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Relevance of nonlocal adatom-adatom interactions in homoepitaxial growth

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The relevance and strength of nonlocal adatom-adatom interactions and their importance for nucleation is critically discussed. Focusing on homoepitaxial growth on Al(111), the analysis indicates that the strength of nonlocal adatom-adatom interactions is overestimated by *ab initio* calculations.

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Adatom-adatom interactions extending beyond the nearest-neighbor site have received considerable experimental and theoretical interest during recent years.[1–8] Nonlocal adatom-adatom interactions have long been known in field-ion microscopy (FIM).[9,10] For example, the orientation-dependent, oscillatory interaction between Pd and W adatoms on W(110) is strongly repulsive at next-nearest-neighbor sites with an energy of about 40 meV, but rapidly decays to amplitudes of a few meV beyond distances of three nearest neighbors (nn).[10]

In recent scanning-tunneling microscopy (STM) experiments, due to the larger field of view and the presence of wider terraces resulting in much better statistics compared to FIM, the adatom-adatom interactions could be determined even for distances up to 70 Å.[1,7] Due to the existence of a partially filled surface-state band, a weak but long-range oscillatory electronic adatom-adatom interaction exists on Cu(111) and Ag(111) surfaces. At short distances, however, the nonlocal adatom-adatom interaction is dominated by a rapidly decaying repulsive part, including an elastic contribution.[3] Experimentally, the maximum nonlocal adatom-adatom interaction for Cu adatoms on Cu(111) is found at second nn distances, is repulsive, and amounts to about 15 meV.[1] Independent STM experiments essentially confirmed this picture, finding a lower bound of 13 meV for the maximum interaction energy.[7] *Ab initio* density-functional theory (DFT) calculations were performed to investigate the magnitude of adatom-adatom interactions for a number of systems. For Cu/Cu(111), the maximum repulsive interaction energy is found for adatoms at second nn sites amounting to 46 meV.[3] A binding-energy variation of about 17 meV is found for Al adatoms on Al(111) due to indirect interactions.[3] For Ag adatoms on strained Ag(111) the maximum repulsive interaction is found at a distance of about four nn and amounts to 50 meV approximately.[2]

Island density analysis within the nucleation theory is a major tool for the determination of the fundamental parameters of adatom diffusion: its activation barrier $E_{d,1}$ and its attempt frequency $\nu_{0,1}$.[11] However, classical theory neglects nonlocal adatom-adatom interactions and it is thus a question of fundamental importance to find out to which extent this negligence invalidates the usual island density analysis. The key issue of the present paper is to contribute to the solution of this question.

Kinetic Monte Carlo (kMC) simulations taking into account the repulsive interactions—calculated according to DFT—result in significant increases of the island densities compared to interaction-free systems.[2,3,5,6] As an example, for the Al/Al(111) system these increases range from a factor of 3 at 25 K (Ref. 3) up to a factor of about 100 at 50 K.[5] A mean-field nucleation theory including the adatom-adatom interactions has been developed and is in good agreement with the kMC simulations.[6] One key finding of the simulations is that the usual island density analysis neglecting adatom-adatom interactions is likely to yield adatom attempt frequencies $\nu_{0,1}$ orders-of-magnitude lower than the expectations of transition state theory (TST),[12] which predicts pre-exponential factors of the order of 10^{12} Hz.[13–15]

Is there any experimental evidence for the failure of the classical mean-field island density analysis due to nonlocal adatom-adatom interactions? To this end, low-temperature island density measurements for Cu adatoms on Cu(111) would be ideal, since the strength and range of the adatom-adatom interaction are known experimentally. In the lack of these, we discuss island density measurements and simulations for Al adatoms on Al(111).

Figure 1 displays two different island density measurements and two sets of kMC simulations. The experimental island densities are renormalized to the deposition rate F of the corresponding simulations in order to allow better comparison. The renormalization was performed by assuming a relation $n_x = n_x'(F/F')^{1/3}$, which is valid if the island densities develop according to $n_x \propto (F/D)^{1/3}$, i.e., assuming a stable and immobile dimer.[16]

