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Atomistic modeling of H absorption in Pd nanoparticles

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ABSTRACT

Size affects the properties of absorption of H in Palladium nanoparticles. Because of their higher proportion of surface atoms compared to the bulk, the pressure–composition (*P–C*) isotherms of the nanoparticles are modified. We performed atomistic simulations for different-sized Pd nanoparticles and for the bulk at different H concentrations using the Monte Carlo technique in the $TP\mu N$ ensemble to calculate the *P–C* isotherms. The Pd–H interatomic potentials are of the Embedded Atom (EAM) type and have been recently developed by Zhou et al. [1]. From the related van't Hoff equation we obtained $|\Delta H^{\circ}| = (28 \pm 7)$ kJ/0.5 mol of H_2 and $|\Delta S^{\circ}| = (71 \pm 19)$ J/0.5 mol of H_2·K for the PdH formation in the bulk. For Pd nanoparticles previous simulations results based on a different set of EAM potentials showed that H was absorbed primarily in the surface before diffusing into the inside of small Pd clusters [2]. Considering the better performance of Zhou's potentials [1] for the bulk, in this work we analyzed the evolution of the equilibrium microstructure of Pd nanoparticles as a function of their size and H concentration. Our simulations predict enhanced hydrogen solubilities and vanishing plateaux when compared to the bulk and that H is absorbed in the subsurface of the nanoparticles.

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1. Introduction

Pressure–composition isotherms are a fundamental tool to investigate the interaction of hydrogen with metals since they can give valuable information concerning thermodynamic properties of metal-hydrogen systems. These curves characterize the phase transition from a low concentration solid solution of H in the metal matrix to a high H concentration hydride phase. For bulk Pd this transition does not involve a structural phase transformation but only a change in the lattice parameter of the metallic host. The hydride phase can be thought of as an expanded fcc metallic lattice with H occupying all the octahedral sites.

The Pd–H bulk system has been extensively studied [3]. The change of hydrogen absorption properties in fine Pd powdered samples and nanometer-sized clusters have motivated recent investigations considering the different physical behaviour expected in bulk and nanometer size systems. Hydrogen solubilities as well as plateau pressures in *P–C* isotherms are sensitive to particle/cluster size and preparation history of the samples. For nanocrystalline Pd samples (Pd-n) composed of nano-sized grains of ~10 nm, *P–C* isotherms and derived thermodynamic properties of the Pd–H system are compared with coarser grain Pd powders [4]. It was found that the hydrogen solubility in the α phase region was significantly larger than that for coarser grained Pd and also that the plateau pressures are reduced with respect to coarser grained Pd. In this study it was shown that the difference in thermodynamic properties between Pd-n and coarser grain Pd could be interpreted by site energy broadening for the hydrogen occupation originated by anisotropic strains in the nano-sized grain [4]. On the other hand for Pd–H clusters embedded in a surfactant tetraoctylammonium bromide shell it was found that isotherms resemble those of the bulk samples above the critical point for the phase transition [5]: they show an increased solubility in the low concentration range, a decreased solubility in the high concentration range and, in between, a sloped isotherm. The enhanced solubility found is attributed to subsurface sites. Although nanoparticle isotherms show no flat plateau region, a phase transition is confirmed through hysteresis and structural measurements. The slope in the nanoparticle isotherm's two-phase region is attributed to mechanical stresses arising during the hydrogen sorption between Pd-cluster and its surfactant [5].

From the theoretical point of view atomistic modeling can be used to calculate *P–C* isotherms. The results however are very sensi-

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tive to the choice of the EAM potentials used to represent the atomic interactions [2,6,7] and for the bulk not every set of potentials gives a flat isotherm as expected [2]. For Pd–H the EAM potentials developed by Wolf et al. [6] successfully predicted the *P–C* bulk isotherms and the qualitative trend experimentally found for nanoparticle isotherms [7]. Unfortunately the specifics of this potential have been lost. Following a similar methodology as in Ref. [6], in this work we apply the new set of EAM functions recently proposed by Zhou et al. [1] for the Pd–H system to analyze the evolution of *P–C* isotherms and equilibrium microstructure of Pd nanoparticles as a function of their size and H concentration. We compare these theoretical results with available experimental data.

2. Theoretical background

The EAM potentials used in this work were developed by Zhou et al. [1]. This potential is better than other potentials available in the literature [2,6,7] since it is applicable to the entire hydrogen composition range and is capable of predicting the miscibility gap.

