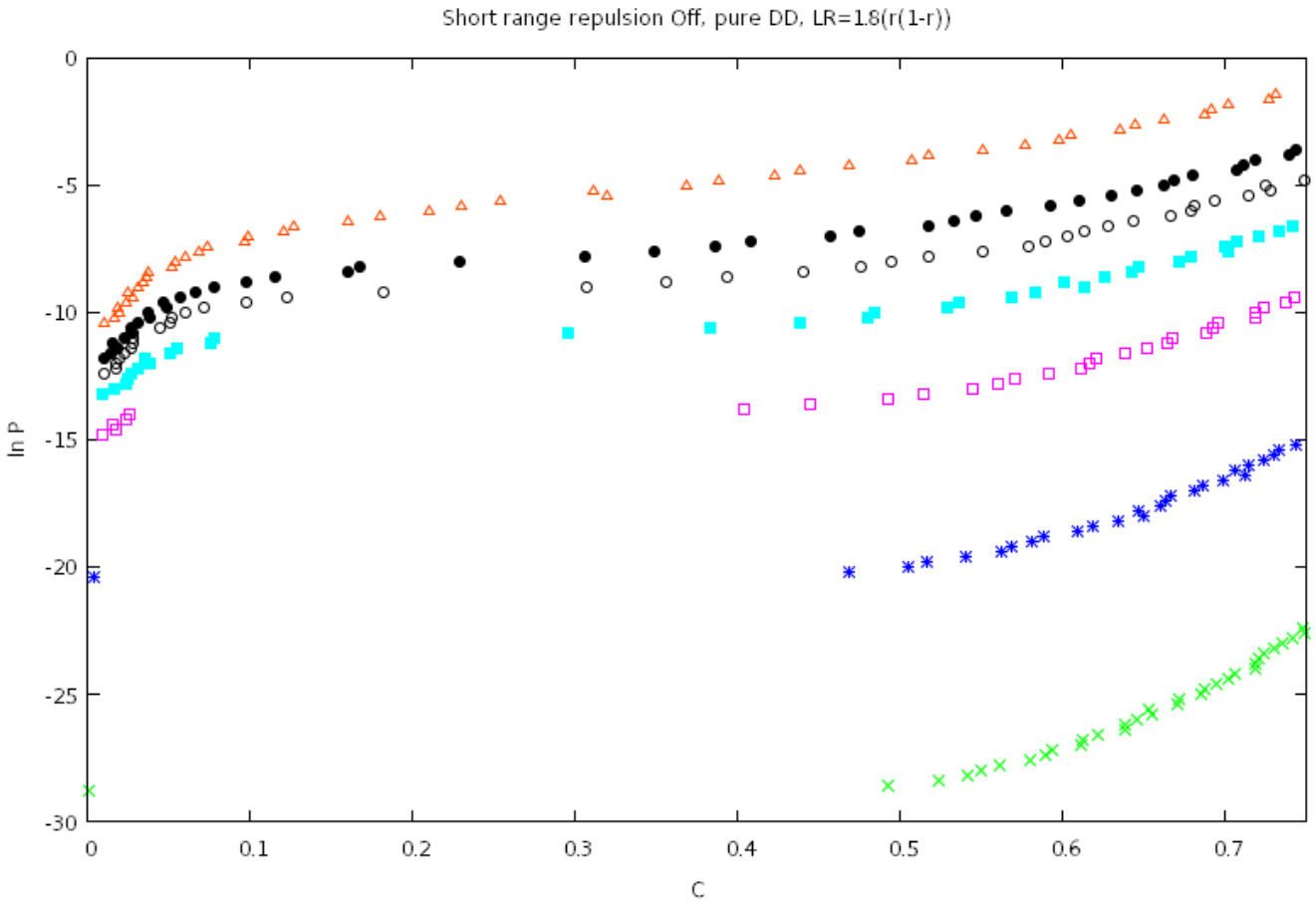
(Left– large long-range attraction present — right absent)

Basic Issues

Bulk pressure composition characteristics are due to attractive forces between lattice and hydrogen.
Ordering appears predominantly due to short range Coulomb repulsion between hydrogen.
Building a simplistic model such as this required investigating:-

