Dynamic response of $Ag$ monolayers adsorbed on $Au(100)$ upon an oscillatory variation of the chemical potential: A Monte Carlo simulation study.

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Abstract

Based on the fact that the underpotential electrochemical deposition of Ag atoms on the Au(100) surface exhibits sharp first-order phase transitions at well-defined values of the (coexistence) chemical potential ($\mu_{\text{coex}}$), we performed extensive simulations aimed at investigating the hysteretic dynamic behavior of the system close to coexistence upon the application of a periodic signal of the form $\mu(t) = \mu_{\text{coex}} + \mu_o \sin(2\pi t/\tau)$, where $\mu_o$ and $\tau$ are the amplitude and the period of the sweep, respectively. For relatively short periods and small enough amplitudes the system becomes trapped either at low or high Ag coverage states, as evidenced by recording hysteresis loops. This scenario is identified as dynamically ordered states (DOS), such that the relaxation time ($\tau_{\text{relax}}$) of the corresponding metastable state obeys $\tau_{\text{relax}} > \tau$. On the other hand, by properly increasing $\mu_o$ or/and $\tau$, one finds that the Ag coverage gently follows the external drive (here $\tau_{\text{relax}} < \tau$) and the system is said to enter into dynamically disordered states (DDS), where hysteresis loops show almost symmetric limiting cycles. This symmetry breaking between limiting cycles driven by an external signal is discussed in terms of the concept of (out-of-equilibrium) Dynamic Phase Transitions between DOS and DDS, similar to those encountered when a magnetic system is placed in the presence of a variable external magnetic field. However, a careful finite-size scaling study reveals that, at least at $T = 300K$, the Ag/Au(100) system does not exhibit true second-order phase transitions but rather a crossover behavior between states. A diagram showing the location of the ordered and disordered states in the $\mu$ versus $\tau$ plane is obtained and discussed.

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I. INTRODUCTION

The term hysteresis is used to describe the lagging of an effect behind its cause. Hysteresis is a common phenomenon that is observed in a great variety of physical, chemical, and biological systems. However, the magnetization response of a ferromagnet in the presence of an oscillatory magnetic field is probably the best known example of hysteresis.

Hysteresis in thermodynamic systems is often related to the existence of first-order phase transitions, which are the sources of nonlinearities always associated with hysteretic behavior. Within this context, systems exhibiting first-order phase transitions and capable of becoming coupled to an external oscillatory drive are excellent candidates for the observation of (out-of-equilibrium) dynamic phase transitions (DPT’s). A DPT takes place between a dynamically ordered state (DOS) and a dynamically disordered state (DDS) when the drive changes from high to low frequencies. Most studies related to DPT’s have been performed by using magnetic systems. Particularly, the Ising ferromagnet on a two-dimensional square lattice has become the subject of great interest \([1, 2, 3, 4, 5]\). In this case, an oscillatory magnetic field causes the occurrence of a second-order DPT that is believed to belong to the universality class of the standard Ising model in the same dimensionality \([1, 2, 3]\). For a recent review see reference \[6]\.

Aside from ferromagnets, sharp first-order transitions are also observed in other physical systems of relevant practical importance, namely upon the underpotential electrochemical deposition (Upd) of metal atoms on metallic surfaces. Upd implies the deposition of a metal on the surface of an electrode of different nature at potentials more positive than those expected from Nernst equation \([7, 8, 9, 10, 11]\). Therefore, this kind of phenomena can be intuitively understood by considering that, under Upd conditions, it is more favorable for the adsorbate to be deposited on a substrate of different nature than on a surface of the adsorbate itself. For a recent review on this subject see e.g. the book by Budevski et al \[8]\ while for the discussion of theoretical aspects see e.g. \[9]\.

