Long-term atomistic simulation of hydrogen diffusion in metals

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ABSTRACT

Whereas great strides have been taken towards the characterization of metal-based nanomaterials for high-speed, high capacity, reversible hydrogen storage applications, most mesoscopic approaches to date have relied on molecular dynamics (MD) as their chief representational and computational paradigm. However, the absorption and desorption of hydrogen in nanomaterials is characterized by an atomic, deformation-diffusion coupled process with a time scale of the order of seconds to hours—far beyond the characteristic time windows of MD-based simulations. In this work, we present an application of a novel deformation-diffusion coupled computational framework, which allows the long-term simulation of such slow processes and at the same time maintains a strictly atomistic description of the material. Specifically, we have studied the diffusion of hydrogen in palladium nanofilms and compared our predictions with previous hydrogen desorption results obtained by electrochemical cycling experiments.

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Introduction

Nanotechnology has extensively contributed to opening up new frontiers in materials science and engineering, in particular designing and manufacturing novel materials for more efficient energy storage. As part of this effort, the predictive characterization of nanostructured materials for energy applications remains a focal area of research of great current theoretical and practical import. The ability to store hydrogen in solid materials depends sensitively on their mechano-chemical properties including, among others, composition, lattice structure, mass and heat transport, phase diagram and structural defects. For some nanomaterials, particularly nanofilms, experimental results by Refs. [1,2] showed that their diffusivities may decrease by two to four orders of magnitude. Thus, the absorption and desorption of hydrogen in nanomaterials is characterized by an atomic deformation-diffusion process on a time scale of the order of seconds to hours, far beyond the time windows accessible to molecular dynamics (MD) and Monte Carlo (MC) methods.

However, most computational simulations to date have relied on first-principles-based molecular dynamics [3,4] as their chief representational and computational paradigm. In order to bridge the atomic and device scales over time scales relevant to the operation of the system, we have proposed a...
computational framework [5] that has the potential for closing this gap. More specifically, we have developed an efficient computational platform that, while based on a detailed understanding of complex atomistic mechanisms taking place at the nanoscale, will enable the design of novel real-world energy storage systems, in which kinetic processes are key to their operation and successful design.

Among the vast array of metal hydrides known at present, the palladium–hydrogen (Pd–H) system was the first metal-hydrogen system to be discovered [6]. Palladium is capable of absorbing a large atomic percentage of hydrogen at room temperature and atmospheric pressure, as required for many applications. The Pd–H system exists in two distinct phases: the α-phase at low hydrogen concentration (up to PdH_{0.013}, and the β-phase at high hydrogen concentration (PdH_{0.609} and above). Attendant to the α/β-phase transition, there is a lattice expansion resulting in 10.4% increase in volume. However, it is remarkable that the palladium sub-lattice remains face-centered cubic (FCC) in both phases, while the hydrogen atoms occupy interstitial octahedral sites, which themselves define a second FCC sub-lattice. Owing to this feature, along with the extensive experimental data presently in existence, the Pd–H system has been the subject of extensive research. In this paper we present an application of the aforementioned computational framework to the study of hydrogen diffusion in Pd nanofilms, for hydrogen concentration rates ranging from low to high values.

### Mass transport model

In this section, we provide a brief account of the theoretical model underlying the long-term non-equilibrium simulation we tackle below. Our model specifically considers systems consisting of \(N\) particles, e.g., atoms or molecules, each of which can be of one of \(M\) species. For each particle \(i = 1, \ldots, N\), and each species \(k = 1, \ldots, M\), we introduce the occupancy function

\[
n_{ik} = \begin{cases} 
1, & \text{if site } i \text{ is occupied by species } k, \\
0, & \text{otherwise.}
\end{cases}
\]  

(2.1)

in order to describe the species of each function. We assume that the statistics of the system obeys Jaynes’ principle of maximum entropy [7,8]. This principle postulates that the probability density function \(\rho(q, p, n)\), characterizing the probability of finding the system in a state \((q, p, n)\), maximizes the information-theoretical entropy

\[
\mathcal{S}[\rho] = -k_b \langle \log \rho \rangle,
\]  

