First-Principles Parameter Estimation for Dynamic Monte Carlo of a Lattice-Gas Model

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Abstract. We present preliminary results demonstrating how dynamic Monte Carlo transition rates for lateral diffusion can be found from quantum *ab initio* calculations. As an example, we consider the specific problem of Br electrosorption onto Ag(100), and we use density functional theory (DFT) to calculate the Br binding energy at the four-fold hollow, bridge, and on-top sites. From these energies, we develop a simplified corrugation potential. Using Langevin simulations, we analyze the motion of a single particle in this corrugation potential and study the transition rates between lattice-gas states. We further test the corrugation potential by comparing results of an off-lattice equilibrium simulation with the previous results for a lattice-gas model. We find that our DFT barrier estimates are consistent with a lattice-gas treatment of the statics and dynamics of the system.

1 Introduction

The static and dynamic properties of surface adsorption models are often treated within a lattice-gas approximation. This approximation has the implicit assumption that the lateral energy barriers at the surface are large compared to the temperature and lateral interaction energies, thus localizing the particles at the lattice-gas sites. This simplification has yielded remarkably accurate equilibrium results for real experimental systems [1,2]. However, the stochastic transition rates needed for dynamic Monte Carlo (DMC) simulations are not known, and although many transition rates satisfy detailed balance (and thus lead to the correct equilibrium distribution), most of these rates do not represent a physically realistic dynamic.

In DMC, the Arrhenius transition rate is often assumed [1,2],

$$R(F|I) = \nu \exp\left[-\left(\frac{E_F - E_I}{2} + \Delta_X\right) \Big/ k_{\mathrm{B}}T\right], \tag{1}$$

where $R(F|I)$ is the probability per unit time of making a transition from the lattice-gas state I to the lattice-gas state F, ν is an attempt frequency, E_I and E_F are the energies of the states I and F, respectively, Δ_X is an energy barrier associated with the process X, k_{B} is Boltzmann's constant, and T is the temperature ($k_{\mathrm{B}}T$=25 meV at room temperature). Here, we consider only the barrier associated with lateral diffusion, Δ, since the barrier associated with adsorption/desorption is much more complex and has yet to be studied.

Here, we demonstrate how density-functional theory (DFT), Langevin simulations, and off-lattice equilibrium Monte Carlo can be used to examine the validity of the Arrhenius behavior and to determine the parameters ν and Δ for lateral diffusion on the surface. As an example, we present results for Br/Ag(100), which has been studied extensively by both experiment [3,4] and simulation [2,5]. No explicit water molecules were considered, although liquid water is one source of noise and damping in the Langevin simulations. This simplification is reasonable since Br/Ag(100) has the same binding site and ordered phase in both vacuum [3] and aqueous solution [4].

2 First-Principles Calculations

The Ag(100) surface is modeled by supercells with five metal layers separated by a vacuum region equivalent to seven metal layers. We used a 3×3 surface cell, so that each metal layer in the supercell contains nine atoms (totaling 45 silver atoms). Br is adsorbed on both sides of the Ag slab, and all the Ag atoms were initially located at their bulk positions. The T=0 K lattice constant of bulk Ag, as determined by our calculations, is 4.17 Å as compared to the experimentally accepted value of 4.09 Å [6].

The total-energy calculations were performed with DFT using the pseudopotential method and a plane-wave basis set. For greater accuracy than the local density approximation (LDA), we used the generalized gradient-corrected exchange-correlation functionals (GGA) developed by Perdew and Wang [7,8] and the Vanderbilt ultrasoft pseudopotentials [9]. The calculations were conducted with a plane-wave energy cutoff of 20 Ry and 9 special $\boldsymbol{k}$-points in the irreducible part of the two-dimensional Brillouin zone of the 3×3 surface. Test calculations with 16 special $\boldsymbol{k}$-points were also carried out to check convergence. Optimization of the atomic structure was performed for each supercell using the conjugate-gradient technique [10], and all the structures were fully relaxed until the forces acting on the atoms were smaller than 0.05 eV/Å.