The interpretation of Upd as a phase transition has been employed by Blum et al \[12]\ in order to model the underpotential deposition of Cu on Au. Subsequently, the concept has been generalized by Staikov et al \[13]\. The formation and growth of well ordered overlayers can be understood as a first-order phase transition that takes place at the electrode-solution interface. This kind of transition can be detected by observing a discontinuity in the adsorp-
tion isotherm that is accompanied by a very sharp peak of the corresponding voltammetric profile [12]. It should also be mentioned that this oversimplified picture is not completely free of controversy and is the subject of current debate [8]. Computer simulations performed by one of us [14] have recently contributed to the understanding of the deposition of Ag on Au (100), where sharp first-order transitions in the adsorption isotherms have been reported.

Within this context, the aim of the present paper is to study the dynamic behavior of the Ag/Au(100) electrochemical system by means of computer simulations. Taking advantage of our experience in the simulation of the equilibrium properties of such system, here we propose investigating its response to periodic variations of the chemical potential. This situation can experimentally be achieved just by changing the applied potential. Of course, the effect of oscillatory variations of different frequency will be studied and discussed.

The organization of this paper is as follows: in Section II we describe the model and the numerical simulation technique. Also, some relevant results corresponding to the system Ag/Au(100) under equilibrium are discussed. The obtained results are presented and discussed in Section III. Our conclusions are stated in Section IV where some experiments that could account for the numerical simulations are suggested.

II. DESCRIPTION OF THE MODEL AND THE SIMULATION METHOD.

Monte Carlo simulations are performed assuming a lattice model, with periodic boundary conditions, to represent the square Au(100) substrate. Each lattice site represents an adsorption site for a Ag atom. It may absorb or desorb. If the crystallographic misfit between the involved atoms is not important, it is a good approximation to assume that the adatoms adsorb on defined discrete sites on the surface, given by the positions of the substrate atoms. This is the case of the very well studied Ag/Au(100) system [15, 16, 17, 18]. The Grand Canonical ensemble is used throughout and the transitions rates are evaluated according to the Metropolis algorithm. That is, for a given temperature \( T \) and chemical potential \( \mu \), a site is selected at random and its state is changed, becoming either empty or occupied by Ag atoms, with probability

\[
W = \min[1, \exp(-\Delta E - \mu \Delta N)/k_B T)],
\]

where \( k_B \) is the Boltzmann constant, \( \Delta N \) is +1 or −1 depending of the change of occupation
(adsorption or desorption) and $\Delta E$ is equal to $E_{\text{ads}}$ or $-E_{\text{ads}}$. These adsorption energies have previously been calculated by employing the embedded atom model (see below) considering the environment of the involved site, taking into account first, second and third neighbors. A careful discussion of the assumptions involved in the lattice model in the light of the available experimental information has already been performed [14] and does not need to be repeated here.

A very important feature of the used method is that the interatomic potentials involved in the Monte Carlo simulations are first evaluated by means of the embedded atom model (EAM). The EAM assumes that the total energy of an arrangement of $N$ atoms may be calculated as the sum of individual energies of the atoms. Thus, the attractive contribution to the EAM potential is given by the embedding energy, which accounts for many-body effects. On the other hand, the repulsion between ion cores is accounted for pair potentials depending on the distance between cores only. For additional details see reference [14] and references therein. For the purpose of the present work, the EAM has been parametrized to fit available experimental data such as elastic constants, dissolution enthalpies of binary alloys, bulk lattice constants and sublimation heats [19].

The Grand Canonical Monte Carlo method allows us to take the chemical potential ($\mu$) as an independent variable that can straightforwardly be related to the electrode potential that is used to control the chemical potential of the species at the metal/solution interface. Also, in our two-dimensional system of size $L \times L = M$, a Monte Carlo step (mcs) involves the random selection of $M$ adsorption sites in order to consider all possible adsorption/desorption events. In these simulations, diffusion events are not considered explicitly, but instead one has an equivalent process since there exists the possibility that an atom may desorb from one site while another one may adsorb on a neighboring site. It should be mentioned that very recently Frank et al. [20] have studied the influence of lateral adsorbate diffusion on the dynamics of the first-order phase transition within the framework of the two-dimensional Ising model. These results are discussed in the context of Upd and one relevant finding is that diffusion may suppress the nucleation processes around clusters.

