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Long-term atomistic simulation of hydrogen absorption in palladium nanocubes using a diffusive molecular dynamics method

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ABSTRACT

Understanding the transport of hydrogen within metallic nanomaterials is crucial for the advancement of energy storage and the mitigation of hydrogen embrittlement. Using nanosized palladium particles as a model, recent experimental studies have revealed several interesting phenomena that occur over long time periods. The time scale of these phenomena is beyond the capability of established atomistic models such as molecular dynamics. In this work, we present the application of a new approach, referred to as diffusive molecular dynamics (DMD), to the simulation of long-term diffusive mass transport at the atomic scale. Specifically, we simulate the absorption of hydrogen by palladium nanocubes with edge lengths in the range of 4 nm and 16 nm. We find that the absorption process is dominated by the initiation and propagation of an atomistically sharp α/β Pd-H phase boundary, with thickness in the range of 0.2 to 1.0 nm, which separates an α phase core from a β phase shell. The evolution of phase boundary and the resulting local lattice deformation are described in this paper in detail. The effects of size on both equilibrium and kinetic properties are also assessed.

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Introduction

Solute-induced phase transformation is a fundamental process in various energy conversion and storage applications. For example, the storage of hydrogen in metals relies on the phase transformation of the hydride (e.g., MgH_x , NaAlH_x), induced by the diffusion of hydrogen atoms [1–4]. Similarly, the operation of lithium-ion batteries relies on a reversible phase transformation in the cathodic material (e.g., Li_xCoO_2 , Li_xFePO_4), induced by the diffusion of lithium ions [5]. For these applications, there has been a continuous push towards

nanostructured systems, as they hold promise to accelerate the charging and discharging process, increase the energy and power density, and extend the life cycle [5–7].

The palladium-hydrogen (Pd-H) system is a prototypical model for studying solute-induced phase transformation, because it allows for relatively fast reaction kinetics at easily accessible temperatures and pressures [8]. The Pd-H system exhibits two distinct phases at room temperature: the dilute α phase at low H concentration (up to $\text{PdH}_{0.015}$), and the β phase at high H concentration ($\text{PdH}_{0.6}$ and above). In both phases, the Pd lattice maintains the face-centered cubic (FCC) structure, while the H atoms occupy the interstitial octahedral sites.

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Attendant to the α/β phase transformation, there is a lattice expansion with approximately 3.5% increase in lattice constant [9] and 10.4% increase in volume, which, in bulk materials, results in the formation of misfit dislocations.

While the behavior of Pd-H is well-understood in the bulk, the phase transformation dynamics within nanostructured Pd-H systems is an active area of ongoing research [10–17]. Specifically, the sloped isotherms of nanoparticle ensembles seem to suggest that the phase transformation is continuous, and hence the two phases may coexist in equilibrium [10]. However, this hypothesis is challenged by several recent experiments at the scale of individual nanoparticles. For example, using scanning transmission electron microscopy, Narayan et al. observed the propagation of a sharp α/β phase boundary in individual Pd nanocubes with edge lengths between 10 and 35 nm [15]. Using coherent X-ray diffractive imaging, Ulvestad et al. measured the evolution of strain within individual Pd nanocubes between 120 and 340 nm, which also indicates a sharp α/β phase transformation [13,16]. Beyond the overall transformation mechanism, i.e., *continuous transformation versus phase boundary propagation*, other unresolved issues include the morphology of the phase boundary, e.g., *spherical shell versus spherical cap* [11,15,16], the effect of particle shape and lattice orientation [12], and the interaction of phase boundary with preexisting defects [14].

