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An emulator for kinetic Monte Carlo simulations of kinetically controlled metal electrodeposition

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Abstract. In recent years there has been an increasing interest in developing models for atomistic-scale simulations of electrochemical metal deposition processes. One of the most interesting and challenging features of such models is their capability to reproduce the physical evolution of the final deposition shape in a practical time scale. To date, most of the available models are limited to the simulation of a few nanoseconds of the physical phenomenon, for instance molecular dynamics, and there are very few methods, including kinetic Monte Carlo, that can reach to reproduce some seconds due to the requirement of an enormous computational cost. In this paper we present a surrogate-assisted kinetic Monte Carlo method based on Gaussian process emulation as a tool for predicting the final electrodeposition shape in a kinetically controlled copper electrodeposition on a gold substrate. The main advantage of this method is its ability to dramatically reduce the computational cost of the kinetic Monte Carlo simulation while yielding accurate results.

1. Introduction

Atomistic scale modelling, e.g., molecular dynamics and kinetic Monte Carlo (KMC), is frequently used to gain fundamental understanding of an enormous variety of physical processes [1] that may be difficult or even impossible to visualise or study experimentally, e.g., there have been very few experimental characterisation studies of copper deposition on a gold substrate (e.g., [2, 3]). Such methods can be combined with *ab-initio* [4] and macroscopic approaches to develop multi-scale models. KMC [5] is a popular method for studying the dynamical evolution of systems of atoms or molecules undergoing various processes, such as adsorption/desorption, reactions and surface diffusion, by approximate solution of a Master equation. In order to achieve this, a hierarchy or transition probabilities is required and detailed balance must be satisfied, which is possible using different approaches [1].

In recent decades there have been several attempts at atomistic-scale simulations of electrochemical metal deposition processes [6, 7, 8, 9, 10, 11], particularly for studying the evolution of the deposition profile. The computational cost increases with the number of deposition sites and deposition thickness required. More generally, for multiple processes, computational cost can be very large for cases in which certain of the processes occur on much faster time scales than the others. In this paper, therefore, we present a surrogate-assisted kinetic Monte Carlo method based on Gaussian process (GP) emulation as a tool for predicting the final electrodeposition shape in a kinetically controlled copper electrodeposition on a gold substrate.



The method is able to dramatically reduce the computational cost of the KMC simulation while yielding accurate results.

The outline of this paper is as follows. In Section 2 we describe the mathematical model, the KMC simulator and data used for the simulations of copper electrodeposition onto a gold substrate. We then describe how to build a GP emulator for the KMC simulator. In Section 3 we show and discuss the numerical results. Concluding remarks are provided in Section 4.

2. Description of the model

The idealized electrodeposition system consists of metal ions M^{2+} present in a given electrolyte solution and metal atoms (M) already deposited on a given substrate (S). The metal atoms are restricted to be on a spatial lattice of a face-centred cubic (fcc) crystal system of (111) orientation (see, e.g., [11, 12, 13]). The substrate is assumed to have the same lattice spacing as the deposit, and any M^{2+} ion is first reduced at the electrode surface, and then deposited or diffused either on the substrate or on a pre-deposited M atom. The deposition process is assumed to be kinetically limited, and thus mass transfer effects can be neglected. In this paper we are considering a simplified 2D cross-sectional KMC model and thus the use of either solid-on-solid approximations [13] or the embedded atom method [12] for computing the activation energies is not considered. The surface diffusion rates are updated from the initial values during the deposition process according to the coordinate number of the diffusing atom and the nature of its neighbour atoms. The details of the substrate and deposited metal were purposely kept simple in order to simulate the range of deposit morphologies that arise from different rates of deposition and surface diffusion.

2.1. Kinetic Monte Carlo Simulator

The two possible events that will be considered in this study are deposition and surface diffusion. The depositions are considered to occur only on the lattice sites having two neighbouring atoms underneath, i.e., a deposited atom has a minimum coordination number of 3. The deposition rates on M and S are taken from the literature [6, 11] and are given by:

$$r_{dep_{M-M}} = k_{M-M}C_{M^{2+}} + e^{-nF\eta_{M-M}/(2RT)}, r_{dep_{M-S}} = k_{M-S}C_{M^{2+}} + e^{-nF\eta_{M-S}/(2RT)} \quad (1)$$

where: F , R and T are Faraday's constant ($s A mol^{-1}$), the ideal gas constant ($J K^{-1} mol^{-1}$) and temperature (K), respectively; k_{M-M} and k_{M-S} the deposition rate constants for M on M and M on S, respectively; $C_{M^{2+}}$ is the concentration of M^{2+} ions at the electrode interface; and $n = 2$ is the number of electrons transferred. The overpotentials η_{M-M} and η_{M-S} are respectively the difference between the applied potential and the equilibrium potential for the M^{2+}/M couple and between the applied potential and the nucleation potential. The charge-transfer coefficients are assumed to be equal to 1/2.