Simulations are performed starting from an empty substrate and subsequently the chemical potential is swept harmonically according to

$$\mu(t) = \mu_{\text{coex}} + \mu_0 \sin(\omega t)$$

(2)
where \( \mu_0 \) is the amplitude of the sweep, while \( \omega = 2\pi/\tau \) is the pulsation such that \( \tau \) is the period of the applied perturbation. Also, \( \mu_{\text{coex}} \) is the coexistence chemical potential measured at the first-order phase transition observed upon deposition of Ag on Au(100) (see e.g. figure 1 and the discussion below). During the simulation we record the time dependence of the Ag-coverage \( \theta(t) \). After neglecting several initial sweeps in order to allow the system to achieve a nonequilibrium stationary state, we calculate the quantities of interest by averaging over many cycles.

### III. RESULTS AND DISCUSSION.

Before starting the discussion of the dynamic behavior of the system, it is instructive to remind the reader that both experiments and numerical simulations performed under equilibrium conditions have confirmed that the adsorption isotherms \( \theta_{\text{Ag}} \) vs \( \mu \) exhibit first-order transitions within a wide range of temperatures, as is shown in figure 1 for the case of Monte Carlo results performed by one of us [14].

In view of these results we performed the study of the dynamic behavior of the system by taking \( T=300\text{K} \), so that the system is far below its critical temperature. At this temperature one has that the chemical potential at coexistence is \( \mu_{\text{coex}} = -3.03\text{eV} \). Therefore, the sweep of the chemical potential, as given by equation (2), is applied over \( \mu_{\text{coex}} \).

Figure 2 shows two examples of the dynamic behavior of the system as obtained by applying oscillatory sweeps of the same amplitude \( \mu_0 = 0.3 \) but different periods \( \tau \).

For the shortest period (\( \tau = 10\text{mcs} \), see figure 2(a)) the system becomes trapped within a low-coverage regime, with \( \theta_{\text{Ag}} < 0.5 \). Since the highest achieved chemical potential is given by \( \mu_{\text{coex}} - \mu_0 = -2.73\text{eV} \), the applied signal clearly drives the system well inside the high-coverage regime of the equilibrium isotherm (see figure 1). So, the behavior observed in figure 2 for \( \tau = 10 \) is clear evidence that such a period is much smaller than the relaxation time \( \tau_{\text{relax}} \) required by the system to jump from the low-coverage to the high-coverage regimes. On the other hand, for \( \tau = 100 \) (see figure 2(b)) the system reaches the high-coverage regime \( \theta_{\text{Ag}} \approx 1 \) during all sweeps, indicating that for this case one has \( \tau > \tau_{\text{relax}} \). So, from figure 2 one concludes that it is possible to identify the dynamic competition between two time scales in the system: the half-period of the external drive and the relaxation time (also known as the metastable lifetime of the system in a given state). For large periods, a complete decay
FIG. 1: Adsorption isotherms for the deposition of Ag on Au(100) obtained under equilibrium conditions by means of numerical simulations. Results corresponding to different temperatures as listed in the figure. For further details see reference [14].

of the metastable phase always occurs during each half-period. Consequently, the coverage describes an (almost symmetric) limiting cycle. In contrast, for short periods, the system does not have enough time to change the coverage from \( \theta \approx 0 \) to \( \theta \approx 1 \) and the symmetry of the hysteresis loop is broken.

It should be mentioned that the phenomenon of symmetry breaking between limiting cycles in an externally driven system has been the subject of considerable attention. It was first reported in the context of numerical and mean-field studies of the magnetization of a ferromagnet in an oscillating magnetic field [21, 22] and subsequently it has been studied by means of Monte Carlo simulations of the kinetic Ising model [1, 2, 3, 4, 6].

