Energy concentration induced by phase transitions in hydrogenated metals

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Abstract: In this paper we discuss a mechanism capable of producing, at least in principle, enough energy concentration to trigger cold fusion reactions like those recently observed by several people in metal deuterium systems. It is based on a release of elastic energy in the lattice of the host metal as a consequence of a phase separation of the absorbed gas in non equilibrium conditions. Quantitative estimates are explicitly given.

§1 Introduction

Several authors have recently reported [1,2,3] neutron emission in deuterated metals like Pd or Ti in experimental conditions which can be characterized as non equilibrium situations. The experiments belong, roughly speaking, to two categories: a) neutrons are observed during low voltage electrolytic infusion of deuterons into the metal; b) neutrons are observed after the infusion of deuterons by electrolytic or other methods. In both situations the system is apparently far from thermodynamical equilibrium.

Experiments of type b), if confirmed, are conceptually simpler and very intriguing because the energy necessary to overcome the Coulomb barrier and trigger the nuclear reaction has to come from the system itself. According to the analysis of [4] the barrier energy is of the order of 100 - 150 eV and it is difficult to think of mechanisms (e.g. partial screening) that could lower it substantially.

The mechanism that we propose in this paper is based on the two following well established facts:

I: In systems like PdH (D), TiH (D) the absorbed gas can exist in at least two phases: a low density phase and a high density phase. The phase diagram is very similar to a gas liquid transition.

II: The metal lattice step size adjusts itself to the density of the absorbed gas. This implies that to the phase transition is also associated a change in the elastic energy of the metal.
One can imagine that if the low density phase nucleates in a high density region by forming expanding bubbles a situation will be reached in which the lattice will suddenly contract creating a dislocation at the surface of the bubble. This will produce an implosion with considerable energy concentration towards the center of the bubble.

In the rest of this paper we will try to make this picture quantitative. As we shall see the model has essentially no free parameters and it is not in disagreement with the experimental situation. In addition the model gives rather precise indications on the conditions in which the phenomenon can take place efficiently.

We have examined also the complementary mechanism associated with bubble explosions. They can also produce energy concentration but on the whole they seem to be less effective.

§2 The model for energy concentration

We consider a metal $M$ which can absorb a gas $G$: our examples will take the metal to be $Pd$ or $Ti$ and the gas to be $H$ or $D$ as these are well known cases in which the absorption is important and easy to realize experimentally.

The metal $M$ forms a f.c.c. lattice with step size $a$ depending on the concentration $c$ of $G$. The graph of $a(c)$ is assumed linear and temperature independent in the whole range of temperatures and concentrations considered: in fig. 1 we report as an example the graph for the $Pd$ at room temperature [5]:

![Graph showing relative volume change $\Delta V/V$ of palladium vs hydrogen concentration.](image-url)
The state diagram of \( G \) in \( M \) has the form reported in fig.2 for the system \( PdH \) (the \( TiH \) system leads to a similar diagram with a somewhat higher \( T_c \)), [5]:

![State Diagram](image)

We describe the interaction of the \( G \) atoms inside \( M \) by an Ising model with nearest neighbour interaction, for simplicity (it has been argued in the literature, [5], that this is a very good model at least if the interaction is allowed to extend over several lattice units: the analysis below would remain qualitatively unchanged if we allowed a long range interaction; this assumption should be regarded merely a way to permit us to perform estimates of the orders of magnitude). The lack of the symmetry \( c \rightarrow 1 - c \) in the phase coexistence curve fig. 2 gives an idea of how much the many body forces play a role. It is known that important metastability phenomena take place inside the coexistence region.

To fix the ideas we take as initial state of our system a point of high concentration \( c_0 \). At time \( t = 0 \) the temperature is dropped from \( T = T_0 > T_c \) to \( T = T < T_c \) at concentration \( c_0 \) intermediate between the equilibrium concentrations \( c_- \) and \( c_+ \) of the two phases, and we suppose, for simplicity, that no \( G \) gets out of \( M \) during the whole experiment.

The system finds itself in a non equilibrium state and the two phases with densities \( c_- \), \( c_+ \) start growing and eventually they will occupy macroscopic volumes proportional to \( c_+ - c_0 \) and \( c_0 - c_- \) (such volumes will be the union of smaller domains in each of which one has a pure phase). The two phases can be described by the droplet model (as appropriate to systems modeled by the Ising model)[6,7].

Let \( O \) be a point around which a low density phase is growing: then \( O \) will be the center of a domain \( D \) occupied by clusters of different size, i.e. consisting of a different number of gas atoms. A simple calculation shows that for \( T < T_c/2 \) the clusters are with a high probability just isolated atoms, see §3.

