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Evaporation of Cold Metallic Hydrogen*

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Abstract

Solid metallic hydrogen is only metastable at low pressures, but the transition to the molecular form may require surface phenomena. The "evaporation" of pairs of adjacent surface atoms (forming free H_2 molecules) is discussed. A monolayer of surface atoms is lost in e^G times a lattice vibration period, where $G \lesssim 20$ at zero pressure and temperature. G increases with pressure and decreases with temperature above $T_c \sim 150^\circ K$.

Recent calculations¹ of the equation of state for cold solid hydrogen indicate a zero-pressure binding energy of ~ 0.8 eV per H-atom (slightly larger than earlier estimates) for the denser metallic phase. Although the equation of state for solid molecular hydrogen is still not known accurately at higher pressures,^{1,2} the phase-transition from the molecular to the metallic solid probably takes place at a pressure $P_{tr} \sim 1$ Mbar. Several experimental facilities³ should soon be able to make metallic hydrogen crystals of macroscopic size (~ 1 mm, say) at high pressures, $P > P_{tr}$, where the metallic phase is the stable form. However, it is also hoped to bring cold metallic hydrogen crystals to lower pressures, where such a crystal represents a metastable state, and one faces the question of how this state "decays" to the stabler molecular form.

For $P < P_{tr}$ the total energy E for a given value of pressure (as well as the Gibbs free energy) is lower for the molecular phase than for the metallic. However, because of the greater compactness of the metallic lattice the situation is reversed for total energy E at constant density. The range of validity of this reversal is not yet known reliably, but at the moment we assume it to hold even at the zero-pressure density¹ of $\rho \approx 0.57 \text{ g cm}^{-3}$ for cold metallic hydrogen. A simultaneous

transition of the whole macroscopic crystal to the molecular form can then be neglected because of an enormous activation energy and presumably the transition is inhibited fairly strongly for even a smaller aggregate of atoms⁴ in the interior of the crystal. We must then rely on surface phenomena and we discuss here the "evaporation" of pairs of adjacent surface atoms to form free H_2 molecules. We first estimate the rates at zero temperature, due to quantum mechanical tunneling, and return to thermal effects later on.

The decay-rate for an atom-pair from an originally intact surface of a metallic crystal could, in principle, be obtained from a six-dimensional WKB-approximation:⁵ Let $\vec{R}$ be the vector position of the center of mass of the proton-pair and $\vec{r}$ their relative coordinate. For fixed values of $\vec{R}$ and $\vec{r}$ one should first evaluate the energy of the electronic ground-state configuration and use this energy as the potential $V(\vec{R}, \vec{r})$ for the six-dimensional Schrödinger equation. Since the total mass $2H$ of the proton-pair is four times the reduced mass for $\vec{r}$, one can use the "adiabatic approximation" once more, i.e. for fixed values of $\vec{R}$ find the energy of the vibrational ground-state in the relative coordinate $\vec{r}$ and use this as a three-dimensional potential $V(\vec{R})$. Let Z be the component of $\vec{R}$ normal to the surface. From symmetry the potential for fixed Z has a minimum value $V(Z)$ when $X = Y = 0$. We further replace the

Schrödinger equation by a one-dimensional one in Z for a particle of mass $2H$ in potential $V(Z)$, which introduces errors in multiplying factors but not in the large exponential terms of the three-dimensional WKB-approximation.⁵

The potential $V(Z)$ is qualitatively as shown in Fig. 1, with $Z = 0$ the average proton position in the intact surface (and Z_1 the zero-point vibration amplitude). The dashed curve, which approaches E_x , the removal energy for a pair of hydrogen atoms, is the hypothetical potential in the absence of any molecular binding. Assuming the remaining protons in the crystal to stay at their original lattice positions, E_x certainly exceeds the total binding energy (per two atoms) in the metal but by not more than a factor of two ($E_x \sim 3\text{eV}$, say, for the zero-pressure crystal with $\rho \approx 0.58 \text{ g cm}^{-3}$ and binding energy 1.6 eV per two atoms). The solid curve in Fig. 1 includes the increasing contribution of molecular binding with increasing Z , approaching the dissociation energy $D = 4.48 \text{ eV}$ of a free hydrogen molecule. The atom-pair has to leak through a barrier with classical turning points at Z_1 and $(Z_1 + x_0)$. The decay-time t_s for one atom-pair to "leak out" of the intact surface is then given by the WKB-expression