The surface diffusion rates on M and S for deposited atoms to nearest neighbouring sites are respectively [11]:

$$r_{dif_{M-M}} = v_{M-M}e^{-E_{act_{M-M}}/(RT)}, r_{dif_{M-S}} = v_{M-S}e^{-E_{act_{M-S}}/(RT)} \quad (2)$$

where the E_{act} denote the activation energies, i.e., the energy barriers that a given atom must overcome to be diffused either on the metal or the substrate. In this study we will assume that those energy barriers depend only on the coordinate number N_{cord} and the energy barriers E_{M-M} and E_{M-S} for the M-M and M-S bonds respectively, and are given by [11]:

$$E_{act_{M-M}} = N_{cord}E_{M-M}, E_{act_{M-S}} = 2E_{M-S} + N_{cord}E_{M-M}. \quad (3)$$

As we wish to build a surrogate model for the KMC method, we need experimentally validated parameter values which allow us to guarantee that the GP emulator is trained properly. For

Table 1. Parameter values used in the KMC simulations. Values obtained from [11].

Symbol	Meaning	Parameter value
ν_{M-M}	Jump frequency for surface diffusion of M on M	$3.9 \times 10^5 \text{ s}^{-1}$
ν_{M-S}	Jump frequency for surface diffusion of M on S	$3.9 \times 10^5 \text{ s}^{-1}$
η_{M-M}	Overpotential for deposition on M	-0.13 V
η_{M-S}	Overpotential for deposition on S	-0.03 V
k_{M-M}	Rate constant for deposition on M	$0.204 \text{ m}^3 \text{ mol s}^{-1}$
k_{M-S}	Rate constant for deposition on S	$0.143 \text{ m}^3 \text{ mol s}^{-1}$
$C_{M^{2+}}$	Concentration of M^{2+} ions at electrode surface	0.32 mol
E_{M-M}	Energy barrier for a M-M bond	0.13 eV
E_{M-S}	Energy barrier for a M-S bond	0.35 eV

that purpose, in this paper we will use the parameter values used in [11], with $M = \text{Cu}$ and $S = \text{Au}$. The values are reproduced in Table 1. Macroscopic dimensions for the parallel and normal directions to the surface of the substrate based on the fcc lattice can be calculated as [11] $l_w a \sqrt{2}/2$ and $l_y a \sqrt{3}/8$, respectively, where l_w denotes the lattice width, l_y the number of the layers of lattice sites, and a the lattice constant (m) for M. In this paper we will set $a = 3.61 \times 10^{-10}$.

The KMC algorithm used follows the approach of Liu *et al.* [11] for the simulating metal electrodeposition by monitoring the whole process, i.e., starting when the first atom is deposited and finishing when the simulation time has been reached. The KMC algorithm works by establishing a dynamical hierarchy for the transition probabilities of the events (e.g., adsorption and desorption), with time increments for successful (independent) events given by a Poisson process. It can be implemented as follows:

- (i) Find initial values for the constants in the expressions introduced in Section 2.1 (experimental or *ab-initio* simulations). Define the type of lattice configuration for the metal atoms that will be considered.
- (ii) Store the initial rates (normalized) for the possible events in three different matrices (for deposition and surface diffusion to the left/right), with each entry denoting a spatial location. Set the simulation time. Build an array r_1, \dots, r_n of the non-zero elements of the rate matrices and normalize this array to form an array with elements $R_i = \sum_{k=1}^i r_k / \sum_{k=1}^n r_k$.
- (iii) Sample a random number ζ from the Uniform distribution $U(0, 1)$. Decide on the event to occur and position by using the first index p from the normalized array that satisfies $R_p \geq \zeta$. Periodic boundary conditions are assumed in the horizontal direction.
- (iv) Update the rates of the deposited atom and its neighbours. Increase the time step with $\Delta = -\ln(\zeta) / \sum_i r_i$. Repeat (iii)-(v) until the simulation time has been reached.