(2.2)

among all probability measures consistent with the constraints on the system. In (2.2) and subsequently, \(k_b\) denotes Boltzmann’s constant. We specifically consider systems consisting of distinguishable particles whose Hamiltonians have the additive structure

\[
H = \sum_{i=1}^{N} h_i,
\]  

(2.3)

where \(h_i\) is the local Hamiltonian of particle \(i\). Note, however, that in general each local hamiltonian \(h_i\) is allowed to depend on the positions, momenta, and species of all the particles in the system. Suppose that the expected particle energies and the expected particle molar fractions, respectively,

\[
\langle h_i \rangle = e_i, \quad \langle n_{ik} \rangle = x_{ik},
\]  

(2.4)

\(i = 1, \ldots, N, \ k = 1, \ldots, M\), are known. The particle molar fraction \(x_{ik}\) may be interpreted as the probability that particle \(i\) be of species \(k\). Unlike the classical equilibrium framework, where only global constraints are enforced, these constraints are now local. Maximizing (2.2) among probability measures results, after a straightforward calculation, in

\[
\rho = \frac{1}{Z} e^{-\langle \beta \rangle \langle h \rangle - \langle \gamma \rangle \langle n \rangle},
\]  

(2.5)

where

\[
Z = \sum_{(q)\in\mathcal{E}} \prod_{i} \frac{1}{\sqrt{2\pi k_b T_i}} \int e^{-\langle \beta \rangle \langle h_i \rangle - \langle \gamma \rangle \langle n_i \rangle} dq dp,
\]  

(2.6)

and \((\langle \beta \rangle, \langle \gamma \rangle)\) are Lagrange multipliers. By analogy to equilibrium statistical mechanics, we may interpret (2.5) and (2.6) as non-equilibrium generalizations of the Gibbs grand-canonical probability density function and the grand-canonical partition function, respectively. By analogy with equilibrium statistical mechanics, we may interpret

\[
\theta_i = \frac{1}{k_b \beta_i}, \quad \mu_i = \frac{\gamma_i}{\beta_i} = k_b \theta_i \gamma_i,
\]  

(2.7)

as the particle absolute temperature and the particle chemical-potential array of particle \(i\), respectively. We emphasize that, unlike equilibrium statistical mechanics, the temperature and chemical-potential fields need not be uniform and may vary from particle to particle when the system is away from equilibrium.

In order to obtain explicit formulations of thermodynamic potentials suitable for computations, we apply the meanfield approximation theory [9] with a carefully designed trial Hamiltonian, and model the interatomic potential energy using the embedded-atom method. As a result, the thermodynamics of the solid is characterized by Gaussian distributions and atom-wise macroscopic variables including atomic temperature and molar-fraction \(x\). In particular, now the diffusion of hydrogen is characterized by the change of hydrogen molar fraction \(x \) over both space and time, whereas the microscopic variable \(n\) is no longer involved. The localized equilibrium conditions can be obtained by enforcing stationarity of free entropy [10] with respect to parameters characterizing the meanfield trial Hamiltonian.

This thermodynamics model is then coupled with discrete kinetic models of Onsager type which governs mass transport and possibly also heat conduction. This in practice defines the evolution of atomic temperature and molar-fraction. In this work, we consider linear models of the form

\[
x_i = \sum_{(i,j)} B_{ij} x_j \gamma_j, \quad i = 1, \ldots, N;
\]  

(2.8)

where \(\gamma\) denotes non-dimensionalized chemical potential, \(x_{ij}=(x_i + x_j)/2\). \(B_{ij}\) denotes the bondwise diffusion coefficient between the (i,j) atom pair; in practice it can be obtained by fitting to experimental measurement.
**Application: hydrogen diffusion in Pd (111) nanofilms**

In Ref. [5], the general thermo-chemo-mechanical coupled computational framework summarized in Section Mass transport model is specialized to hydrogen diffusion within rigid, single-crystalline Pd at constant temperature. Specifically, the following closed-form local equilibrium condition that relates $\{\gamma\}$ and $\{x\}$ is established:

$$\gamma_i = -\log \frac{1-x_i}{x_i} + B_i \frac{k_B T}{\text{e}g_i} + \sum_{j \in I_{ij}} C_{ij} \frac{k_B T}{\text{e}g_j} x_j, \quad \forall i \in I_{H},$$