$$t_s \sim (2\nu_D)^{-1} e^{G_s}, \quad G_s = 2(4H/h^2)^{\frac{1}{2}} \int_{Z_1}^{Z_1+2x_0} dZ [V(Z) - E_0]^{\frac{1}{2}} \quad (1)$$

where ν_D is the Debye frequency of the lattice.

Reliable estimates for $V(Z)$ are not available at the moment but we can obtain a rough order of magnitude estimate (or at least a limit) for the exponent G_s as follows. Approximating $V(Z)$ by an inverted harmonic oscillator potential with barrier height V_0 and width X_0 gives

$$t_s \sim e^{G_s} \times 10^{-14} \text{ sec}, \quad G_s = 48.5(V_0/\text{eV})^{\frac{1}{2}}(X_0/\text{\AA}) \quad (2)$$

I obtained an estimate for X_0 by using $E_r = 3\text{eV}$ and calculating $V(Z)$ for large Z by using a potential $\phi(r)$, between each atom of the molecule at $(X = 0, Y = 0, Z)$ and the remaining atoms of a bcc-lattice, of form

$$\phi(r) \sim \exp[-(r - 1.8\text{\AA})/0.3\text{\AA}] \times 0.23 \text{ eV} \quad (3)$$

For small Z , I used a harmonic oscillator potential appropriate to a Debye temperature¹ of $\sim 2,000^\circ\text{K}$ ($Z_0 \sim 0.15\text{\AA}$) and interpolated $V(Z)$ by eye and found $V_0 \sim 1.2 \text{ eV}$, $X_0 \sim 0.7\text{\AA}$. These "visual estimates" for V_0 and X_0 are obviously rough, but are likely to be overestimates for both because the potential in equation (3) holds^{1,6} only in cases where all H-atoms are in saturated molecules and the repulsion of protons plus "metallic" electrons is presumably smaller (but presumably larger than for completely free atoms⁷). Provisionally, we have only the rough inequality $G_s \lesssim 37$.

G_s is the Gamow barrier penetration factor for an atom-pair leaking away from an originally intact surface, calculated first under the assumption that the hole left behind on the surface does not "anneal". In this case further evaporation proceeds more rapidly from the vicinity of the hole, which then grows. Consider a rectangular hole, one lattice spacing deep with its four edges $\sim \eta$ lattice spacings long. Let G_e be the barrier penetration factor for an atom-pair leaking away from such an edge, defined in analogy with G_s but numerically smaller. The removal of one molecule from an edge leaves behind two "corners" and the penetration factor G_c for pair-evaporation from a corner is presumably still smaller than G_e . The removal energy $E_r \approx 1.6$ eV for evaporation from a corner is smaller by only a factor of two than for an intact surface. Nevertheless, we expect the double inequality $G_c < G_e < G_s$ to be rather strong: the equilibrium position of atoms near an edge (and much more so near a corner) lies appreciably above the intact surface and we expect the barrier width x_0 to be decreased appreciably and the "activation energy" (the barrier height V_0) to be a smaller fraction of the removal energy E_r .

