

Dynamics of Surface Migration in the Weak Corrugation Regime

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We report a systematic study for metal-on-metal surface migration in the weak corrugation regime, i.e., with migration barriers falling below ≈ 100 meV. The migration characteristics are elucidated by variable-temperature scanning tunneling microscopy observations in the 50–200 K temperature range, which are analyzed by means of nucleation theory. The results demonstrate that, upon entering the weak corrugation regime, the dynamics of the systems are characterized by increasingly reduced effective preexponential factors, while Arrhenius behavior prevails.

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The thermal migration of adsorbed atoms on the periodic lattice of a surface offers an ideal test case to systematically investigate the energetics and dynamics of a rate phenomenon in chemical physics. Surface migration requires the overcoming of an energy barrier E_m separating two identical states, a process usually obeying an Arrhenius law [1–3]. In particular, the mobility of atoms on metal surfaces has been extensively studied due to its importance for a variety of processes in science and technology, such as heterogeneous catalysis or epitaxial growth [4–6]. The phenomenology is simple: Atoms or small molecules are preferentially adsorbed at specific high-symmetry sites of the surface periodic atomic lattice, which are separated by energy barriers being generally a mere fraction of the adsorption energy. The lateral mobility of the adspecies is driven by the substrate heat bath providing stochastic excitations whose characteristic energy is given by the Debye temperature (~ 25 meV for metals). When the density is low, a two-dimensional random motion of isolated adspecies or *tracer diffusion* [5] is operational; i.e., adsorbates hop from energy minima to neighboring energy minima. This process can be adequately described in terms of transition state theory (TST) [7], when the thermal energies are much smaller than the migration barrier, i.e., $k_B T \ll E_m$, and when the coupling of the adspecies to the substrate is sufficiently effective to ensure equilibration between the individual jumps. These conditions normally hold for metallic adsorbates on metal surfaces, and the corresponding tracer diffusion coefficient D^* is given by [5]

$$D^* = \frac{1}{4} a^2 \nu_0 e^{-\beta E_m} \equiv D_0 e^{-\beta E_m}, \quad (1)$$

where $\beta = 1/k_B T$, a is the periodicity of the surface lattice, and ν_0 is the attempt frequency, frequently associated with the lateral vibrational mode of the adatom; D_0 is the preexponential factor.

The situation becomes more intricate when the thermal energy increases such that $k_B T \sim E_m$ and it is anticipated that TST breaks down, until for $k_B T \gg E_m$ a free two-dimensional Brownian motion of the adatoms is expected,

where the diffusivity is directly proportional to the temperature [8]. Another complication may arise when the coupling of the adatom to the substrate is weak or strong. The resulting effect is twofold: On the one hand, a decrease of the attempt frequency is expected, which lowers the mobility [9–11]. On the other hand, for the case of weak coupling, adspecies in the process of migration are deexcited less efficiently and may hop further than just to a neighboring minimum. Such “long jumps” effectively increase the mobility, and the parameter a^2 in the diffusion Eq. (1) has to be substituted by a mean square jump length $\langle l^2 \rangle$ [12].

Very recently, the first experimental observations for the extreme situation of an unrestricted two-dimensional Brownian motion at a surface have been reported: Quasielastic helium atom scattering (QHAS) data indicate that with the Xe/Pt(111) system the adatoms at low coverage and $T = 105$ K form a fully mobile two-dimensional gas due to an extraordinarily small lateral potential corrugation falling below 10 meV [13]. However, the *dynamics* of this weak corrugation system could not be elucidated, since the results were obtained at a single temperature with $k_B T \approx E_m$. In the present Letter, we address this question on the basis of variable temperature scanning tunneling microscopy (STM) observations. As a model case, we discuss the self-diffusion of Al adatoms on Al(111), where E_m was predicted by *ab initio* density functional theory calculations to be only ≈ 40 meV [14–16].