The growth of the low density phase around \( O \) is a random process taking place because of the diffusion of the \( G \) atoms: the diffusion constant is of the order of magnitude of \( 1 \mu/\text{sec}^{1/2} \) and therefore the diffusion processes are very slow compared to the propagation of the elastic waves. The radius \( R(t) \) of the ball of low density phase will grow in the average at some rate and during the process we can suppose that the metal lattice is in equilibrium because in it the energy is carried at the speed of sound (of the order
of $4 \times 10^3 \text{m/sec})$. The actual rate of growth of $R(t)$ can be made as slow as we wish by adjusting $c_0$ close enough to the value $c_-$ corresponding to the temperature $T$: in fact we can make use of the metastability phenomena present close to $c_-$.

If the domain $\mathcal{D}(t)$ had a free boundary the lattice $M$ inside $\mathcal{D}(t)$ would adjust to a size $a_-$ corresponding to the density $c_-$ according to the equation described by fig. 1. But its boundary is constrained to keep the same size $a(c_0) > a_-$. Therefore the metal in the domain $\mathcal{D}(t)$ keeps the step size $a(c_0)$ accumulating elastic energy in the bulk of $\mathcal{D}(t)$ and elastic strains develop, strongest at the boundary.

The displacement off equilibrium (with free boundary) of the metal atoms at distance $\vec{r}$ from $O$ will be $\vec{r}E$ if $E$ is the elastic energy corresponding to the equation described by fig. 1: $E = \eta(c_0 - c_-)$ if $M = Pd$. When $\vec{r}E(t) = (\text{maximum displacement})$ grows beyond the lattice step the bonds can break and the lattice can proceed to acquire the new lattice step $a_-.$

At this point the elastic energy accumulated is the energy corresponding to the fact that the metal atoms find themselves displaced by $\vec{r}$ away from $O$. To estimate the elastic energy $E_R$ we suppose the domain spherical, neglect the variation in the elastic parameters of $M$ (and its anisotropy) and use the formula:

$$E_R = \frac{1}{2} \int_0^R \sum_{ij} (\partial_i E \partial_j E) d^3 \vec{r}$$

Hence $E_R = 3(1/2)(4\pi/3)k\varepsilon^2 R^3$, which can be related to the speed of sound $c = (k/\rho_M)^{1/2}$ (where $\rho_M$ is the density of the metal) by:

$$E_R = 2\pi \rho_M c^2 R^3 \varepsilon^2 = 2\pi (\rho_M a^3) c^2 \left(\frac{R}{a}\right)^3 \varepsilon^2 = 2\pi c^2 m_M \left(\frac{R}{a}\right)^3 \varepsilon^2$$

where $m_M = \rho_M a^3$ is mass of the unit cell of metal ($m_M = 4$ times the atomic mass of $M$ if the lattice is a f.c.c. lattice).

The energy is released by an implosion and we are interested in the amount of energy $E$ that can be concentrated in a region of size $a$: this is the part of energy contained in a layer of width $a$ around the surface of $\mathcal{D}$, assuming that no shock wave develops and, therefore, using a linear wave equation. Hence:

$$E = (2\pi c^2 m_M) (R/a)^3 (4\pi a R^2 / (4\pi/3) R^3) \varepsilon^2 = 6\pi c^2 m_M (R/a)^2 \varepsilon^2$$

If shock waves develop (as it seems inevitable from the order of magnitude of $E_R$ found below) the concentration of energy could be much larger (up to a maximum of the order of $E_R$ itself). We assume $R = a/c$, which should be the right order of magnitude taking
into account that a displacement of size $a$ would shift a metal atom from one minimum to the nearest one. Inserting the data for $Pd$ we find:

$$E_R = 18 \text{ KeV} \quad E = 1.3 \text{ KeV} \quad (2.4)$$

This should be compared with 150 $\text{eV}$ which is the threshold above which nuclear phenomena become relevant.

If we are interested in using the above energy to bring the $G$ atoms close, we must take into account that the domain $D$ is a low density region: therefore the probability that in a imploding domain $D$ there are near the center two $G$ atoms has the order of magnitude of the square of the concentration, $c_+^2$.