Let $l = \exp[\frac{1}{2}(G_e - G_c)]$ and $\eta_0 = \exp[\frac{1}{2}(G_s - G_e)]$ and assume that $l \ll \eta_0$ (for a macroscopic crystal with N^3 atoms in it, we also expect $\eta_0 \ll N$). If the number η of atoms along

a hole edge satisfies $l \ll \eta < \eta_0$ one finds an average spacing of $2l$ atoms between "corners" (or "nicks") along each edge: In a time $t_r \sim (4v_D)^{-1} \exp[\frac{1}{2}(G_c + G_e)]$ new "nicks" are created in a fraction l^{-1} of the lattice sites along an edge and evaporation from existing corners denudes one row of atoms (and eliminates old "nicks") in the same time. In a time $\sim (\eta_0/2)t_r$ each hole has grown to an area of η_0^2 lattice sites and the probability of a new hole arising from an intact surface of this area in this time is $\sim \frac{1}{2}$. The time for evaporating a monolayer of atoms from each crystal surface is then not t_s but

$$t_{\text{mono}} \sim \left(\frac{7/3}{2v_D}\right)^{-1} e^G, \quad G = \frac{1}{3}(G_c + G_e + G_s) \lesssim 20 \quad (4)$$

(the natural edges of the crystal are unimportant because $N \gg \eta_0$ and we assume dislocations are absent).

We now consider the effect of annealing and of a finite temperature T on the surface evaporation rate $\propto e^{-G_s}$. For excitation energy E the width of the barrier is $x_0 \propto (V_0 - E)^{\frac{1}{2}}$ and the penetration factor becomes $G_s(E) = (1 - E/V_0)G_s$. In averaging over the Boltzmann distribution the integrand contains a factor $\exp[-(1-E/V_0)G_s - E/kT]$ and we define a critical temperature T_c by

$$kT_c = V_0/G_s \sim 0.03 \text{ eV} \quad (5)$$

(for "edge" and "corner" evaporation the ratios V_o/G are similar). The evaporation rate from a rigid lattice is almost constant for $T < T_c$ but increases rapidly ($\propto e^{-V_o/kT}$) for $T > T_c$. However, metallic hydrogen may undergo a partial melting⁸ at a considerably lower temperature T_m . For $T > T_m$ the surface is not rigid enough to support holes, edges or corners and we have a single evaporation process from a liquid surface with $t_{\text{mono}} \sim (2v_D)^{-1} e^{G_l}$. The barrier width x_o for G_l is probably similar to that for G_s but the barrier height V_o is appreciably smaller, so that G_l is smaller than G_s but comparable with G in equation (4). However, $kT_c = V_o/G_l \propto V_o^{1/2}$ is now slightly smaller and the critical temperature is probably $T_c \sim 150^\circ\text{K}$.

If an originally cold crystal of metallic hydrogen is left in vacuum, it will heat up slowly as each evaporated molecule leaves behind some small fraction of an eV in lattice excitation energy. Thermal diffusion times from the crystal surface to the interior are probably short enough for the temperature T to rise uniformly. Evaporation of an appreciable fraction of the crystal is required for the remaining body to have acquired $\sim 10^{-2}$ eV/atom and for T to exceed T_c , at which stage the evaporation rate increases and results in a "thermal runaway". Typical lifetimes of a whole macroscopic crystal of metallic hydrogen at zero pressure are then of order $\sim 10^7 t_{\text{mono}} \lesssim 100$ sec. As discussed above, the numerical uncertainties in

these lifetimes are enormous at the moment. However, the imposition of a relatively "small" positive pressure also increases the lifetimes enormously, partly because the energy increases much more rapidly with pressure for molecular than for metallic hydrogen (e.g. 0.3 eV/molecule versus <0.01 eV/atom at 0.1 Mbar).

The quantum mechanical evaporation of cold metallic hydrogen may appear as an unwelcome complication for experiments on the bulk properties of this substance. It can probably be inhibited by pressure, but the experimental study of this evaporation should in any case be rewarding. Similar quantum phenomena are probably important in other systems as well (e.g. Pd-H mixtures) but can be studied most simply in a pure hydrogen system (e.g. the isotope effect is enormous instead of being a minor perturbation, because replacing H by deuterium increases the large exponents G by a factor of about $\sqrt{2}$).

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Figure Caption

Fig. 1: A schematic plot of the potential energy $V(Z)$ for an atom pair as a function of height Z above the surface.

Footnotes

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Figure 1