(3.1)

where $T$ is the constant temperature, and $I_{H}$ denotes the set of octahedral interstitial sites in the Pd lattice, which can occupied by H atoms. $B_i$ and $C_{ij}$ are parameters in the dimension of energy resulting from the linearization of the embedding energy in an EAM potential for the Pd–H system. Their values depend on the choice of $\rho_0^{el}$ and $\rho_0^{el}$, about which the embedding energy is linearized.

In this work, we apply this new computational model to simulate hydrogen diffusion in two specific Pd (111) nanofilms, for which experimental data is available. We use the EAM potential proposed in Ref. [11], and propose a specific approach to calibrate $B_i$ and $C_{ij}$. Our main objective is twofold: to validate this computational model; and to demonstrate its capability of capturing highly nonlinear material behaviors, particularly phase separation and transition, at atomic scale, while allowing a long simulation time window in the order of seconds to minutes.

Specifically, we consider the hydrogen desorption experiment described in Ref. [1]. In their work, three Pd (111) films with thickness $L = 220$ Å, 460 Å and 1350 Å are fabricated by physical vapor deposition of Pd onto a gold-coated nickel substrate. For each specimen, the hydrogen diffusion coefficient $D_H$ for $\alpha$-phase Pd–H was determined by an electro-chemical stripping method. The time history of electric current at film surface, which is proportional to the spatial gradient of hydrogen molar fraction, is reported for the 460 Å and 1350 Å films. We first validate our computational model for this $\alpha$-phase hydrogen desorption experiment. Next, using the same computational setup, we simulate hydrogen diffusion problems with higher H concentration, which involves the separation of $\alpha/\beta$-phases and phase transition.

**A one-dimensional simulation approach**

The surface area of the films is 1.2 cm$^2$. Therefore the hydrogen diffusion process is essentially one-dimensional in the film thickness direction, that is, the [111] direction (see Fig. 1). Therefore, the H molar fraction $\{x\}$ and the non-dimensional chemical potential $\{\gamma\}$ can be safely assumed to be constant over each (111) plane of the FCC H sub-lattice. Let $N$ be the number of (111) planes in a specific film. We denote by $x_k$ and $\gamma_k$, $k = 1, \ldots N$ the hydrogen molar fraction and non-dimensionalized chemical potential in the $k$-th (111) plane. The particular plane $k = 1$ corresponds to the film surface, in contact with the electrolyte solution (i.e. a hydrogen reservoir), and $k = N$ corresponds to the other side of the film in contact with the substrate. Taking into account the FCC lattice geometry and the cut-off radius in the EAM potential of [11], the discrete kinetic equation (2.8) and the local equilibrium condition (3.1) reduce to

$$\dot{x}_k = B_H \frac{x_k + x_{k-1}}{2} (\gamma_{k-1} - \gamma_k + \frac{x_k + x_{k+1}}{2} (\gamma_{k+1} - \gamma_k)), \quad k = 2, \ldots, N - 1,$$

(3.2)

and

$$\gamma_k = -\log \frac{1-x_k}{x_k} + B \frac{k_B T}{\text{e}g_k} \left((2C_1 + 2C_2 + 4C_3)x_k + (C_1 + 2C_2 + C_3)(x_{k-1} + x_{k+1})\right) + \frac{B}{k_B T} \text{e}g_k, \quad k = 1, \ldots, N,$$