We applied the Monte Carlo technique in the ($TP\mu_H N_M$) statistical ensamble where the temperature T, pressure P, chemical hydrogen potential μ_H and number of metal atoms N_M are kept constant [6]. The system is open to the interchange of H from a reservoir at μ_H, which is in contact with a constant P reservoir and a constant T reservoir. P and μ_H are kept related through Eqs. (1) and (2) [7].

$$\mu_H = \frac{1}{2}\mu_{H_2} = \frac{1}{2}\left[k_B T \ln\left(\frac{P}{P_0(T)}\right) - E_d\right] \quad (1)$$

$$P_0(T) = \frac{(4\pi M k_B T)^{3/2} 8\pi^2 I_r k_B T}{h^5} \quad (2)$$

where k_B is the Boltzmann's constant, h is the Planck's constant, T the absolute temperature, P the pressure, P_0 is the reference pressure, M is the atomic mass of H atom, I_r is the H_2 molecule moment of inertia and E_d is the H_2 molecule dissociation energy (4.4781 eV).

In the ($TP\mu N$) Monte Carlo simulation we carried out four different trial procedures: (1) change of the volume of the system; (2) particle relaxation; (3) creation and (4) destruction of an H atom. The bulk is simulated by an fcc cell of 864 Pd atoms and 864 H atoms in the octahedral interstitials with periodic boundary conditions. The program executes 5×10^6 steps; 5% are trials type (1), 45% of the trials are type (2) and the rest of the moves are distributed evenly between the other two trials. For the nanoparticles we generate spherical crystallites of 1–2 nm in which hydrogen atoms are created at random positions.

3. Results and discussion

3.1. Bulk Pd–H system

Our simulated isotherms at T = 298 K, 323 K and 373 K are presented in Fig. 1, together with the experimental data of [4] for coarser grained Pd and the 300 K isotherm as calculated by Wolf et al. [6]. Reasonable agreement with experimental data is found at the lower temperatures; however as the temperature increases the calculated plateaux become larger than the experimental ones. These errors could be a consequence of the EAM potential chosen; still, our results are closer to the experiments than the simulation of Ref. [6] for bulk at 300 K, therefore representing an improvement over Wolf et al. predictions [6].

We calculated the thermodynamic parameters for the formation of the hydride (PdH) from the van't Hoff equation:

$$\ln\left(\frac{P_{eq}}{P_0(T^*)}\right) = 2\frac{\Delta H^\circ}{RT} - 2\frac{\Delta S^\circ}{R} \quad (3)$$

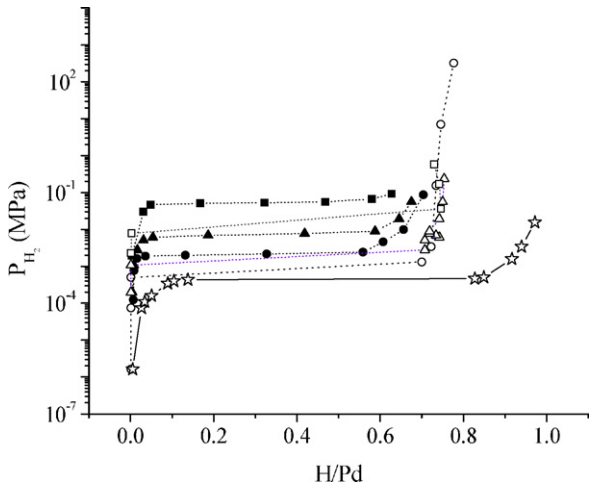

Fig. 1. Pd–H pressure–composition isotherms at T = 298 K (circles), 323 K (triangles) and 373 K (squares). Filled symbols are experimental values from [4]. Stars represent Wolf et al. [6] calculated values at 300 K. Open symbols represent our calculated values. Lines are meant as a guide to the eye.

where P_{eq} is the plateau pressure and $P_0(T^*)$ is equal to 0.1 MPa. The results were sensitive to the range of the temperatures included in the calculation. Using isotherms up to 373 K we obtained $|\Delta H^\circ| = (28 \pm 7)$ kJ/0.5 mol H_2 and $|\Delta S^\circ| = (71 \pm 19)$ J/0.5 mol H_2·K, which are close to the experimental values for the corresponding $\alpha' \leftrightarrow \alpha$ transition [3]: $|\Delta H^\circ| = (18.7 \pm 0.15)$ kJ/0.5 mol of H_2 and $|\Delta S^\circ| = (46.3 \pm 0.4)$ J/0.5 mol of H_2·K. The results are quite satisfactory, considering that the calculation of the *P–C* isotherms pose a difficult challenge to the EAM potentials, which normally are developed at 0 K and are then required to be able to predict the whole range of the composition and temperature of the different isotherms.