Note that the number of atomic layers in a simulation corresponds to the simulation time specified in the KMC algorithm.

2.2. Gaussian process emulation of electrodeposition profiles

In this section we show how to build a surrogate model based on GP regression [14] for the KMC simulator. This will keep the qualitative features of the original simulator and will reduce considerably the overall computational cost. The GP emulator is provided with prior mean and covariance functions, which are updated in light of observed data obtained from KMC simulations. The updated (or posterior) functions are then used for inference [14].

In this paper, the KMC simulator outputs (or observed values) correspond to the final thickness of the deposit measured at carefully selected spatial locations (or design points) within the lattice. These spatial locations are taken to be the inputs. The data set formed by the design points and the observed values is called the training set. To generate the set of design points we simply spread the points to cover the simulation domain of the input space $[0, l_w] \subset \mathbb{R}$. Then for each spatial location $x \in [0, l_w]$, we can estimate the thickness of the deposit by setting $y = f_{kmc}(x)$, where f_{kmc} represents the KMC simulator which returns the thickness of the deposit at a desired lattice site. Note that a design point $x' \in [0, l_w]$ might not match any of the lattice sites, and, in that case, we take as $f_{kmc}(x')$ the value (or noisy output) of $f_{kmc}(x'')$ at the nearest neighbour x'' on the lattice.

There are various methods available for sampling the design points [15]. In this paper, we used a low discrepancy (Sobol) sequence [16]. The GP emulator inputs are denoted by ξ and are distributed according to $\mathcal{U}(0, l_w)$. We choose the uniform distribution to be consistent with the sampling procedure of the KMC algorithm (step (iii)). Other distributions for the GP inputs, for instance $\mathcal{N}(0, 1)$, may be also considered. To distinguish the GP emulator inputs from the training data, we will denote the design points by $\hat{\xi}$. Thus, to form the set, we first generate d Sobol points in $[0, 1]$, and second, we compute the inverse cumulative distribution function of a $\mathcal{U}(0, 1)$ random variable.

In this paper, we use a zero mean function and a square exponential (SE) covariance function for the prior specification, which is given in terms of three hyperparameters as follows [14]:

$$k(\xi, \xi') = \sigma_f^2 \exp\left(-\frac{1}{2\ell} \|\xi - \xi'\|^2\right) + \sigma_n^2 \delta_{ij}, \quad (4)$$

where σ_f^2 is the process variance, ℓ is the length scale, σ_n^2 is the noise variance, δ_{ij} is the Kronecker delta and $\|\cdot\|$ is the Euclidean norm. To find suitable values for the hyperparameters above, we used a maximum likelihood estimate (MLE) by minimizing the negative log marginal likelihood with respect to the hyperparameters (see, e.g., [17, 18]). Finally, we can make predictions for new untested inputs $\xi^* \in [0, l_w]$ by using the following equations [14]:

$$m_*(\xi^*) = \Sigma(\xi^*, \mathbf{X}) [\Sigma(\mathbf{X}, \mathbf{X}) + \sigma_n^2 \mathbf{I}]^{-1} \mathbf{y}, \quad (5)$$

and

$$k_*(\xi^*, \xi^*) = k(\xi^*, \xi^*) - \Sigma(\xi^*, \mathbf{X})^T [\Sigma(\mathbf{X}, \mathbf{X}) + \sigma_n^2 \mathbf{I}]^{-1} \Sigma(\xi^*, \mathbf{X}) \quad (6)$$

in which $\Sigma(\xi^*, \mathbf{X}) = (k(\xi^*, \hat{\xi}_1), \dots, k(\xi^*, \hat{\xi}_d))^T$. The (i, j) -th entry of $\Sigma(\mathbf{X}, \mathbf{X}) \in \mathbb{R}^{d \times d}$ is given by $k(\hat{\xi}_i, \hat{\xi}_j)$. Expression (5) for the GP posterior mean m_* can be then used to emulate the simulator output at any new input ξ^* , i.e., we can write $m_*(\xi^*) \approx f_{kmc}(\xi^*)$. Expression (6) provides the predictive variance (error bound) in this estimate of the output.

3. Results

In this section we report the results obtained for a set of six KMC simulations of copper deposition onto a gold substrate. The simulations were obtained over continuous intensive CPU computations on a 12-core Intel Xeon cluster processor. All the Cu atoms are restricted to be on an fcc lattice of (111) orientation, as previously described. For this set of experiments the lattice width was set to $l_w = 650$. This means that we are considering a lattice with 650 sites in the x -axis (horizontal) direction for atom occupancy. The simulations were performed for six different simulation times which correspond to the number of atomic layers deposited in each simulation.

