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Role of solvent in metal-on-metal surface diffusion: A case for rational solvent selection for materials synthesis

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ABSTRACT

The effect of solvent on diffusion at metal surfaces is poorly understood despite its importance to morphological evolution during materials processing, corrosion and catalysis. In this article, we probe the metal-solvent interfacial structure, effective nature of interactions and dynamics when a solvent is in contact with a metal using a novel accelerated molecular dynamics simulation technique called temperature programmed molecular dynamics (TPMD). TPMD simulations reveal that surface diffusion of metal-on-metal can be made to vary over *orders-of-magnitude* by tuning the metal-solvent interaction. Ultimately, the solvent can have an indirect effect on diffusion. As the solvent tugs at the metal surface the separation between the adsorbed metal atom (adatom) and the surface layer can be modulated via metal-solvent interactions. The resulting adatom-surface separation can cause stronger/weaker binding of the adatom to the metal surface, which in turn results in the observed slower/enhanced diffusion in the presence of solvent. We believe this effect is ubiquitous in pure metal and metal alloys and in principle one could rationally select solvent to control the material structural evolution. Implications on materials synthesis are discussed in the context of formation of nanoporous materials.

1. Introduction

Metal-on-metal diffusion in the presence of a solution is an important phenomenon in catalysis [1], corrosion [2], materials synthesis [3] and electrochemistry [4]. Surface diffusion plays the crucial role of the rate-limiting step in the time-dependent evolution of the material structure in nucleation and crystal growth [5–7], particle aggregation and coalescence [8], Ostwald ripening [9], self-assembly [10], leaching [11], elemental distribution within metal alloy particles [12,13], and nanoporous materials synthesis [2,14]. These examples highlight that the material structural evolution can be tuned by controlling the diffusion rates.

The surface diffusion coefficient D for a metal can be approximated as $D \sim \exp(-N\epsilon/k_B T)$ where N is the number of metal-metal bonds, ϵ is the metal-metal (M-M) binding energy, k_B is the Boltzmann constant and T is the absolute temperature. One possible way of tuning D involves altering the solvent composition which in turn affects ϵ at a fundamental level. Despite its practical importance, relatively little is known about how the metal-solvent (M-S) interactions may influence ϵ. Unlike extensive studies of surface diffusion in vacuum [15], experimentally probing surface diffusion in solution at the nanoscales is challenging. From a theoretical point of view, the lack of accurate interatomic potentials describing interactions at the M-S interface [16] constitutes a major challenge.

In this work, we employ a coarse-grained model for the solvent to capture the M-S interactions approximately. The M-S interaction strength is varied to gain insights into the role of this parameter on diffusion. Different aspects need to be taken into consideration. In vacuum, several thermally-activated diffusion mechanisms including single adsorbed atom (adatom) hop and many-atom moves are present with *well-defined* minimum energy paths on a smooth potential energy landscape [17–19]. On the other hand, solvent molecules can arrange themselves in a myriad ways. Unlike in vacuum, diffusion in the presence of a solvent entails an ensemble of reactive trajectories on a corrugated potential energy landscape [20,21]. Specifically-adsorbed species are ignored in this work to clearly elucidate the effect of solvent on diffusion. In the absence of specifically-adsorbed species the M-S interaction will be weaker than metal-metal (M-M) interaction, which raises a question about the extent to which the M-S interactions can have an effect on surface diffusion. It is necessary to investigate the relative contribution of the potential energy and entropy terms in solvent and vacuum. Traditionally, corrugated energy landscapes have been studied using free-energy calculations [22–24].

To understand these aspects, our investigation is carried out in the following steps. First, assuming surface diffusion is thermally-activated and that the Arrhenius rate law is obeyed, the activation barrier for

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single Ag adatom hop on Ag(001) surface is calculated using a recently developed rare-event technique called the temperature programmed molecular dynamics (TPMD) method [25,26]. TPMD method samples the activation barriers using high temperature MD calculations and provides a list of dominant pathways for surface diffusion. Using TPMD we find that the activation barrier in the presence of solvent is significantly different in comparison to vacuum conditions, resulting in orders-of-magnitude variation in diffusion rates. Similar behavior is observed with other metals. Second, umbrella sampling technique [27], which complements the TPMD method, is used for calculating the free energy barrier along the reaction coordinate. Based on the calculated barriers, we find that the entropy difference between the saddle and reactant configuration is relatively small. The orders-of-magnitude speed-up in the hopping rate constant in solvent is purely an energetic effect that is modulated by the strength of the M-S interaction. Third, M-S interfacial structure at the saddle location and at the reactant configuration are inspected for Ag/Ag(001). The M-S interfacial structure provides an explanation for the variation in the hopping rate constant. In addition, the M-S interfacial structure is studied for different M-S interaction strengths, where M = Au, Ag, Pt and Pd. To extend our conclusions to environments beyond single adatom on a surface we calculate the hopping barriers for multiple adatom cluster arrangements for Ag/Ag(001) and demonstrate that the same solvent effect on diffusion is witnessed even in these arrangements. Finally, implications on material synthesis is briefly discussed by considering nanoporosity evolution in binary metal alloy. The outline of the paper is as follows. First, we describe the computational methodology used in Section 2. Next, we describe the main results of the paper in Section 3. Finally, conclusions are provided in Section 4.