Using these first-principles methods, we calculated the binding energy for Br on Ag(100) in vacuum at the four-fold hollow, two-fold bridge, and on-top sites. In agreement with experiment [3,4], we find that the four-fold hollow site has the highest binding energy. The energy differences for 9 $\boldsymbol{k}$-points are $E_{\mathrm{bridge}} - E_{\mathrm{hollow}} = 155 \pm 1$ meV and $E_{\mathrm{top}} - E_{\mathrm{hollow}} = 483 \pm 3$ meV, where the error is estimated from the difference between the 9 and 16 $\boldsymbol{k}$-point calculations. The convergence with slab thickness has yet to be checked.

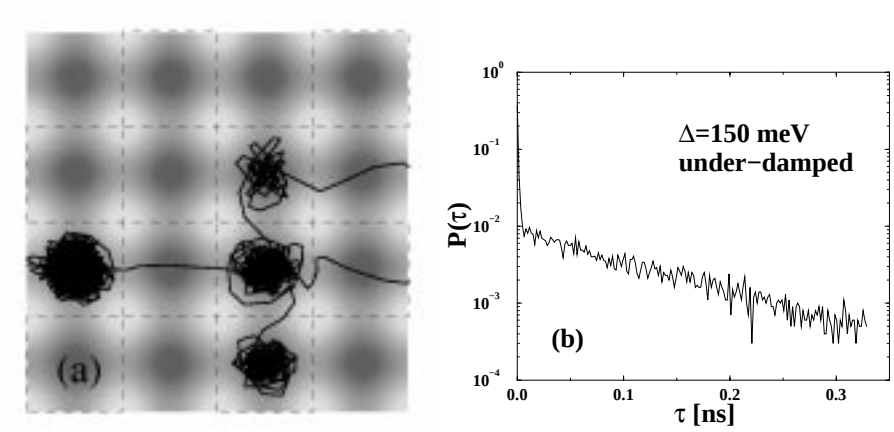

Fig. 1. Single Br adparticle in a sinusoidal corrugation potential simulated with an under-damped Langevin dynamic. The parameters are Δ=150 meV and $k_{\mathrm{B}}T$=25 meV (room temperature). (**a**) A typical particle trajectory in the corrugation potential of a 4×4 section of a much larger lattice. The grayscale indicates the magnitude of the potential, where lighter shades indicate less favorable binding. The dashed lines indicate boundaries between lattice-gas states. (**b**) The probability density of the crossing time, τ, for 10,000 crossings between lattice-gas states. The exponential tail at large τ indicates Arrhenius behavior, and the significant deviation from this behavior at short τ indicates the under-damped "running" behavior seen in (**a**), which is also discussed in the text

3 Langevin Dynamics in a Corrugation Potential

We approximate the full corrugation potential for Br/Ag(100) as a simple two-dimensional sinusoidal function,

$$U(x,y) = \frac{\Delta}{2}\left[\cos\left(\frac{2\pi x}{a}\right) + \cos\left(\frac{2\pi y}{a}\right)\right] + \Delta\,, \tag{2}$$

where 2Δ is the difference between the maximum and the minimum binding energy, and a is the lattice constant of the Ag(100) surface. More negative U represents stronger binding energy. This form has the expected lateral symmetries from Section 2, but with the additional symmetry that $E_{\mathrm{top}} - E_{\mathrm{bridge}} = E_{\mathrm{bridge}} - E_{\mathrm{hollow}}$.

