Capturing local atomic environment dependence of activation barriers in metals using cluster expansion models

Nimish Kulkarni and Abhijit Chatterjee*
Department of Chemical Engineering, Indian Institute of Technology Bombay, Mumbai 400076 India

*Email: abhijit@che.iitb.ac.in

Abstract. It is well known that surface diffusion in metals can proceed via multiple mechanisms, such as hop, exchange and other types of concerted moves. However, the manner in which kinetic rates associated with a mechanism can depend sensitively on local atomic environment is relatively less understood. We describe recent attempts in our research group to capture the atomic environment dependence using the cluster expansion model (CEM). In particular, we focus on hop and exchange moves at the (001) surface in homoepitaxy, and show that while CEM can work remarkably well in most cases, it can sometimes provide inaccurate predictions for concerted moves.

1. Introduction
Far from the idealized picture that atoms at crystalline surfaces remain frozen at locations corresponding to the minimum energy configuration, one finds that surfaces tend to be dynamic. Understanding how surfaces can evolve is important to applications like catalysis and electrochemistry as well as materials processing. For instance, the surface density of reactive sites for a catalyst particle, or the nature of the surface roughness during corrosion can evolve with time. While most dynamical models for surface phenomena contain parameters that capture the role of atomic scale processes in a coarse-grained manner, inclusion of detailed kinetic rates could provide unprecedented insights into the surface phenomena. Unfortunately, the situation is incredibly complex for 3D structures and multicomponent materials where a plethora of kinetic mechanisms and atomic environments are encountered, i.e., the problem lies in tackling the combinatorial complexity. We report some of the preliminary advances from our group that can be used to predict kinetic rates from the local atomic environment in metal homoepitaxy. These developments indicate that one can be cautiously optimistic that our approach could pave the way for tackling more complex environments.

Metal-on-metal surface diffusion is essential to a number of applications like thin film growth [1], catalysis [2], and corrosion [3]. Fig. 1 shows an example of a metal alloy surface undergoing selective dissolution of the electrochemically active metal species in the presence of an electrolyte solution. Although the starting material was atomically flat, the dealloying process results in formation of 3D porous structures over a period of several minutes to hours. Interestingly, one finds a large number of atomic arrangements at the surface. While a large number of experimental and computational studies have identified important principles of surface diffusive processes a general understanding of how the diffusion barrier will change with the environment or admetals/substrate species is lacking. A conventional view is that surface diffusion proceeds mainly via the hopping mechanism where an
adsorbed atom (adatom) hops from one lattice site to a nearest neighbor vacant site [4]. Contrary to the view that concerted pathways are unimportant, recently, we have shown that in some situations concerted pathways can play an important role in the long term evolution of the material [5]. Kinetic rates associated with the pathways have been calculated for simple cases such as a single adatom on a surface [4]. The rates can change dramatically as adatoms are introduced in the vicinity of a moving atom, i.e., its local atomic environment [6]. Predicting the rates for all possible relevant mechanisms and atomic environments that can be encountered in the dynamics presents a major challenge.

Figure 1. Large number of atomic environments can be encountered in the dynamics as a bimetallic alloy undergoes corrosion.

A promising approach to capture the local atomic environment involves the use of a cluster expansion model (CEM) [7]. CEM have been employed extensively for predicting thermodynamics properties [8], and only recently for predicting kinetic properties [6]. We describe the CEM in Sec. 2. The CEM parameters can be trained using a database of kinetic rates collected for a large number of atomic environments. However, this raises several questions, such as what is the size of the atomic environment associated with metal systems and how well can the CEM predict the environment dependent rates. The answer to these questions are provided in Sec. 2.

2. Cluster expansion model for metal homoepitaxy

Assuming that the lattice approximation is valid for the crystalline material, one can define a local environment \( \varepsilon \) consisting of \( N \) sites that can affect the kinetic rate. The value of the occupancy \( \sigma_\alpha \), which may be 0 or 1, denotes the absence or presence of an atom at the site \( \alpha \), respectively. Environment selected for the hop and exchange mechanism are shown in Fig. 2. Assuming that the Arrhenius law is obeyed, i.e.,

\[
k(\varepsilon) = \nu(\varepsilon) \exp\left(-\frac{E_a(\varepsilon)}{k_B T}\right),
\]

a CEM can be separately generated for the pre-exponential factor \( \nu \) and the activation barrier \( E_a \). Here \( k_B \) is the Boltzmann constant and \( T \) is the temperature.

We employ the embedded atom method (EAM) potential of Ref. [9] to describe the interactions between the metal atoms. Consider the example of a single Ag adatom hop. The activation barrier for a hop move is 0.5 eV. The barrier remains unchanged when one adatom is introduced into the environment at either \( \sigma_9 \) or \( \sigma_{19} \) of Fig. 3a. However, presence of adatoms at both sites \( \sigma_9 \) or \( \sigma_{19} \) results in an increase in the barrier by 0.14 eV – a synergistic effect that cannot be described by the bond-counting method. This also shows that the barriers depend on the environment in a non-intuitive manner. Fig. 2c shows that the pre-exponential factor can vary over two-orders of magnitude, whereas the activation barrier, which varies between 0.06 eV to about 1 eV depending on the environment,
results in a 14 order-of-magnitude variation in the rates at 300 K. Similar behavior is observed for Al, Cu, Pd, Pt and Ni [6]. For this reason, we focus our attention on the activation barrier.

Figure 2. Atomic environments selected for a) hop and b) exchange mechanism. Only adatom locations are included in the environment. Color denotes symmetrically equivalent sites. Variation in pre-exponential factor and barrier for more than 7500 randomly selected environments is shown in panels c and d.