The first published data set (EXP-I) for Al island densities on Al(111) (Ref. 17) is represented by filled circles in Fig. 1. The mean-field island density analysis applied to this data resulted in $E_{d,1} = (42 \pm 4)$ meV and an extraordinarily small attempt frequency $\nu_{0,1} = 8 \times 10^{6 \pm 0.25}$ s^{-1}. The analysis of two additional systems by the same group also resulted in unexpected low attempt frequencies.[17] These results stimulated the hypothesis that the extraordinarily small preexponential factors obtained for low corrugation potential-energy surfaces indicate some hidden physics.[17] Later on, kMC simulations, taking into account interaction energies calculated by DFT, found enhanced island densities for Al on Al(111) in the presence of nonlocal adatom-adatom interactions compared to the system neglecting these interactions.[3,5] The results of Ref. 5 including adatom-adatom interactions (KMC-I) are displayed in Fig. 1 as open circles. Apparently, the data EXP-I and simulated island densities KMC-I match perfectly in the overlapping temperature range. To see the influence of the assumed adatom-adatom interactions, the kMC simulation data without adatom-adatom interactions

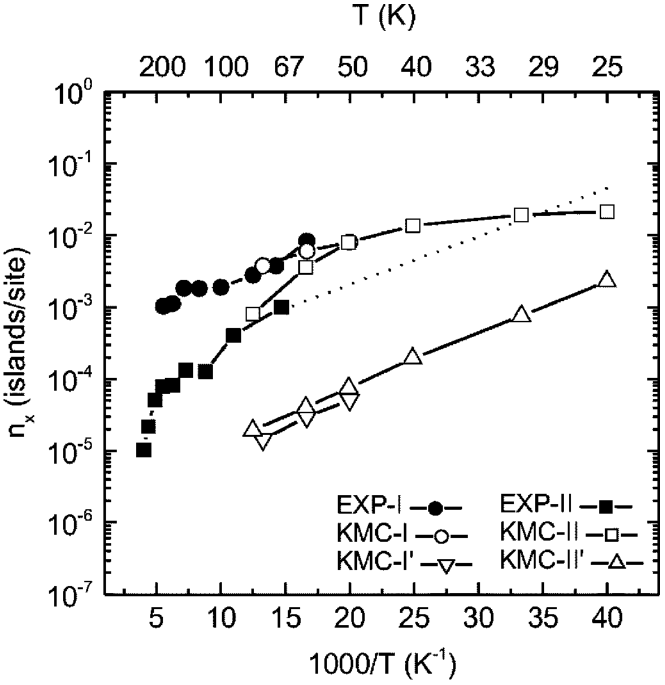

FIG. 1. Comparison of the temperature dependence of the Al island density on Al(111) derived from different works. Down and up triangles correspond to island densities computed by kMC simulations without adatom-adatom interactions in Ref. 5 and Ref. 6 for a flux of $F=0.01$ ML/s, and $F=0.03$ ML/s respectively. Open circles and squares correspond to kMC-computed island densities with adatom-adatom interactions: open circles are derived from Ref. 5 ($F=0.01$ ML/s) and open squares are derived from Ref. 6 ($F=0.03$ ML/s). Filled symbols correspond to experimental data: circles correspond to STM data measured in Ref. 17 [$F=6.2\times10^{-4}$ ML/s] renormalized to $F=0.01$ ML/s for comparison (see text), and squares correspond to the experimental data of Ref. 18 [$F=(7.2\pm0.6)\times10^{-3}$ ML/s] renormalized to $F=0.03$ ML/s for comparison. The dotted line corresponds to an extrapolation of the island density curve represented by filled squares (see text).

yielding island densities two orders-of-magnitude lower (KMC-I′) are also reproduced in Fig. 1 as down triangles. The agreement between EXP-I and KMC-I seemed to be a striking confirmation for the relevance of adatom-adatom interactions in the nucleation theory island density analysis. The enhanced island densities due to adatom-adatom interactions imply an explanation for the extraordinarily small $\nu_{0,1}=8\times10^{6\pm0.25}$ s^{-1}. This value could be understood knowing that $\nu_{0,1}\propto(1/n_{x,\infty})^3$ in the usual island density analysis. Here $n_{x,\infty}$ is the intercept of the linear fit of the relevant data with the y axis. Thus, an enhancement of the island density by a factor of 100 causes a decrease of $\nu_{0,1}$ by factor of 10^6, explaining just the difference between the measured value 10^6 and the TST estimate of about 10^{12} s^{-1}.