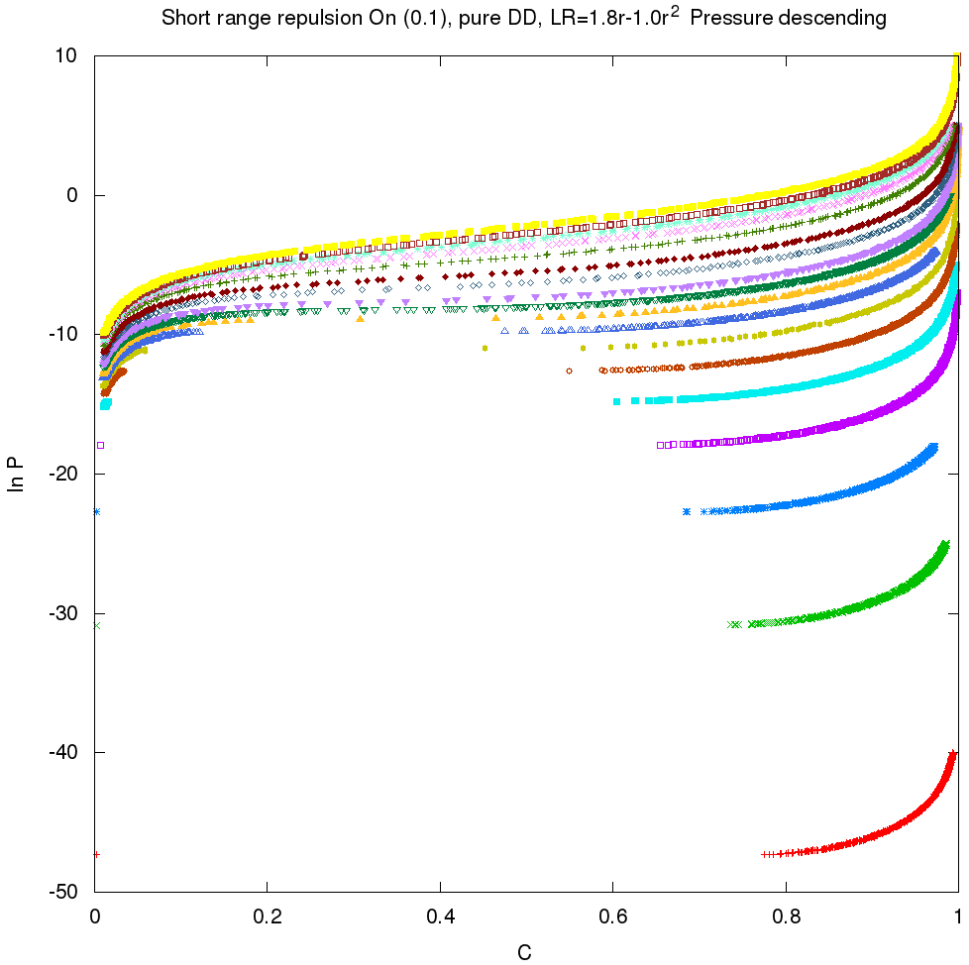
1. A suitable mathematical model for long-range attraction.
2. A suitable ratio between this and the established Bond-Ross pairwise repulsive model.
3. Testing how well these reproduce both pressure composition and local ordering effects.

Long-Range Attraction



Long-range attractive force alone will reproduce the pressure composition isotherms well *(ascending temperature bottom to top)*

Long-Range Attraction



A number of models were investigated with

$$\text{L:R} = 1.8c - 1.0c^2$$

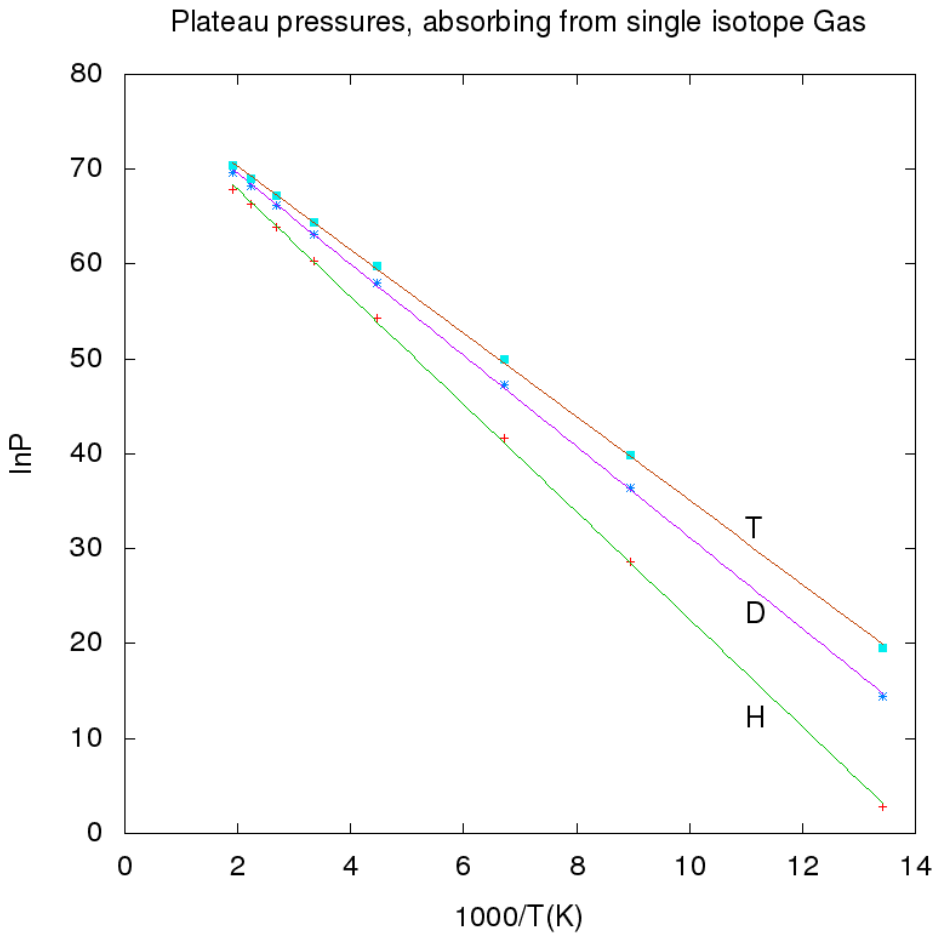
giving the best fit to experimental pressure composition isotherms *(ascending temperature bottom to top)*