As an example we consider a grammoatom of $Pd$, 107g, and a gas of $D$ in concentration $c_0 = 0.5$ at $T = 20^\circ C$ with $c_+ = 0.6$, $c_- = 0.01$ (see diagram in fig. 2). Then the metal volume eventually occupied by the pure $c_-$ phase will contain $N_A(c_+ - c_0)/(c_+ - c_-) = N_A/6$ metal atoms distributed in $(N_A/6)/4$ cells (each cell contains 4 atoms in the f.c.c. lattice), $N_A$ is Avogadro's number.

The value of $\varepsilon$ estimated from the graph in fig. 1 is $\varepsilon = 0.025$. The linear size of the regions of the $c_-$ phase will be of the order of $1/\varepsilon$ cell sides: hence the number of regions which can implode is of the order of $N_A\varepsilon^3/24$: assuming perfect efficiency we can then say that the number of pairs brought togther by the implosions should be $c_+^2\varepsilon^3 N_A/24 = 0.4 \times 10^{14}$.

If each of the implosions produced a nuclear fusion the total energy released by the fusion (assuming a yield of $2 MeV$ per reaction) would be of the order of $0.8 \times 10^{20} \text{ eV} = 1.3 \times 10^8 \text{ erg} = 13 \text{ joule} \approx 3 \text{ cal}$ carried by the $10^{14}$ neutrons or other nuclear products.

This figure does not seem to be in disagreement with the experiment reported in [2], if one considers that perfect efficiency is unrealistic, and their concentration could be very low.

The time duration of the whole phenomenon is a function of how long the metastability time of the unstable density $c_0$ is: since in the experiments there is no direct control on the exact values of $c_0$ this may depend on the experiment itself even when the preparation of the samples has been done in apparently the same way.

Metastability, on the other hand, can be useful to slow down the processes keeping control of their speed.

One can also consider experiments in which the initial situation is in a state at low temperature inside the two phase region and the final state has the same density but high temperature outside the coexistence region. Also in this case one expects energy concentrations by implosions: the mechanism could be that large domains of high density $c_+$ phase (which may be present due to a convenient preparation of the sample) start evaporating: lower density bubbles develop in the domain and implosions can accumulate the elastic energy as in the previous case. This time the low density is $c_0 > c_-$ and we can expect a larger effect at least as far as the main loss factor $c_0^2$ in the previous case is concerned.
The latter remark also suggests that one should try to perform the experiments at temperatures where $\varepsilon_-$ is larger than the one considered in the above example: however if $c_0$ is too close to $\varepsilon_-$ the value of $\varepsilon$ becomes too small, hence $R = a/\varepsilon$ may become so large that we cannot any longer suppose that the crystal is perfect over this range of length and the formulae for $E_R$ and hence $E$ change.

More generally, by suitably changing the position on the phase diagram one can produce implosions by performing some cycle going from inside the two phase region to the outside of it or even somewhere else inside it. The above example suggests a detailed analysis of the two phase diagram to maximize the energy output.

Various causes can diminish the efficiency of the above implosions as concentration mechanisms: for instance a non spherical shape greatly reduces the amount of energy that can be concentrated in the center of the imploding regions. Furthermore even if the energy is high enough there is a non negligible probability that it will be dissipated without a fusion taking place.

It is also clear that a sample of metal cannot be used more than once: large enough microcrystals must be recreated in every experiment.

In our opinion the lack of experimental control of the thermodynamics of the system in its various aspects may explain the still uncertain status of the empirical findings.

§§ Droplet model estimates.

For convenience we summarize here some estimates based on the droplet model of phase transitions supporting the physical picture used in the previous section.

Let $O$ be a point around which a low density phase is growing: then $O$ will be the center of a domain $D$ consisting of $1, 2, \ldots G$-atoms with a probability proportional to:

\[ e^{-2\beta J_q}, e^{-2\beta J(2q-2)}, \ldots \]  

where $q$ is the coordination number (number of nearest neighbours, $q = 12$ for f.c.c. lattices) and $J$ is related to the critical temperature $T_c$ by [8]:

\[ kT_c/qJ = 0.81 \]  

We see that 2-atoms clusters have a frequency, relative to the single atoms clusters, estimated by:

\[ e^{-2\beta(2q-2)} / e^{-2\beta J_q} = e^{-2\beta J(q-2)} \approx e^{-2(T_c/T)} \]  

Hence the low density domain can be considered consisting of isolated atoms if $T < T_c/2$. 

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Furthermore the probability that in an imploding domain there are two G atoms is given (for low concentration c_0) by:

\[ p_2 = c_0^2 = e^{-4\beta_J(g-1)} = e^{-4(T_0/T)} \]  

(3.4)

which indeed reproduces correctly the order of magnitude of \( c_0^2 \).

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References