3.2. Pd–H nano-sized particles

In order to calculate pressure–composition isotherms in nano-sized particles, we built spherical particles of Pd with H, of

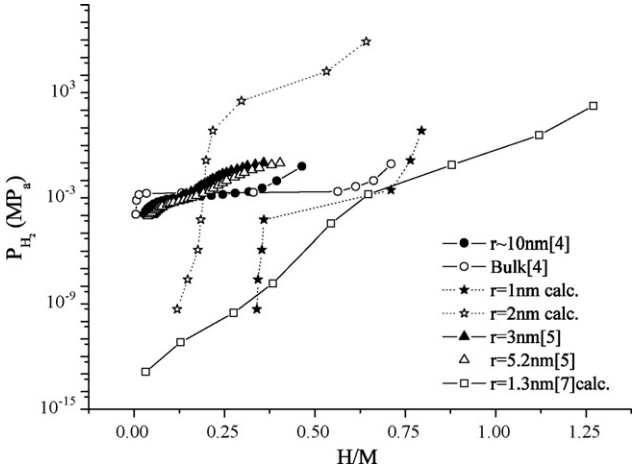

Fig. 2. Pressure–composition isotherms at 298 K. Stars stand for calculated values of spherical nanoparticles, radii = 1.0 nm (filled symbols) and 2.0 nm (open symbols). Circles are experimental values from Ref. [4] for $r \sim 10$ nm Pd-n (filled circles) and the bulk (open circles). Triangles stand for experimental values from Ref. [5] for r = 3.0 nm particles (filled) and r = 5.2 nm particles (open triangles). Squares represent calculated values from Ref. [7] for $r \sim 1.3$ nm Pd particles. Lines are meant as a guide to the eye.

radii = 1.0 nm and 2.0 nm. Sloped *P–C* isotherms, with absence of the typical plateau present in the bulk, were obtained at 298 K as shown in Fig. 2. Enhanced solubilities are deduced from these isotherms. These qualitative trends are also observed in isotherms measured for 3.0 and 5.2 nm clusters [5]. The values of the pressures predicted in our calculations are lower than those for the bulk systems in the case of the $r = 1.0$ nm particle, however for the $r = 2.0$ nm particle the sloped plateau appears at pressures where the bulk isotherm shows its plateau for the transition. In Fig. 2 we compare our calculated isotherms with experimental data available for larger size clusters; we observe that the slopes in our calculated isotherms are sharper than those of the experimental ones. We can also see from Fig. 2 that isotherms for fine powder samples resemble more closely the bulk ones, in the sense that a clear plateau can be distinguished [4]. Besides the difference in the size of the particles (measured and calculated), the difference in the results can be attributed to the fact that the grains are not isolated as in our calculations. Concerning the difference with respect to the measurements performed in [5], it is not clear to us the role of the surfactant present in their cluster samples. Our results here show modifications in the slope of the plateau pressure, even with our isolated particles, so that mechanical stresses arising during