In order to study the DPT’s involved in the already discussed symmetry breaking process in magnetic systems it is useful to define the dynamic order parameter \( Q \) as the period-averaged magnetization. Since in the present work we are interested in the surface coverage with Ag atoms, we take advantage of the lattice gas-spin system equivalence. In fact, if
FIG. 2: Plots of the temporal dependence of the coverage and the chemical potential (upper panel), and the coverage-chemical potential loops (lower panel). (a) Results obtained using lattices of side $L = 100$ and by taking $\mu_0 = 0.3$ and $\tau = 10$. (b) As in (a) but for $\tau = 100$. In (a) the coverage is amplified by a factor 10 for the sake of clarity. So, in order to properly obtain the actual coverage the $\theta$—scale has to be divided by a factor 10.

The spin variable can assume two different states ($s = \pm 1$) corresponding to two occupation states of lattice gas ($n = 0$ (empty)) and $n = 1$ (occupied)), one has that $s = 2n - 1$ and the suitable order parameters is

$$ Q = \frac{1}{\tau} \oint (2\theta_{Ag} - 1)dt. \quad (3) $$

Notice that for finite systems, as in the present study, one actually computes $\langle|Q|\rangle$, where $\langle\rangle$ means averages over different cycles of the time series $\theta_{Ag}(t)$. So, if $\tau < \tau_{relax}$ the coverage cannot change from $\theta \sim 0$ to $\theta \sim 1$ (and vice versa) within a single period, and therefore one has that $\langle|Q|\rangle > 0$. This situation is regarded as the DOS. In contrast, when $\tau > \tau_{relax}$ and the coverage follows the applied chemical potential one has that $Q \approx 0$ in the so called DDS. Between these two extreme regimes, one expects that the existence of a critical period such
as $\langle |Q| \rangle$ should vanish in the thermodynamic limit. This behavior may be the signature of a nonequilibrium DPT.

Further insight into the nature of DPT’s can be obtained by measuring the fluctuations of the order parameter ($\chi$), given by

$$\chi = L^2 \text{Var}[|Q|] = L^2[\langle |Q|^2 \rangle - \langle |Q| \rangle^2],$$

(4)

where $\text{Var}[|Q|]$ is the variance of the order parameter. This measurement is motivated by the fact that, as is well known, systems undergoing second-order phase transitions exhibit a divergency of the susceptibility. Of course, for equilibrium systems the fluctuations of the order parameter are related to the susceptibility through the fluctuation-dissipation theorem (FDT). It is not obvious if such a theorem would hold for our out-of-equilibrium dynamic system. However, if our system obeyed the FDT, both quantities would be proportional.

Figures 3 and 4 show typical snapshot configurations obtained during the adsorption and desorption half-cycles of the sweep, respectively. Recall that all parameters are set as in figure 2 (a) for the sake of comparison. Figure 3 suggests that by sweeping the chemical potential, the decay of the metastable (with $\theta_{Ag} = 0$) phase takes place by random homogeneous nucleation of many critical clusters of Ag (recall that for the applied chemical potential the stable phase corresponds to a fully covered Ag surface). These critical droplets grow and coalesce driving the system into the stable phase, resulting in an almost deterministic process. This kind of behavior is very well documented for the case of the Ising model and the outlined mechanism is known as a multiple droplet (MD) regime [1, 2, 3]. In fact, in the Ising magnet the decay of the metastable phase under a sudden reversal of the applied magnetic field may proceed according to different mechanisms, depending on the magnitude of the field, the temperature $T$, and the lattice size $L$. The system crosses over from the MD to a single droplet (SD) regime at a crossover field called the dynamic spinodal. Within the SD regime the decay of the metastable phase occurs by random homogeneous nucleation of a single critical droplet of the stable phase. For a detailed discussion of the different decay modes of the Ising system see references [1, 2, 3]. Roughly speaking, the MD regime is observed when both the system size and the amplitude of the applied oscillatory field are large enough [3]. We found that our simulations of the Ag/Au(100) system correspond to the MD regime, presumably due to the application of large amplitude signals ($\mu_o \geq 0.1$), the use of relatively large lattices ($L \geq 100$), and the relatively low temperature ($T = 300K$) used
FIG. 3: Typical snapshot configurations obtained during the **adsorption** half-cycle. For the sake of comparison, relevant parameters are taken as in figure 2(a), namely $\mu_o = 0.3$ and $\tau = 10$. The chemical potential increases from top-left ($\mu = \mu_{coex} = -3.03$) to bottom-right ($\mu = -2.73$) in the simulations. However, we expect that the system may also display a SD regime for appropriate selections of the parameters, but undertaking systematic studies on this issue is beyond the scope of the present paper.