(3.3)

where $a_0 = 3.885$ Å is the lattice parameter of the FCC H sub-lattice at room temperature, predicted by the EAM potential proposed in Ref. [11]. To determine $B$ and $C_i$, $i = 1,2,3$, we set $\rho_0^{el} = 10.035$, which is the EAM electron density evaluated at equilibrium Pd lattice constant $a_0 = 3.885$ Å. Then, we calibrate $\rho_0^{el}$ to achieve a good agreement between the proposed model (Eq. (3.3)) and the classical entropy-of-mixing relation $\gamma = \log x_H$ at low H concentration ($x < 0.02$), which results in $\rho_0^{el} = 21.0$. Plugging this pair of $\rho_0^{el}$ and $\rho_0^{el}$ into Eq. (6.19) in Ref. [5] yields $B = -2.3844$ eV, $C_1 = -0.01117$ eV, $C_2 = -0.003556$ eV, and $C_3 = -0.0005190$ eV. The equilibrium condition (3.3) is

**Fig. 1** – (a) A (111) plane in the FCC unit cell. (b) (111) planes in the FCC H sub-lattice in the Pd–H system.
plotted in Fig. 2 for uniform H molar fraction (i.e. \(x_k = \text{const} \), \(k = 1, \ldots, N\)) and compared with the classical mix-of-entropy relation \(g = \log x\). Remarkably, the proposed model exhibits an up-down-up equilibrium relation characteristic of phase transitions. In particular, the two local extrema points, namely \(x_a = 0.192\) and \(x_b = 0.810\), can be interpreted as the \(\alpha\) and \(\beta\) phase of the Pd–H system, respectively. This feature will be further explored in Section Phase separation and transition to predict phase separation and transition in the process of H diffusion.

It is notable that although the equilibrium condition (3.3) is highly nonlinear, the coupled mass transport model (3.2) and (3.3) conserves mass, as

\[
M_k \equiv \sum_{i=1}^{k} x_i = \frac{D_H}{2} \left( x_{k+1} - x_{k-1} \right) + \frac{x_k + x_{k+1}}{2} \left( \gamma_{k+1} - \gamma_{k-1} \right), \quad \forall k_1 < k_2 < N.
\]

We close Eqs. (3.2) and (3.3) by the following initial and boundary conditions suggested by Ref. [1] based on their experimental set-up:

\[
x_k(0) = x_0, \quad k = 2, \ldots, N; \quad (3.5a)
\]

\[
x_1(t) = x^*, \quad 0 < t < t_{\max}; \quad (3.5b)
\]

\[
x_N(t) = x_N(0), \quad 0 < t < t_{\max}. \quad (3.5c)
\]

where \(x_0\) denotes the initial uniform H molar fraction in the film interior, and \(x^*\) denotes the fixed H molar fraction at the film surface in contact with the electrolyte solution. No-flux boundary condition is imposed at the other side of the film, given that H diffusion between the Pd film and the gold-coated nickel substrate is negligible.

**Model validation for \(\alpha\)-phase Pd–H**

We simulate the films of thickness \(L = 460\) Å and 1350 Å for which time-dependent data is provided in Ref. [1]. In both cases, \(x_0\) corresponds to the saturation H molar fraction at a cathodically polarized potential of \(-0.830\) V, in which the films are held before desorption starts. It is set to 0.009 in the computation based on the measurement of [2] (see Fig. 1 therein). \(x^*\) denotes the H molar fraction at the surface of the film. The experimental data of \(x^*\) is not direct provided in Ref. [1], however, an estimate can be easily derived from Figs. 6(a) and 7(a) therein using the exact solution of Fick’s second law. The estimated \(x^*\) used in the computations are reported in Table 1, together with the experimental data of other case-dependent coefficients involved in Eqs. (3.2)–(3.5).

Equation (3.2) is discretized in time by the mid-point rule which is second-order accurate. The computational time step is set to \(\Delta t = 5.0 \times 10^{-6}\) s and \(1.0 \times 10^{-6}\) s in Case I and II.
respectively. In both cases, simulation is terminated at \( t_{\text{max}} = 1.0 \text{ s} \).

The spatial variation of \( x \) at film surface is converted into electric current and plotted in Fig. 3 in comparison with the experimental data reported in Ref. [1]. In both cases, the predicted electric current agrees well with the experimental measurements in terms of both the initial transient as well as the long-term behavior.