2. Computational methods

2.1. System preparation

Ag adatom on Ag(001) surface is studied both in vacuum and in presence of a solution (see Fig. 1(a)). A periodic box of size 28.623 Å × 28.623 Å × 67.402 Å is employed. The bottom three layers of the 12-layer metal slab is kept frozen to mimic the bulk system. The embedded atom method (EAM) formalism of Daw and Baskes [28] has been the interatomic potential of choice to describe the environment-dependent interactions between the metal atoms in a transferable manner. The pure metal embedded atom method (EAM) potential of Ref. [29] is used to treat interactions between the metal atoms including the studies for Ag, Au, Pt, Pd and Ni. The EAM energy is calculated as

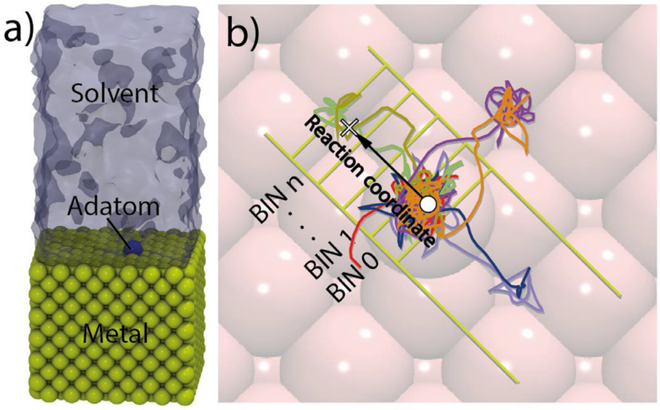

Fig. 1. (a) Metal-solvent interface with an adsorbed metal atom (adatom) shown in blue color present at the interface. (b) Reactive MD trajectories starting with the adatom at the white circle. The reaction coordinate for one of the pathways with adatom hopping to cross symbol is also shown. Bins constructed along the reaction coordinate are used for free energy calculations. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$$E_{EAM} = \sum_i F_i(\rho_i) + \sum_{i,j} V_{ij}(r_{ij}) \tag{1}$$

where the function $F_i(\rho_i)$ is the embedding energy for metal atom i, ρ_i is the electron density at metal atom i arising from neighboring atoms and V_{ij} corresponds to the pair interactions between atoms i and j. The EAM potential results in activation barriers in vacuum [17,19] that are in good agreement with experiments. The lattice constant for Ag is 4.089 Å from the EAM potential.

A solvent molecule (S) is represented by a coarse-grained particle. The interaction between solvent-solvent (S-S) particles separated by distance r_{ij} was modelled using the Lennard-Jones pair potential of the form

$$V^{\mathrm{LJ}}_{S-S}(r_{ij}) = 4\epsilon_{\mathrm{S-S}}((\sigma_{\mathrm{S-S}}/r_{ij})^{12} - (\sigma_{\mathrm{S-S}}/r_{ij})^{6}) \tag{2}$$

where $\sigma_{S-S} = 2.95$ Å and $\varepsilon_{S-S}/k_B = 61.6\,K$ (0.5 kJ/mol). Water models such as the SPC [30], TIP3P [16] and TIP5P [31] employ a value of $\epsilon/k_B \sim 100\,K$ (see [32]) but additionally involve other terms including electrostatic interactions between charged sites, which are missing from Eq. (2). Thus, the parameters used with Eq. (2) only approximately captures the liquid-structure and does not pertain to any particular solvent.

Selecting an appropriate metal-solvent (M-S) interaction has separate issues. Attempts have been made to develop LJ potentials for M-S systems wherein the M-M and M-S interactions are described by the LJ potential [33]. The M-S interaction parameter ε_{M-S} can be obtained using a mixing rule such as $\varepsilon_{M-S} = (\varepsilon_{M-M}\varepsilon_{S-S})^{1/2}$. Typical values of ε_{M-M} and ε_{S-S} in this context are 1 and 0.5 kJ/mol, respectively [33]. The parameter σ for Ag is 2.95 Å, while Au, Pt and Pd lies between 2.8 and 2.96 Å [33]. Such an approach has been reported to provide reasonable values for the surface tension even though polarization effects are missing in the model. Unfortunately, the potential has not been tested for the calculation of the activation barriers with metal systems. At the electronic structure level, tight-binding, density function theory (DFT), other more accurate quantum-mechanical approaches and solvation models [34] have been used to study effect of water. Proper handling of the dispersion interactions [35] and electronic self-interaction effects [36] involving water is required in DFT calculations to obtain reliable properties [37]. The revised version of the PBE functional [38] with dispersion corrections [39] is able to provide a good description of the water-water as well as water-metal interactions by including a non-directional van der Waals interaction. However, employing computationally expensive electronic structure calculations will make the problem intractable.

A general form of the M-S interaction to be used with EAM is not known. Consequently, we assume that M-S interaction will contain a LJ-type interaction

$$V^{\mathrm{LJ}}_{M-S}(r_{ij}) = 4\epsilon_f\epsilon_{\mathrm{M-S}}((\sigma_{\mathrm{M-S}}/r_{ij})^{12} - (\sigma_{\mathrm{M-S}}/r_{ij})^{6}) \tag{3}$$

with $\sigma_{M-S} = 2.95$ Å and $\varepsilon_{M-S}/k_B = 61.6\,K$ (0.5 kJ/mol). In addition, a solvent molecule can contribute an electron density $\chi_S(r)$ to a metal atom at a distance r. We have chosen the solvent density to be identical to the electron density from metal atom. This density term would result in a stronger attractive interaction between metal and solvent than possible with only the LJ interaction. As shown later in the study we will consider M-S interactions both with and without the density term to understand the effect of density-like term. All calculations will apply the density terms unless explicitly mentioned. In addition, the LJ interaction will be varied later using ε_f in Eq. (3).

Table 1 shows the interfacial energy of the Au, Ag, Pt and Pd (100) surface in vacuum and solvent at 300 K calculated using $\sigma_{M-S} = 2.95$ Å, $\varepsilon_f = 1$ and $\varepsilon_{M-S}/k_B = 61.6\,K$. The interfacial energy was calculated in vacuum using