Moreover, these experimental studies suggest that in nanosized particles, the α/β phase boundary may be atomistically sharp, and it may propagate very slowly at around 1 nm/s. This confluence of atomistic length scale and a long time scale (i.e., minutes or longer) challenges theory and simulation. Phase-field models have been applied to interpret some of the experimental results from nanosized Pd particles [11,13]. However, continuum models fail to account for the fine atomistic structure (e.g., local lattice distortion and dislocations) across the phase boundary. By way of contrast, classical Molecular Dynamics (MD) does supply full atomistic detail [18], but the need to resolve the thermal vibrations of the atoms places slow diffusive processes such as phase boundary propagation outside its scope. Transition state theory based accelerated MD methods [19] and kinetic Monte Carlo (kMC) methods [20] have been developed to expand the simulation time window of MD while maintaining full atomistic fidelity. However, for mass transport problems, such as hydride phase boundary propagation, the total time window accessible to these methods is limited by the frequency of individual atom hops within the material sample and is typically less than one second [21]. Besides the aforementioned kinetic models, the equilibrium MC method has also been applied to investigate H absorption by Pd nanoparticles and nanofilms, which predicted isotherms at different equilibrium states [22–24].

In this work, we apply a novel computational model, referred to as diffusive molecular dynamics (DMD), to the investigation of the detailed dynamics of H absorption and hydride phase propagation within Pd nanocubes with edge lengths in the range of 4 nm to 16 nm. DMD is a new paradigm for simulating long-term diffusive mass and heat transport while maintaining full atomic resolution [17,25–30]. Its defining idea is to couple a calibrated empirical kinetic model for the evolution of lattice site occupancy with a non-equilibrium statistical thermodynamics model that supplies

the requisite driving forces for kinetics. The basic assumption underlying DMD is that the time scale of diffusion is much larger than that of microscopic state transitions. Therefore at an intermediate time scale, the microscopic state variables can be considered as random variables. In comparison to the established atomistic models mentioned above, DMD has a larger simulation time window as it does not explicitly resolve thermal vibrations nor individual microscopic state transitions. It has been applied to nanoindentation and sintering [25], dislocation extension [26], nanovoid growth [31], solute-defect interactions [32] and silicon lithiation [33]. In particular, a recent study by Wang et al. [17] shows that the DMD model, when equipped with an embedded atom method (EAM) potential function [34], is capable of capturing the separation of the α and β phases of Pd-H. In Ref. [17], the DMD model is also validated against experimental data for the desorption of hydrogen in Pd nanofilms. Nonetheless, the study was limited to a one-dimensional analysis of hydrogen diffusion within thin Pd films. Also, the lattice deformation induced by hydrogen diffusion was neglected. The application of the DMD theory to investigate three-dimensional Pd-H systems — accounting for the deformation-diffusion coupling — is therefore the main novelty of the present paper.

The large time window and atomic resolution of DMD renders it an excellent tool for studying hydride phase transformations within Pd nanoparticles, which operates on time scales of seconds to minutes. In this work, we begin by presenting a succinct summary of DMD in the interest of completeness, in Section **Methodology**. The assumptions and computational setup are subsequently described in Section **Simulation setup**. Simulation results concerned with the final equilibrium state, the morphology of the α/β Pd-H phase boundary, the attendant local lattice distortion, the absorption transient, as well as the effect of nanoparticle size are presented in Section **Results and discussion**. A summary and concluding remarks are consigned to Section **Conclusions** by way of closing.

Methodology

We consider an FCC Pd sample, which includes host sites occupied by Pd atoms and interstitial octahedral sites that can be either occupied by H atoms or unoccupied. For ease of reference, we denote the host sites by I_{Pd} , and the interstitial sites by I_H . At each interstitial site $i \in I_H$, we introduce an occupancy function defined as

$$n_i = \begin{cases} 1 & \text{if the site } i \text{ is occupied by H atom} \\ 0 & \text{if the site } i \text{ is unoccupied} \end{cases} \quad (1)$$

The instantaneous position and momentum of each site i are denoted by \mathbf{q}_i and \mathbf{p}_i , respectively. Based on the assumption of scale separation and the ergodic hypothesis, these microscopic state variables can be viewed as random variables that have a joint probability distribution characterized by density function $\rho(\{\mathbf{q}\}, \{\mathbf{p}\}, \{n\})$, where $\{\mathbf{q}\} = (\mathbf{q}_i)_{i \in I_{Pd} \cup I_H}$, $\{\mathbf{p}\} = (\mathbf{p}_i)_{i \in I_{Pd} \cup I_H}$ and $\{n\} = (n_i)_{i \in I_H}$. We determine ρ by applying Jaynes' principles of maximum entropy [35,36], i.e., by maximizing the information-theoretical entropy

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