Phase separation and transition

As discussed in Section A one-dimensional simulation approach, the equilibrium condition (3.3) is able to capture the phase structure of the Pd–H system. Here, we further explore this feature in simulations that take the Pd–H system into its \( \beta \)-phase, and highlight the capability of the proposed computational model in capturing complex phase separation and transition behaviors in slow diffusion processes with time scale in the order of seconds or minutes. In this work, we focus on the absorption of H into Pd and, therefore adsorption is accounted for implicitly through the flux boundary conditions.

To observe phase separation, we consider H diffusion in the 460 Å Pd film, with initial condition

\[
x_k(0) = \begin{cases} 0.6, & k = 2, 3, \ldots, N/2, \\ 0.4, & k = N/2 + 1, \ldots, N. 
\end{cases}
\]  

(3.6)

No-flux boundary condition is applied at both ends of the 1D computational domain, that is,

\[
x_1(t) = x_2(t), \quad x_N(t) = x_N/\text{C}_0, \quad 0 < t < t_{\text{max}}.
\]

(3.7)

The mass transport equation (3.2) is integrated in time using the mid-point rule with time step \( \Delta t = 5.0 \times 10^{-7} \text{ s} \). The termination time \( t_{\text{max}} \) is set to 80 s, at which point the steady state is already reached. The H molar fraction over the entire computational domain is shown at \( t = 0, 3.2 \times 10^{-4} \text{ s}, \) and 80 s in Fig. 4. Unlike the classical diffusion model, which would predict a uniform steady state \( x_k(t_{\text{max}}) = 0.5 \), \( k = 1, \ldots, N \), the proposed model predicts a fine mixture of two distinct states (\( x = 0.05 \) and \( x = 0.95 \)) with a periodic alternating pattern and sharp interfaces. These two states can be identified as the \( \alpha \)- and \( \beta \)-phases of the Pd–H system. Therefore, the capability of the proposed computational model in capturing phase separation is clearly evident.

Next, we simulate hydrogen absorption in the 460 Å Pd film characterized by a high H concentration at film surface \( x^* = 0.99 \). The H molar fraction at six time instances are plotted in Fig. 5(a). Clearly, the H diffusion process is characterized by the propagation of an \( \alpha/\beta \) phase boundary. The displacement and instantaneous velocity of the phase boundary are shown in Fig. 5(b). Notably, the phase boundary velocity is in the order of 100 nm/s. In general, the prediction of phase boundary mobility is an important task in multiscale analysis, as typically phase boundaries move slowly, hence cannot be analyzed using brute-force MD. Therefore, the capability of the proposed model in predicting the phase boundary velocity in a long-term analysis is remarkable.

A similar hydrogen absorption simulation is performed with boundary condition \( x^* = 0.5 \). As shown in Fig. 6(a), at steady state, the H molar fraction in the film interior does not reach \( x^* \); instead, it dwells at 0.095, close to the H concentration in \( \alpha \)-phase Pd–H. This indicates the existence of a threshold in \( x^* \) for the formation of \( \beta \)-phase Pd–H. To further...
explore this “threshold behavior”, we perform a series of 25 absorption simulations with \( x^* \) ranging from 0.01 to 0.99. The steady-state H concentration obtained from each and every simulation is shown in Fig. 6(b), in comparison of the corresponding result obtained using the classical model \( \gamma = \log(x) \). It can be observed that the threshold for the formation of \( \beta \)-phase is around 0.95. Moreover, for \( 0.2 < x^* < 0.95 \), the H molar fraction in the film interior is not able to reach the boundary state \( x^* \).

### Conclusions

We have applied a theory of non-equilibrium statistical thermodynamics for groups of atoms, recently presented by the authors [5], to the study of hydrogen diffusion in Palladium nanofilms. In this work, our preliminary kinetic model presented in Ref. [5] has been improved in order to achieve a better agreement between the proposed model and the classical equilibrium relation derived from entropy-of-mixing.

In general, the prediction of phase boundary mobility is an important task in multiscale analysis, as typically phase boundaries move slowly, hence cannot be analyzed using brute-force MD. Our results show the remarkable capability of the proposed model for predicting the phase boundary velocity as part of a long-term analysis. The model also predicts threshold phenomena for hydrogen absorption, as well as providing quantitative estimates of charging times.

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