On the other hand, figure 4 shows that the desorption process involves the detachment of individual particles from all clusters formed upon adsorption. So, in this sense desorption and adsorption are also MD processes. Also, the very low rate of nucleation of $Ag$–free regions within $Ag$–clusters, observed in figure 4 is in agreement with the fact that due to the interactions, adsorption (figure 3) and desorption (figure 4) are not be symmetric processes (the model lacks of symmetry under the exchange empty $\leftrightarrow$ occupied sites).

In view of these results suggesting the existence of DPT’s in the $Ag/Au(100)$ system we performed extensive numerical simulations in order to study the dependence of the order parameter (see equation 3) and its fluctuations (see equation 4) on both the chemical potential and the period of the applied signal, as shown in figures 5 and 6, respectively. For
FIG. 4: Typical snapshot configurations obtained during the desorption half-cycle. For the sake of comparison, relevant parameters are taken as in figure 2(a), namely $\mu_o = 0.3$ and $\tau = 10$. The chemical potential decreases from top-left ($\mu = \mu_{coex} = -3.03$)) to bottom-right ($\mu = -3.33$)).

a given period and low enough values of $\mu_o$ one has that $\langle |Q| \rangle > 0$, although it decreases smoothly and monotonically when $\mu_o$ is increased (see figure 5(a)). On the other hand, by fixing the chemical potential, the order parameter also decreases when $\tau$ is increased (see figure 6(a)). It is worth mentioning that figure 6(a) is qualitatively similar to figure 15 of the paper of Kornis et al. [23], that corresponds to the MD process and has been obtained during the study of DPT’s in the Ising model in two dimensions. So, the behavior of $\langle |Q| \rangle$ suggests the existence of continuous transitions between a DOS (for $\langle |Q| \rangle > 0$) and a DDS (for $\langle |Q| \rangle \simeq 0$). This preliminary conclusion, which has already been anticipated within the context of discussion of figure 2 may also be supported by the characteristic peaks observed by plotting the variance of the order parameter, as shown in figures 5(b), 6(b), and 6(c).

In view of these findings it would be desirable to perform a systematic study of finite-size effects. In fact, it is well known that continuous (second-order) phase transitions become shifted and rounded due to the finite size of the samples used in numerical simulations,
FIG. 5: Plots of the (a) order parameter and (b) the fluctuations of the order parameter versus the amplitude of the applied (oscillatory) chemical potential, respectively. Results obtained by using lattices of side $L = 100$ and by taking different periods $\tau$ of the applied signal, as listed in the figures.

The shortcoming can be overcome by applying the finite-size scaling theory to the numerical results obtained by using a wide range of sample sizes $L \to \infty$. Therefore we performed simulations up to $L = 1024$ for few typical values of the parameters (not shown here for the sake of clarity). Our first finding was that the dependence of $\langle |Q| \rangle$ on $\mu_o$ does not show any appreciable finite-size effect (not shown here for the sake of space). Furthermore, the fluctuations of the order parameter ($\chi$, as measured according to equation (4)) are independent of the lattice size, as shown in figure 7. Since one has that $\chi = L^2 \text{Var}(Q)$, it follows that the variance of the order parameter actually vanishes in the thermodynamic limit. Due to this evidence we conclude that for the range of parameters used, rather than undergoing a true phase transition, the Ag/Au(100) system actually exhibits a crossover between the DOS and the DDS. This finding may be consistent with the observation that
FIG. 6: Plots of (a) the order parameter and (b) the fluctuations of the order parameter versus the period $\tau$ of the applied chemical potential, respectively. Results obtained by using lattices of side $L = 100$ and by taking different values of the amplitude of the applied signal, as listed in the figures.