The experiments were performed in a standard UHV chamber equipped with a variable temperature STM [17]. The Al(111) single crystal surface was prepared by cycles of Ar^+ sputtering ($\approx 1 \mu\text{A}/\text{cm}^2$, 500 eV, 20 min) at 300 and 800 K flash annealing followed by slow cooldown. Aluminum was evaporated *in situ* from a Knudsen cell at background pressures below 5×10^{-10} mbar. Auger electron spectroscopy revealed the absence of contaminations for Al films as thick as 10 ML [1 monolayer (ML) corresponds to 1 Al atom per Al(111) substrate atom]. STM data were acquired in the temperature range 60–180 K isothermally to or at lower temperatures than deposition.

The extraordinary small value of the calculated lateral corrugation potential of the Al/Al(111) system implies that even at low temperatures the thermal energy is a substantial fraction of the migration barrier ($k_B T/E_m \approx 1/5$ at $T = 100$ K). The diffusion characteristics of the Al adatoms are derived by directly determining the temperature dependence of the nucleation island density n_x , which is analyzed by nucleation theory. This method has proven to be a powerful means for the elucidation of tracer diffusion at metal surfaces [18–20]. When the temperature is sufficiently low, the only mobile species on the surface is the isolated adatom. Then the dimers are stable and represent immobile nuclei (i.e., the critical cluster size is $i = 1$). With the present system, the stability of dimers is guaranteed up to elevated temperatures due to the high dimer dissociation energy, determined by *ab initio* calculations to 0.54 ± 0.06 eV [21]. Dimer mobility can be similarly excluded for the present temperature range, based on the theoretical value of the dimer migration barrier [21] and on the scaling laws in the presence of cluster diffusion [22,23]. The saturation island density is thus solely controlled by the tracer diffusion coefficient and the deposition flux F . Then the following scaling law relates D^* to n_x [19,24]:

$$n_x = 0.25 \left[\frac{D^*}{F} \right]^{-1/3} = 0.25 \left[\frac{F}{D_0} \right]^{1/3} e^{\beta E_m/3}. \quad (2)$$

Hence, both migration barrier E_m and preexponential factor D_0 can be obtained by determination of n_x at different temperatures. An advantage of this approach is that the density of simultaneously diffusing adatoms on the surface can be kept very small, and thus the tracer diffusion

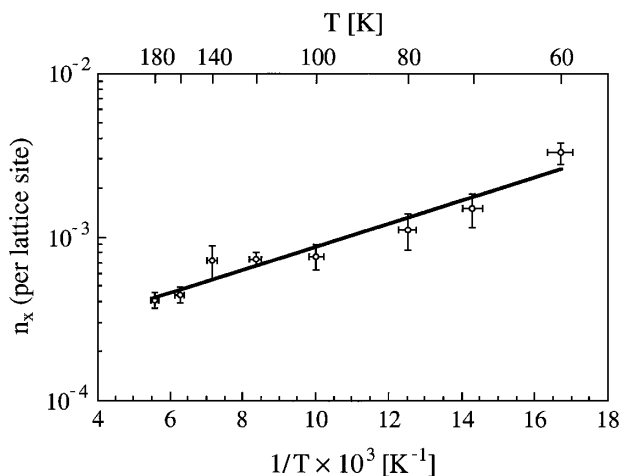


FIG. 1. Arrhenius representation of the saturation island density for Al nucleation on Al(111) derived from a series of STM images in the temperature range from 60 to 180 K ($\theta = 0.15$ ML; $F = 6.2 \times 10^{-4}$ ML/s). From the slope of the line fit, the migration barrier is determined to be 42 ± 4 meV; the extrapolation for $T \rightarrow \infty$ yields a preexponential factor of $2 \times 10^{-9 \pm 0.25}$ cm²/s.