The filled squares in Fig. 1 display a second experimental data set (EXP-II) measured by us and published in Ref. 18. Preliminary data belonging to the same experimental series were published as a comment[19] to EXP-I.[17] Apparently the island number densities of EXP-II are one order-of-magnitude lower than those of EXP-I. Renormalizing both experimental data sets to the same flux would even increase this difference. The explanation is straightforward: for EXP-II the deposition rate ($F=(7.2\pm0.6)\times10^{-3}$ ML/s) was one order-of-magnitude larger and the background pressure ($P=5\times10^{-11}$ mbar) one order-of-magnitude lower than for EXP-I ($F=6.2\times10^{-4}$ ML/s, $P=5\times10^{-10}$ mbar). Both factors thus decrease the rate at which unwanted impurity atoms adsorb on the surface in EXP-II compared to EXP-I. This difference influences decisively the probability of island nucleation by impurities for a system as reactive as Al. Therefore, in our opinion EXP-II is a much better representation of the island density for a clean homoepitaxial island density on Al(111). Thus the agreement between EXP-I and KMC-I becomes questionable as support for the relevance of adatom-adatom interactions on Al(111). We note here that the rapid decrease of the island density for temperatures above 200 K in EXP-II is due to the onset of dimer dissociation, as analyzed in detail in Ref. 18. Later, another set of kMC simulations for the island density taking into account adatom-adatom interactions (KMC-II) was published[6] (reproduced as open squares in Fig. 1). An analytical expression for the interaction potential representing the elastic contribution calculated by DFT for the Al/Al(111) system was used in order to compute the interaction energy. The resulting data set KMC-II fits much better to EXP-II in the narrow-temperature range around 75 K where they almost overlap, though the simulated island densities are larger than the experimental ones for low temperatures.

At this point one might stop the discussion with the statement that, after some experimental and calculational settlements, a reasonable agreement between measured island densities and those obtained from kMC simulation taking adatom–adatom interaction into account is achieved. However, we want to extend the discussion a little further and ask two questions: (i) Are there any inconsistencies if the standard island density analysis neglecting adatom-adatom interactions is applied to EXP-II, inconsistencies similar to the extraordinarily small prefactor resulting from the analysis of EXP-I? (ii) Are there any inconsistencies in the assumptions underlying the kMC simulations?

As discussed in Ref. 18, by assuming a stable immobile dimer the island densities of EXP-II yield an activation barrier $E_{d,1}=(0.07\pm0.01)$ eV and $\nu_{0,1}=5\times10^{11\pm0.5}$ s^{-1}. Thus, within the limits of error, the prefactor coincides with the universal TST estimate for $\nu_{0,1}=kT/h$ which amounts to 2×10^{12} s^{-1} at 100 K. The activation energy is nearly twice as large as the adatom activation energy of 0.04 eV calculated by all DFT studies,[20–23] but in view of the experimental error and of the small absolute calculated value, emphasizing errors of the calculation, the agreement is satisfying. However, one has to consider the possible influence of dimer diffusion on the island density. In Ref. 22 an activation energy of dimer diffusion $E_{d,2}=0.13$ eV is found by using DFT with both the local-density approximation (LDA) and generalized gradient approximation for the exchange-correlation functional, while in Ref. 23 a value of $E_{d,2}=0.08$ eV results by using DFT with the LDA. Based on these two calculated values and assuming the TST estimate $\nu_{0,2}=kT/h$, dimers reach a jump frequency of 1 s^{-1} at temperatures between 34 and 54 K. In order to influence island formation, dimers need not only to be mobile, but also to be able to reach stable nuclei at a rate comparable to or faster than the rate at which dimers combine with single atoms. According to Villain *et al.*[16] this condition prevails if the jump rates ν_1 and ν_2 for adatoms and dimers, respectively, satisfy the requirement $\nu_2^3/\nu_1^2 > F$. By using the calculated energy barrier for monomer diffusion $E_{td,1} = 0.04$ eV and a value in the range $E_{d,2} = 0.08$-0.13 eV for dimer diffusion, the temperature at which dimer diffusion becomes relevant for island formation is within the range 57–108 K. On the basis of the experimental data it is not possible to unambiguously distinguish scaling regimes without and with dimer diffusion [as it is possible for Pt on Pt(111) or Ir on Ir(111) (Ref. 18)]. Therefore, besides the no-dimer-mobility scenario discussed above, we consider here two additional scenarios. First we assume dimer mobility to be irrelevant below 100 K and relevant above 130 K, establishing its own scaling behavior. We then obtain $E_{d,1} = 0.06$ eV, $E_{d,2} = 0.09$ eV, and $\nu_{0,1} = 8 \times 10^{10}$ s^{-1}. Second we assume the entire measurement below 200 K to be located within the dimer diffusion regime and choose, for lack of better knowledge, the theoretical value $E_{d,1} = 0.04$ eV to be the correct adatom diffusion barrier. Then $E_{d,2} = 0.08$ eV and $\nu_{0,1} = 2 \times 10^9$ s^{-1} is obtained. The latter has been deduced by assuming a slope consistent with $E_{d,1} = 0.04$ eV, as indicated by the dotted line in Fig. 1. Apparently, the quality of the data and the lack of island density data at temperatures below 60 K prevent unambiguous conclusions. Nevertheless, the resulting activation energies agree reasonably well with the available DFT calculations and the possible attempt frequencies, which range from 2×10^9 s^{-1} to 5×10^{11} s^{-1}, do not indicate adatom-adatom interactions of the strength assumed in KMC-I and KMC-II. If present at all, adatom-adatom interactions might have caused an increase in island density by a factor of 10. An island density enhancement by a factor of 100 appears to be inconsistent with the lower-bound estimate of the apparent prefactor of 2×10^9 s^{-1}. We believe that the island density enhancement is even lower (see below).