the multidomain growth regime always prevails in our simulations (see also the discussion related to figures 3 and 4). In fact, one may expect that the random growth and subsequent dissolution of many domains, as well as the absence of a well-defined critical nucleus, would show a weak (if any) size dependence of the physical observables. However, one has to recognize that Sides et al [3] have found evidence of a DPT in the kinetic Ising model only within the MD regime, although the size-dependence reported in that work is rather weak. However, in a subsequent paper Korniss et al [23] have reported an extensive study of the finite-size effects that can clearly be understood within the framework of the finite-size scaling theory. On the other hand, a possible reason for the observation of a crossover instead of a true DPT could be the absence of symmetry between the adsorption and desorption processes, as already pointed out upon the qualitative discussion of the snapshots shown in figures 3 and 4. In order to test this possibility we measured the relaxation times for
FIG. 7: Plots of the fluctuations of the order parameter, as defined by equation (14), versus the period $\tau$ of the applied chemical potential. Results obtained by using lattices of different side as listed in the figure.

$Ag$–covered and uncovered surfaces as a function of the applied overpotential (see figure 8). Two relaxation times are measured for each process, namely: i) $\tau_{\text{des}}^{1/2}$ and $\tau_{\text{des}}^{0}$ for the desorption processes up to $\theta_{Ag} = 1/2$ and $\theta_{Ag} = 0$, respectively; and ii) $\tau_{\text{ads}}^{1/2}$ and $\tau_{\text{ads}}^{1}$ for the adsorption processes up to $\theta_{Ag} = 1/2$ and $\theta_{Ag} = 1$, respectively. The obtained results, plotted in figure 8, shown that for low overpotentials the relaxation times corresponding to both processes are different, quantitatively confirming the asymmetry between them. Also, for large overpotentials the relaxation times tend to be almost the same, suggesting that in this limit the asymmetry may be irrelevant. However, if should also be noticed that in that case neither crossovers nor DPT’s are observed due to the fact that one would need to apply signals with periods smaller than 1 mcs (see figure 6). Within this context, it is worth mentioning that the response to a pulsed perturbation of the Ziff-Gulari-Barshad (ZGB) model [24] for the catalytic oxidation of CO, has also very recently been studied [25]. The ZGB model exhibits a first-order irreversible phase transition between an active state with
FIG. 8: Plot of the relaxation times versus the applied overpotential. $\tau_{des}^{1/2}$ and $\tau_{des}^0$ are shown by means of full diamonds in figures a) and b), respectively. These data corresponds to the desorption processes up to $\theta_{Ag} = 1/2$ and $\theta_{Ag} = 0$, respectively. $\tau_{ads}^{1/2}$ and $\tau_{ads}^1$ are shown by means of full circles in figures a) and b), respectively. These data corresponds to the adsorption processes up to $\theta_{Ag} = 1/2$ and $\theta_{Ag} = 1$, respectively. Results obtained by averaging over 100 different configurations. More details in the text.

$CO_2$—production and an absorbing (or poisoned) state with the surface of the catalyst fully covered by $CO$, such that in this regime the reaction stops irreversible [24] (for a recent review see e.g. reference [26]). In order to study DPT’s in the ZGB model it is convenient to perform a generalization by introducing a small probability for $CO$ desorption that, on the one hand preserves the first-order nature of the transition [27], and on the other hand prevents the occurrence of $CO$—poisoning. Measurements of the lifetimes associated with the decay of the metastable states of the ZGB model indicate that they depend on the direction of the process, showing a marked asymmetry as in the case of our adsorption-desorption simulations. In fact, the contamination time $\tau_d$ (measured when the system is quenched from high to low $CO$—coverage) is different from the poisoning time $\tau_p$ (measured from
FIG. 9: Linear-logarithmic plot of the crossover chemical potential versus the crossover period. Data obtained from the peaks observed in plots of $\text{Var}(|Q|)$ versus $\mu_o$ (full circles), and $\text{Var}(|Q|)$ versus $\tau$ (full squares). The full line showing the border between dynamic ordered states (DOS) and dynamic disordered states (DDS) has been drawn in order to guide the eyes. Also, the (vertical) dashed line corresponds to the minimum period at which DDS’s were observed. More details in the text.