The CEM is written as a sum of contributions from clusters of sites of different sizes, e.g., single, pair, etc., weighted by an interaction parameter such that

$$E_n(e) = e_0 + \sum_i e_i \sigma_i + \sum_{i\neq j} e_{ij} \sigma_i \sigma_j + ...$$  \hspace{1cm} (2)

Here $e$ denotes the cluster interaction (CI) parameter of a particular cluster, and $e_0$ is the barrier only due to interactions with substrate atoms when the environment atoms are absent. CIs are estimated using a training set containing barriers for a large number of environments. Barriers are obtained by locating saddle points on the multidimensional energy landscape using the nudged elastic band method [10]. Next, we describe some of the key findings from our analysis.

2.1. Hop mechanism

CEM including terms up to triplet CIs in Eq. (2) were created for Ag, Al, Pt, Pd, Ni and Cu [6]. For the environment shown in Fig. 1a, the total number of CIs that need to be estimated are 3683. This number could have been lowered by arbitrarily choosing a smaller environment at the risk for sacrificing accuracy or by exploiting the symmetry in the lattice positions. After training the CEM, most CIs are found to be negligible small and in fact less than 40 CIs are found to be sufficient to capture the effect of the atomic environment with a correlation coefficient exceeding 0.99. Thus, CEM can reliably model the local environment effects. The relevant CIs include singlet, pair and triplet interactions.

Fig. 3a-d shows that most sites that give rise to the relevant CIs are common to all metals studied. Nearest neighbor (NN) interactions play a key role, however, the interactions are anisotropic. For e.g.,
sites such as $\sigma_9$ and $\sigma_{19}$ are found to be more important than $\sigma_{13}$. Similar behavior is observed with next NN atoms. Minor differences observed in the relevant environments shown in Fig. 3 arise because of the strength of the CIs. Interactions weaker than 0.03 eV in magnitude are considered to be too weak and are therefore ignored. Since the CIs for Pt and Pd are approximately two times larger than the ones for Ag, one finds that the relevant environment of Pt and Pd is also larger. The implication is that atoms distant from the hopping adatom can alter the rate constant by a significant amount. For instance, see locations $\sigma_{11}$ and $\sigma_{21}$ in Fig. 3d.

Figure 3. Environment atoms that influence the activation barrier are shown for a) Ag and Al, b) Cu, c) Ni and d) Pt and Pd.

2.2. Exchange mechanism

The ability of the CEM to predict the environment dependence of the hopping rates motivates its extension to concerted moves such as the exchange mechanism. In metals such as Pt, the exchange move involving a single adatom is preferred over a hop move. CEM of concerted moves have not been developed in the past. Here we describe some aspects of the model, while more details will be provided in an upcoming publication.

The first question that arises is how well the CEM is able to predict the activation barriers. A database of barriers was constructed using more than 10000 randomly selected environments for each metal from Fig. 1b. Most data (70%) was used for training the 352 CEM parameters, while remaining 10% and 20% was used for testing and validation, respectively. Triplet and larger cluster interactions were ignored. Finally, the number of interactions with magnitude greater than 0.01 eV was found to be 39, 81, 59, 70 and 169 for Ag, Pt, Pd, Cu and Ni. The agreement between the trained CEM and the NEB is excellent for Ag, Pt and Pd as shown in Fig. 4a-c. However, the agreement is not spectacular for Cu and Ni (Fig. 4d-e).

The poor agreement observed for Cu and Ni may point to the need for triplet interactions. The number of CEM parameters to be trained increases to 2952 when triplet interactions are included. Unfortunately, the dataset was insufficient for training such a large number of parameters, i.e., more barriers should be included. Moreover, the computational time required to estimate the parameters can be few days even using efficient optimization methods like the L-BFGS method. For this reason, we restrict ourselves to the pair interactions.
Figure 4. Parity plot for barriers calculated using CEM and NEB. While good agreement is observed for a) Ag, b) Pt and c) Pd, the agreement is poor for d) Cu and e) Ni.

The CEM reveals the relevant local environment (see Fig. 5) that influences the barrier for the exchange move. A relatively small local environment is associated with Ag and Pd, while Cu and Ni have large environments associated, i.e., longer-range interactions are present in Cu and Ni. This may result in large number of CIs for the latter, and explain the source of the difficulties encountered while training the CEM for Cu and Ni.

Figure 5. Environment atoms that can influence the activation barrier are shown for a) Ag and Pd, b) Pt, c) Ni and d) Cu.

Several common features are also observed. Presence of adatoms at sites labelled $\sigma_6$ and $\sigma_{10}$ results in an increase in barrier by 0.27-0.56 eV depending on the metal. However, the interaction $e_{6,10}$ denoting the simultaneous presence of adatoms at $\sigma_6$ and $\sigma_{10}$ is negligible. Similarly, interactions $e_7$ and $e_{15}$ are also important as they raise the barrier. However, the next NN sites $\sigma_{11}$ and $\sigma_{16}$ are
generally unimportant. Presence of an adatom at $\sigma_{17}$ and $\sigma_{21}$ results in a decrease in the barrier. The remaining sites participate through the pair interactions.

3. Conclusions

The cluster expansion model (CEM) has been employed for predicting the atomic environment dependence of the hop and exchange moves in homoepitaxies of Ag, Pt, Pd, Cu and Ni. The CEM containing up to triplet interactions can capture the dependence reasonably well for hop moves for all metals studied, and exchange moves in Ag, Pt and Pd. However, the model is inappropriate for Cu and Ni presumably the long-range cluster interactions present in these metals.

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