The goal of this experiment was to use a GP emulator to replace the KMC simulator and predict the final shape of the deposits much more rapidly. The GP emulator was trained



Figure 1. Simulated KMC (top) and GP predicted (bottom) deposition shapes for a lattice size of 650 atoms and 200 atomic layers.

using 128 design points and the estimation of the hyperparameters was done on-the-fly and independently for each different KMC simulation time. Table 2 shows the CPU time spent in each of the KMC simulations and the corresponding CPU time for the GP predictions. The range of times were chosen in order to compare the performance between quick (computationally cheap) and fast (computationally expensive) simulations. The corresponding final lattice sites (l_y) obtained from each simulation is also provided.

From Table 2 we can see that while for the quickest KMC simulation (simulation time = 200) the CPU times between the KMC and GP methods are very similar, for higher simulation times (e.g., 350, 400 and 450) the difference in CPU times is considerable. We remark that the simulation times are dimensionless and refer to the number of atomic layers deposited in one cycle of the KMC algorithm, i.e., simulation time = 1 means that the KMC algorithm will stop after 1 atomic layer has been deposited. Note also that for augmenting the thickness of the deposit by a factor of four, i.e., from 10.39 nm (simulation time 200) to 41.33 nm (simulation time 450), the CPU KMC time resources are ten times higher, while the difference between the CPU GP times for the same simulation times remain very close to each other. We can conclude that for long simulation times, the use of GP emulators is of huge benefit.

A selection of three final shapes (simulation times = 200, 300 and 400) computed with the KMC simulator and the GP emulator are shown in figures 1, 2 and 3. The reason why successive KMC simulations show different morphologies is a consequence of the stochasticity of the KMC simulator. In this paper our goal was to develop a benchmark GP emulation model to reproduce KMC simulated electrodepositions. Thus, each of the GP results are based only on a single KMC simulation, i.e., the one shown above in each of the figures. Thus each of the simulations are computed independently from different random processes. These figures show excellent agreement between the emulator and simulator. GP emulators have been shown to perform well for relatively smooth response surfaces. In this case, the deposition profile is discontinuous yet the GP emulator is successful in predicting the profile with great accuracy. The case shown in figure 1, with fewest atoms being deposited and therefore with the highest number of peaks (or local maxima), presents the most challenging scenario. Nevertheless, the deposition shape predicted by the GP (figure 1 (bottom)) shows excellent agreement with the KMC simulation. It is then expected that along with an increase in the number of atoms deposited, and consequently a smoother target deposition surface, the GP emulator accuracy increases (figures 2 and 3) and the computational cost reduces.

4. Conclusions

In this paper we use Gaussian processes regression to emulate the early stages of metal electrodeposition. The GP emulator performs the simulations in a much shorter time than the original KMC simulator and is able to reproduce the final morphology of the deposition



Figure 2. Simulated KMC (top) and GP predicted (bottom) deposition shapes for a lattice size of 650 atoms and 300 atomic layers.



Figure 3. Simulated KMC (top) and GP predicted (bottom) deposition shapes for a lattice size of 650 atoms and 400 atomic layers.

Table 2. Sequence of the KMC simulation and GP emulation results for different deposition times on a substrate of width 165.75 nm (lattice size of $l_w = 650$ atoms).

CPU KMC time (s)	CPU GP time (s)	Simulation time	l_y	Deposit thickness (nm)
13.52	3.25	200	17	10.39
17.83	4.11	250	29	17.02
20.54	5.75	300	30	17.24
41.20	5.77	350	33	19.01
107.58	5.89	400	48	27.85
153.10	5.90	450	71	41.33

process for different simulation times with high accuracy. Furthermore, the GP emulator allows us to extrapolate the micro-structure of the KMC simulations to a practical size of the problem.

Several extensions are the focus of ongoing research. The first is the incorporation of physical constants such as adsorption/desorption rates, as well as the consideration of the simulation time as an input. This would permit a rapid extensive study of the deposition profiles for (simultaneously) different physical systems, domain sizes, and simulation times. Another possibility is to extend the existing model to a higher dimensional output spaces by considering a 3D model. In both cases a dimension reduction method on this output space becomes necessary either using a linear [19] or non-linear [20] approaches. Such an emulator could form the basis for sensitivity and uncertainty analyses.

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