Therefore, DPT’s are observed by applying a periodic external -asymmetric- signal of period $\tau = \tau_p + \tau_d$ [25]. Based on these evidence, we conclude that the observation of the crossover in our simulations should -most likely- be related to the fact that we have applied a periodic -symmetric- potential and the involved adsorption-desorption processes are not symmetric. Of course, it could also be possible that at higher temperatures the asymmetry may become irrelevant. However, in the present work we have restricted ourselves to $T = 300K$ since we expect to contribute to the understanding of the dynamic behavior of the Ag/Au(100) system under a standard electrochemical environment.

In order to further characterize the crossover between different states we take advantage of the well defined peak exhibited by $\chi$ and $\text{Var}(|Q|)$ (see figures [5, 6, and 7]). So, the
crossover period ($\tau^{\text{cross}}$) and the corresponding crossover chemical potential ($\mu_o^{\text{cross}}$) are identified with the location of the above-mentioned peak. The obtained results are displayed in figure 9, which shows a logarithmic dependence of $\mu_o^{\text{cross}}$ on $\tau^{\text{cross}}$. In the “state diagram” of figure 9, the full line shows the border between DOS’s obtained for intermediate values of both $\mu_o^{\text{cross}}$ and $\tau^{\text{cross}}$, and DDS’s that are found for large enough values of the period. It should be noted that for very low periods (i.e. $\tau^{\text{cross}} < 6$) we were unable to observe DOS (see e.g. figure 6) even after largely increasing the chemical potential. A similar effect has been reported by Korniss et al. [23] in the case of the Ising model, see e.g. figure 15 of reference [23]. Therefore, a (vertical) dashed line was drawn in the diagram of figure 9 in order to properly confine the region where DOS’s are found. An analog phase diagram has been reported by Korniss et al for the case of DPT’s in the Ising model, see e.g. figure 16(a) of reference [23].

IV. CONCLUSIONS.

The Ag/Au(100) system previously simulated by means of the Monte Carlo method under equilibrium conditions, is analyzed in the present work from another point of view, namely by studying its dynamic behavior due to the application of an external drive. The physical situation that motivates this paper is the adsorption isotherm of Ag on the Au(100) surface, which exhibits an abrupt jump between a low-coverage state and high-coverage state, for a well-defined (coexistence) chemical potential at $T = 300K$. In this work, we analyze the situation where the chemical potential is varied periodically around $\mu_{\text{coex}}$ and we study the influence of the period and the amplitude of that variation on the dynamic behavior of the system.

Our results show that a silver layer adsorbed on Au(100) smoothly changes from a dynamically ordered state (DOS) to a dynamically disordered state (DDS) when the period (amplitude) of the chemical potential is increased by keeping $\mu_o (\tau)$ constant. Since the size dependence of the order parameter is negligible and its fluctuations scale with the system size, we conclude that the system does not exhibit a true dynamic phase transition, but rather it exhibits a crossover between two different dynamic states, namely DOS and DDS, respectively. The absence of true DPT’s is due to the asymmetry between the adsorption and desorption processes of Ag–atoms. The crossover points are identified by the position...
of the peaks of the fluctuations of the order parameter. In this way we are able to draw the corresponding diagram of states characteristic of the system. The amplitude of the chemical potential at the crossover point exhibits a logarithmic dependence on the crossover period. However, for low enough periods the DOS is no longer observed.

The experiments that we propose in order to verify these theoretical results consist in the study of the adsorption of silver on a gold 100 surface, under Upd conditions, and the subsequent analysis of the influence of a periodic variation of the applied potential. One has to recognize that it would be difficult to establish a correlation between the actual time scale of the experiments and the Monte Carlo time step, although qualitative similar observations are expected. Furthermore, by determining the rate constants of the relevant electrochemical processes, one may perform real-time Monte Carlo simulations [31].

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