Next we ask for inconsistencies within the assumptions underlying the simulations. A first point of concern is the negligence of dimer diffusion in the simulations. This is only justified if the upper value calculated by DFT, $E_{d,2} = 0.13$ eV,[22] is in fact correct (which, if valid, forces to assume $\nu_{0,1} \approx 10^{11}$ s^{-1} from the island density analysis). Second, it must be considered that the DFT calculations might overestimate the strength of the adatom-adatom interactions. Indeed, for Cu adatoms on Cu(111) the experimental values of 13 meV and 15 meV (Refs. 1 and 7) for the maximum repulsive strength of the adatom-adatom interactions do not compare favorably with the corresponding DFT result of 46 meV.[3] The directness and independence of the experimental measurements leave little doubt that DFT fails this time and overestimates the strength of the adatom-adatom interactions by more than a factor of 3. There is no reason to rule out a similar overestimation of the adatom-adatom interaction by DFT for Al adatoms on Al(111), which could explain the difference between the kMC-computed and experimental island densities.

Due to their generic origin, the short-range repulsive adatom-adatom interactions should be relevant also for other metallic, homoepitaxial systems. In order to obtain an estimate for their possible strength and their effect on the validity of the standard island density analysis, it is useful to briefly consider experimental results for Ir/Ir(111) and Pt/Pt(111). For these two systems $E_{d,1}$, $E_{d,2}$, and $\nu_{0,1}$ obtained from the standard island density analysis neglecting adatom-adatom interactions match perfectly with the corresponding results from field-ion microscopy.[18] By field-ion microscopy the quantities were derived through direct observation of the mean-square displacement of single adatoms and dimers, thus ruling out *a priori* the influence of adatom-adatom interactions. The agreement of the two methods is so tight that within the limits of error there is no space for the relevance of adatom-adatom interactions. The values for $E_{d,1}$ agree within 10 meV or less and the attempt frequencies $\nu_{0,1}$ within a factor of 4 or less. The deviation in the attempt frequency by a factor of 4 allows thus at most for island density enhancement by a factor of 1.6 due to adatom-adatom interactions, and not 100 as proposed for Al/Al(111). It would thus be a good test for the reliability, with which the strength and consequences of adatom-adatom interactions for island nucleation can be predicted, to perform kMC simulations with DFT values as an input for one of the two experimental cornerstone systems. The scaling of the Al(111) island densities with those of Ir(111) and Pt(111) (Ref. 18) makes the relevance of the adatom-adatom interactions for Al(111) even less likely.

In conclusion, from the analysis of Al island densities on Al(111) and the arguments presented above, it seems likely that the effect of nonlocal adatom-adatom interactions on nucleation is weaker than currently assumed on the basis of kMC simulations with DFT values as an input. Presently, two pathways might be choosen to clarify the role of adatom-adatom interactions in nucleation. First, low-temperature island density measurements for Cu islands on Cu(111) are desirable, the only homoepitaxial system for which the strength and range of these interactions are known. Second, measurements and calculations for the strength of adatom-adatom interactions for Ir/Ir(111) or Pt/Pt(111) are desirable, systems for which their effect on nucleation appears to be negligible.

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