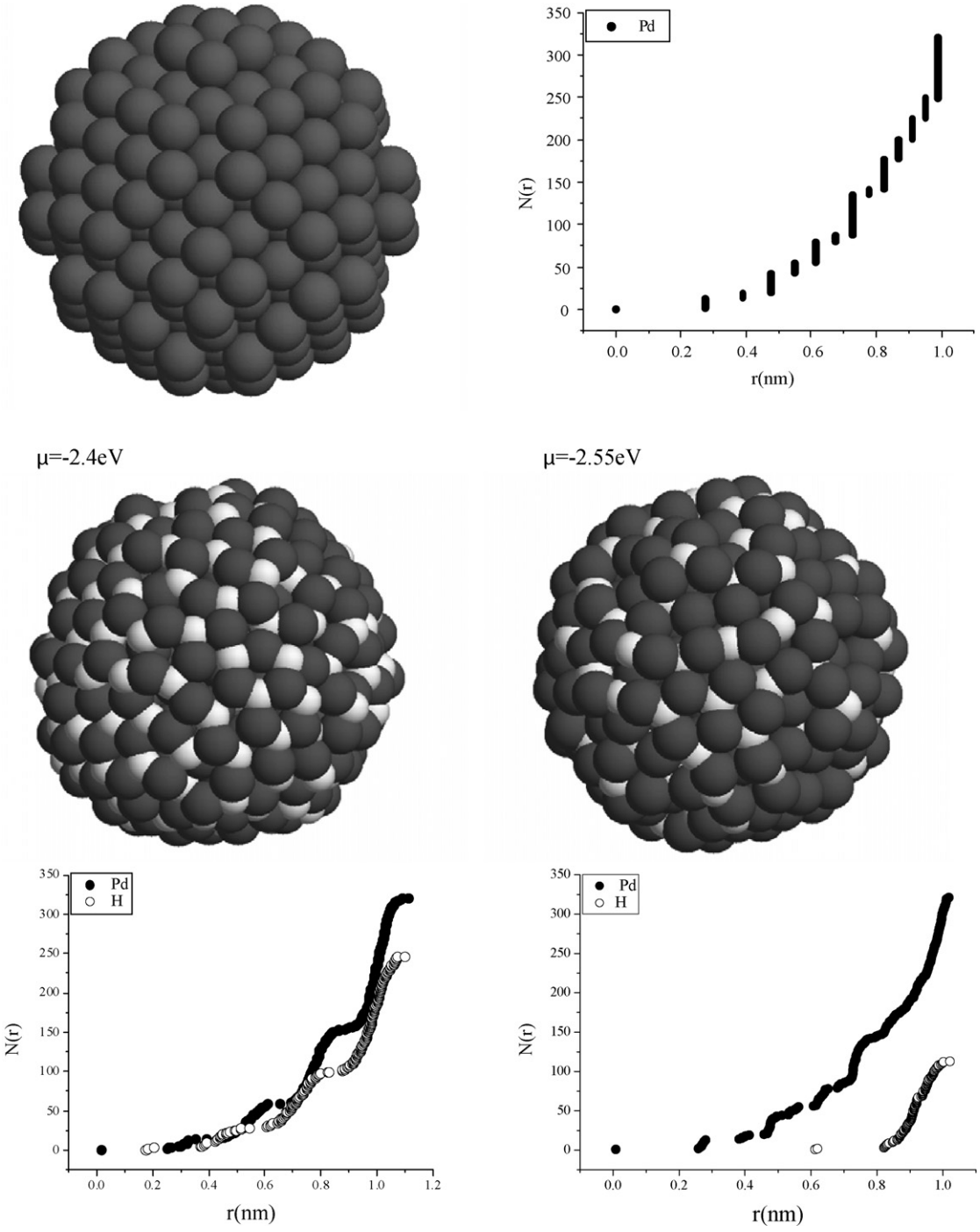

Fig. 3. $n(r)$, number of H atoms inside a sphere of radius $r = 1$ nm centred at the center of mass of fcc Pd nanoparticles and Pd–H nanoparticles at two different hydrogen chemical potentials. There is an important segregation of H atoms towards the subsurface of the particles. $T = 298$ K.