Ratio S:R – L:R

- Too high a value of short-range repulsion causes *steps* to occur in the pressure-composition isotherms
- At concentrations below ~ 0.75 structures generated appeared unaffected by the long-range attraction however anneal times increased.
- Interestingly at higher concentrations the long-range attraction caused more complex behaviour esp. in the region of $C \simeq 0.8$.

Extensive finessing produced a ratio of long-range to short-range site potentials which reproduced both the pressure composition behaviour and local ordering well in the range $C0.01 \rightarrow 0.8$

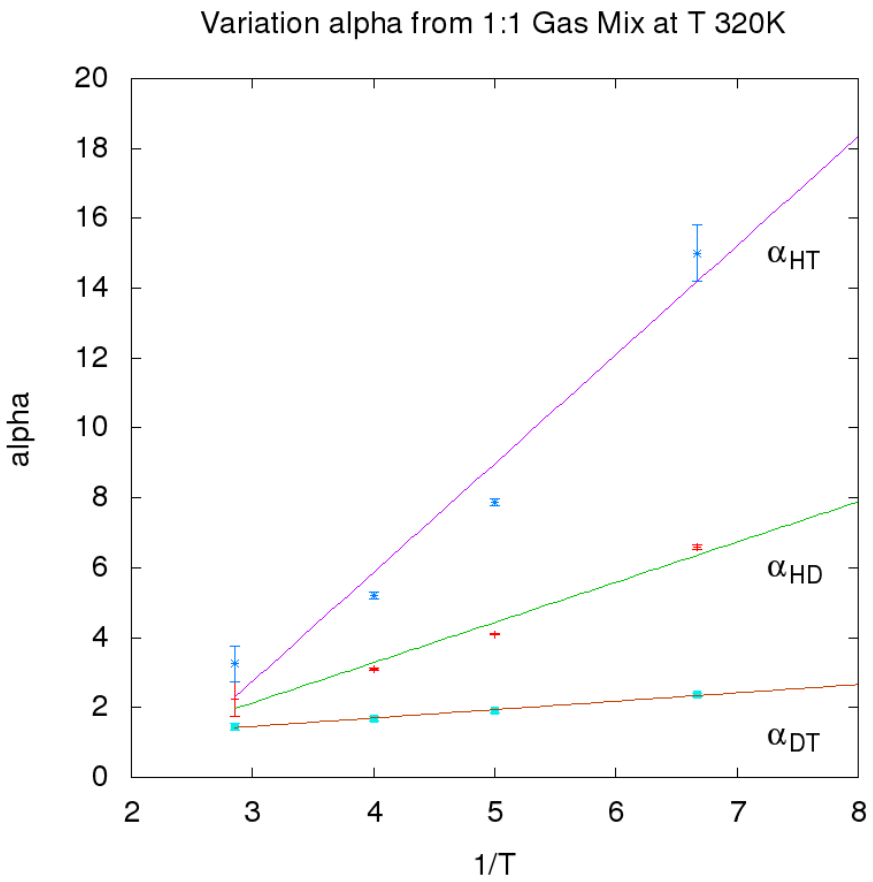
Isotopic variation of Plateau Pressure



Model appears to reproduce experimental results of the variation in plateau pressure in the $\alpha - \beta$ region tolerably well.

Separation Factor

G.C.M.C. simulation, external pressure lowered such that the lattice concentration dropped from a 100% fill of the two isotopes in a 1:1 ratio. Gas bath fixed 1:1 composition. α varied approximately linearly over a temperature range of $\sim$ 100K to 400K though diverged outside this range. Plots similar to experiments reported by Andreev and others. Investigations curtailed due to lack of time.



Other Investigations

A number of other investigations were performed particularly:-

- Exploring ordering in the two-phase plateau. These were of limited success due to the very unstable nature of the region.
- Attempts were made to model surface effects.

Summary

It has been shown that a relatively simple and computationally efficient model can reproduce much *both* the internal ordering and absorption/desorption characteuristics of H in bulk Pd.

There are indications of unusual ordering processes at higher concentrations when long-range attractive forces are present which are absent from the simple pairwise model.

It appears that simple energy parameters may allow valid modeling of isotopic effects.

It seems that more sophisticated interactions *may* be required to reproduce the Ni_4Mo structure at high concentrations.