of noninteracting adatoms is truly probed. A second advantage is that diffusion and nucleation are not influenced by the presence of the STM tip. Results for the Al/Al(111) system are shown by Arrhenius representation for n_x reproduced in Fig. 1. The data reveal that n_x obeys an Arrhenius law, even if the thermal energies in the individual experiments range from approximately 10% to 40% of the expected migration barrier. This clearly indicates that the adatom mobility varies exponentially with the reciprocal temperature in accordance with (1). Thus, (2) can be applied to obtain E_m , which is determined to 42 ± 4 meV, in very good agreement with the theoretical predictions. By contrast, the corresponding preexponential factor $D_0 = 2 \times 10^{-9 \pm 0.25}$ cm²/s is exceptionally minute. This value should be compared with the usual magnitude for D_0 of $\approx 10^{-3}$ cm²/s, resulting from the typical dimensions of a surface lattice ($a \approx 3$ Å) and the universal TST value of the attempt frequency $\nu_0 \approx 1 \times 10^{13}$ s⁻¹ for rate processes at surfaces [25]. Upon assuming that hopping takes place exclusively between neighboring sites, an effective attempt frequency for adsorbed Al atoms is determined to $\nu_0 = 8 \times 10^{6 \pm 0.25}$ s⁻¹, i.e., ν_0 is 6 orders of magnitude smaller than commonly expected. Note that this calculation of ν_0 represents an upper bound for the effective attempt frequency if long jumps were present.

The tremendous decrease of ν_0 is associated with the smallness of the migration barrier, which is close to the Al Debye energy (37 meV), and the magnitude of the thermal energies involved. It is by no means a singular property for the present system. In a recent investigation of the Al/Au(111) system, we found Arrhenius behavior with a minute migration barrier ($E_m = 30 \pm 5$ meV) along with an even more pronounced reduction of the preexponential factor, which was determined to $D_0 \approx 5 \times 10^{-13}$ cm²/s corresponding to an effective attempt frequency of $\nu_0 = 2.4 \times 10^3$ s⁻¹ [26]. Similar, albeit less drastic effects, exist for the migration of Ag on various fcc surfaces [18,24,27], where, with the migration barrier decreasing from 168 ± 5 to 60 ± 10 meV, the corresponding preexponential factor drops from the universal value $D_0 = 1.4 \times 10^{-2 \pm 0.3}$ ($\nu_0 = 7 \times 10^{13 \pm 0.3}$ s⁻¹) to $D_0 = 2 \times 10^{-7 \pm 0.6}$ cm²/s ($\nu_0 = 1 \times 10^{9 \pm 0.6}$ s⁻¹). Note that with all these systems dimer stability ($i = 1$) and the absence of cluster mobility were ensured by investigating the onset of coarsening for dimers [24] or by analyzing the island size distributions [26].

Since all investigations were performed under comparable conditions in the temperature range 50–200 K, the results clearly show a systematic downward shift of the effective attempt frequency with shrinking migration barriers. This trend is visualized by the data compilation in Fig. 2, where we plot ν_0 as a function of E_m . In order to put these results into perspective, the data set is complemented by additional field ion microscopy (FIM) and STM-nucleation theory results for metal on fcc metal surface migration. Note the excellent agreement between the

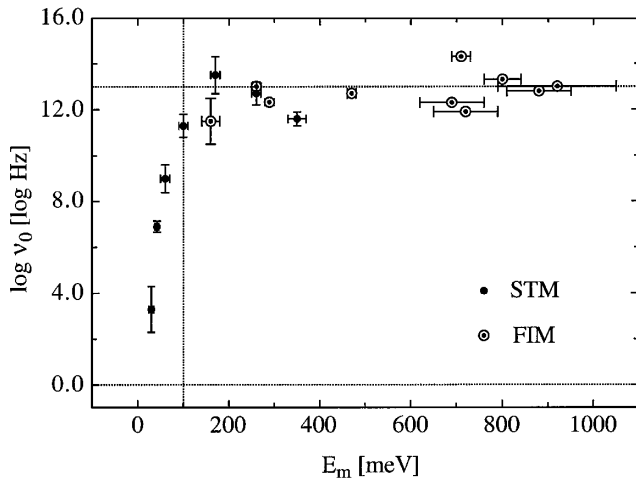


FIG. 2. The effective attempt frequency for intrinsic surface migration of metal atoms on fcc metal surfaces as a function of the migration barrier. In the low-energy regime (E_m below ≈ 100 meV) the dynamics of the rate process is characterized by drastically reduced effective attempt frequencies.