We place a single Br adparticle within this potential, where it is evolved under the Langevin equation of motion. A typical under-damped trajectory is shown in Fig. 1(a) for Δ=150 meV. This Δ is consistent with the corrugation found by DFT in Section 2. For this under-damped motion, a significant amount of "running" behavior is seen, in which the particle hops multiple barriers within a very short time [see Fig. 1(b)]. We define the crossing time, τ, as the time spent in one lattice-gas state before hopping the lattice-gas boundary into another state. The probability density of τ is shown in Fig. 1(b). The

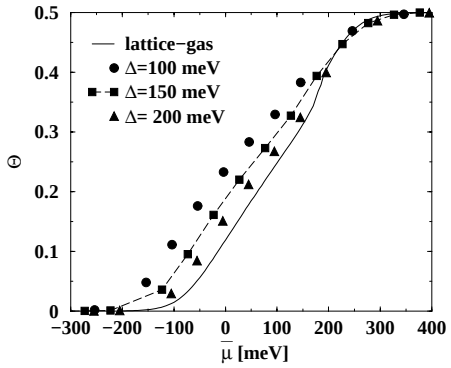

Fig. 2. Off-lattice equilibrium Monte Carlo isotherm for $k_{\mathrm{B}}T$=25 meV, L=32, and various Δ. The coverage, Θ, is shown. The previously determined lattice-gas isotherm [2] is shown for comparison as the heavy solid line and is consistent with the isotherm for $\Delta \geq 150$ meV. No attempt to fit the off-lattice model directly to experiment has yet been made

Arrhenius behavior can be seen for large τ as an exponential tail in the distribution; however, the "running" behavior caused by the weak damping creates significant deviations at short τ. These short-time deviations are expected to decrease for stronger damping, where DMC is most valid. An obvious drawback of using Langevin simulations is that the physically relevant damping is unknown.

4 Off-Lattice Equilibrium Monte Carlo

The validity of the corrugation potential can be tested separately from the Langevin simulation by performing an off-lattice equilibrium Monte Carlo simulation. The Hamiltonian for the off-lattice model is

$$\mathcal{H} = -\frac{1}{2}\sum_{ij}\phi_{ij} + \sum_{i=1}^{N_{\mathrm{surf}}} U(x_i, y_i) - \bar{\mu} N_{\mathrm{surf}}\,, \tag{3}$$

where i and j index adsorbed Br, $\frac{1}{2}\sum_{ij}$ is a sum over all Br pairs where the factor of 1/2 prevents double counting, ϕ_{ij} is the lateral Br-Br interaction energy for the pair i, j within the adlayer, $\sum_{i=1}^{N_{\mathrm{surf}}}$ is a sum over all adsorbed Br, $U(x_i, y_i)$ is the value of the corrugation potential for the i-th Br, $\bar{\mu}$ is the electrochemical potential, and N_{surf} is the number of Br on the surface. The sign convention is such that negative ϕ_{ij} implies repulsion and $\bar{\mu} > 0$ favors adsorption. A surface of $L \times L$ adsorption sites with periodic boundary conditions was used.

In order to compare with the previous lattice-gas model [2], similar interactions, $\phi(r)$, were used. We define R_{ion} as the ionic diameter of Br. For $r > R_{\mathrm{ion}}$, a repulsive Lennard-Jones potential was used. For $5a \geq r > R_{\mathrm{ion}}$ a repulsive $1/r^3$ potential was used, identical to that of Ref. [2]. For $r > 5a$, the interactions were truncated. Furthermore, we required that $\phi(r)$ be continuous for all r and that $\mathrm{d}\phi(r)/\mathrm{d}r$ be continuous at R_{ion}.

The thermal properties of this system were determined by equilibrium Monte Carlo using a ghost-particle method with the appropriate corrections for a grand-canonical ensemble [11]. A corrugation amplitude Δ=150 meV is reasonably consistent with the previous lattice-gas results, see Fig. 2.

5 Summary and Conclusions

We have used density-functional theory (DFT) to estimate the corrugation potential for Br adsorbed onto Ag(100) in vacuum. Langevin simulations are consistent at large crossing times with the Arrhenius behavior assumed previously for dynamic Monte Carlo (DMC) simulations [2]. However, underdamped Langevin trajectories show significant deviations from the Arrhenius behavior at short crossing times, which is associated with "running." Off-lattice simulations of Br on Ag(100) using the simplified corrugation potential are consistent with the previous lattice-gas model.

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