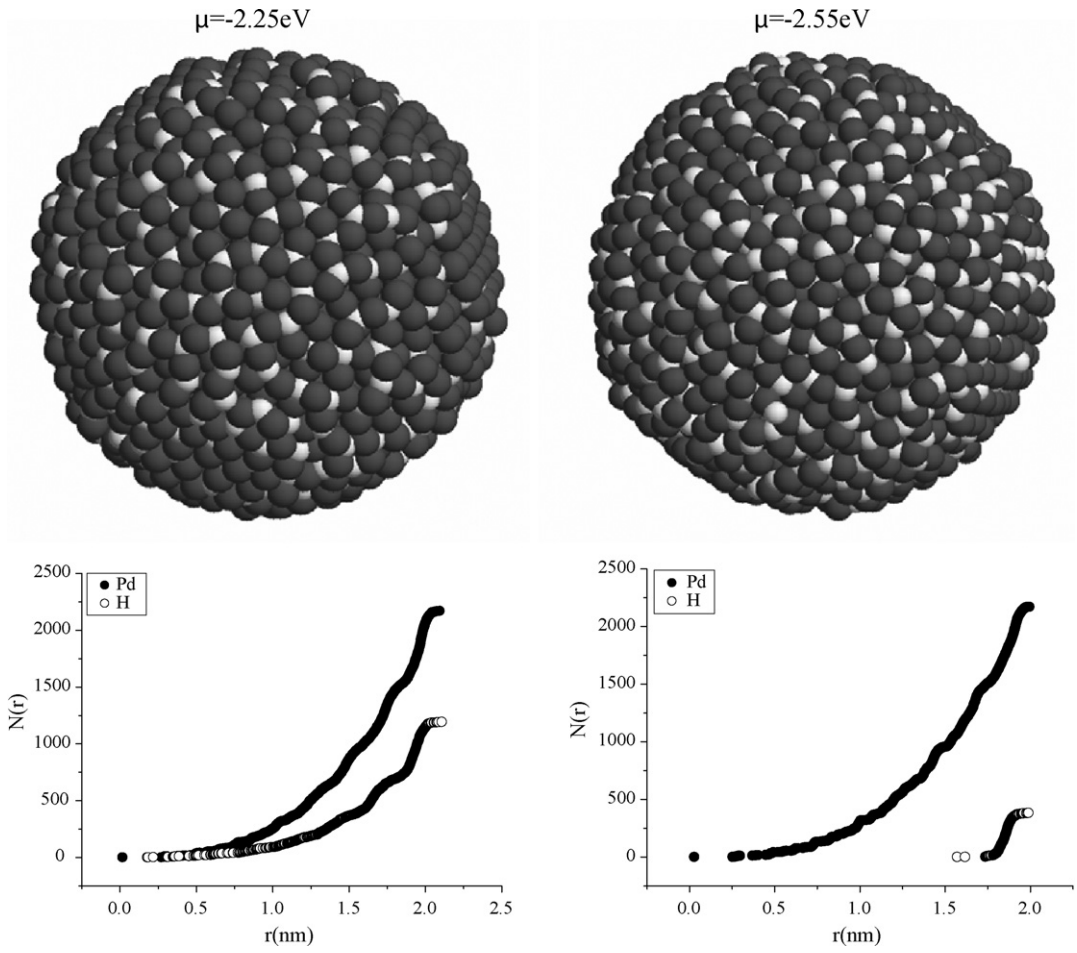

Fig. 4. $n(r)$, number of H atoms inside a sphere of radius $r = 2$ nm centred at the center of mass of Pd–H nanoparticles at two different hydrogen chemical potentials. There is an important segregation of H atoms towards the subsurface of the particles. $T = 298$ K.

the hydrogen sorption between Pd-cluster and its surfactant might not be the only origin of sloped plateux as stated in Ref. [5]. More experimental as well as theoretical investigations about this point are desirable.

H atoms are segregated to the subsurface of the particles in our simulations. In order to quantify these effects we calculated the parameter $n(r)$, which represents the number of atoms (Pd or H) inside a spherical (radius = r) metal nanoparticle. In Fig. 3 we plotted the values of $n(r)$ vs. the radial distance to the centre of the particle for fcc Pd nanoparticles of $r = 1.0$ nm and for the same particles with interstitial H at $\mu_H = -2.4$ eV (H/$M = 0.76$) and $\mu_H = -2.55$ eV (H/$M = 0.35$). In Fig. 4 we repeated the calculations for $r = 2.0$ nm particles at $\mu_H = -2.25$ eV (H/$M = 0.53$) and -2.55 eV (H/$M = 0.17$). In both cases we found that the H atoms prefer the subsurface layers of the particles, leaving the centre of the cluster practically free of H atoms.

The segregation of H atoms to the surface or subsurface of the Pd particles in the simulation is also dependent on the EAM potentials chosen. Using the potentials from Refs. [2,7] H atoms segregate to the surface of the Pd particles. However, in Ref. [5] experimental changes in the solubility of H in $r = 3$–6 nm particles were attributed by the authors to hydrogen sorption in subsurface sites, and further experimental results in Ref. [8] for other particle sizes also agree with these results. Also a statistical thermodynamics two-site model of hydrogen occupancy in Pd nanoparticles employed by Srivastava and Balasubramaniam [9] has shown that the subsurface sites are preferentially occupied by hydrogen in clusters when compared with the situation in bulk Pd. Our results are in line with these experimental [5,8] and statistical thermodynamic model [9].

4. Conclusions

We have calculated pressure–composition isotherms to characterize H absorption in Pd, both in the bulk and in nano-sized particles. The simulations were performed at an atomistic level using EAM potentials and a Monte Carlo technique. Our results show a good agreement to experimental values for the bulk Pd–H isotherms at room temperature, but the plateaux range tend to increase at higher temperatures. The thermodynamic calculations using our results and the van't Hoff equation agree within reasonable limits with experimental data.

For Pd–H nanoparticles of radii = 1.0 nm, 2.0 nm the isotherms predict sloped isotherms with vanishing plateaux. Enhanced solubilities are obtained with H segregating to subsurface sites.

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