STM and FIM derived migration barriers and prefactors with the Pt/Pt(111) system [20,28]. The corresponding numerical values are comprised in Table I. The compilation reveals that in the weak corrugation limit a novel regime for the dynamics of surface migration is entered, where drastically reduced effective attempt frequencies prevail. This may suggest a breakdown of TST for the present metal-on-metal systems caused by violation of the condition $k_B T \ll E_m$ with migration barriers falling below a critical value of ≈ 100 meV and simultaneously coming close to the typical excitation energies of the substrate phonon bath. The increasing reduction of ν_0 with shrinking migration barriers lends support to this idea.

We note that, as E_m decreases, one becomes susceptible also to small lateral interactions between diffusing monomers. Kinetic Monte Carlo simulations show that long-range repulsions ranging over several sites can indeed delay island nucleation which leads to an increase in n_x and thus perturbs the scaling law (2) (cf. [35]). However, to explain our observations, these interactions would have to gain importance as E_m decreases, whereas the natural expectation would be that also the lateral interactions scale with E_m . Consequently, the ensemble of our results can hardly be reconciled with failures of density scaling. The data in Fig. 2 can similarly not be described in terms of a compensation effect for phonon-activated Arrhenius processes as suggested in a molecular dynamics study of surface migration on metals [36]. The curved falloff in the approach of the small barriers does not allow for a reasonable fit with the suggested formulas [36], even when exclusively the STM data are considered. This is presumably related to the smallness of the present barriers, coming close to the characteristic excitation energies. Accordingly, the related molecular dynamics simulations reveal an unusual lowering for the effective attempt frequency in this limit [36].

It should be emphasized that our observations are by no means singular, albeit the reported trend could not be extracted thus far due to a lack of systematic observations. On the one hand, the Xe/Pt(111) QHAS observation provides evidence that with the thermal energy approaching E_m the nature of the surface migration mechanism undergoes a severe change [13]. On the other hand, related anomalies in the dynamics of surface diffusion with small barriers have been observed earlier by field emission microscopy for adsorbed Xe on W(110) [37,38], direct STM observations for CO on Cu(110) [39], and, very recently, also by the integral linear optical diffraction technique for

TABLE I. Characteristics of tracer surface migration for metal atoms on fcc metal surfaces. Effective attempt frequencies were obtained via the relation $D_0 = (1/2d)a^2\nu_0$, with $d = 1, 2$ for one- or two-dimensional diffusion, respectively.

System	E_m [meV]	D_0 [cm ² /s]	ν_0 [s ⁻¹]	Method	Ref.
Al/Au(111)	30 ± 5	5×10^{-13}	2×10^3	STM	[26]
Al/Al(111)	42 ± 4	$2 \times 10^{-9 \pm 0.25}$	$8 \times 10^{6 \pm 0.25}$	STM	present work
Ag on strained Ag(111)	60 ± 10	$2 \times 10^{-7 \pm 0.6}$	$1 \times 10^{9 \pm 0.6}$	STM	[27]
Ag/Ag(111)	97 ± 10	$4 \times 10^{-5 \pm 0.5}$	$2 \times 10^{11 \pm 0.5}$	STM	[27]
Rh/Rh(111)	160 ± 20	$5 \times 10^{-5 \pm 1}$	$3 \times 10^{11 \pm 1}$	FIM	[29]
Ag/Pt(111)	168 ± 5	$1.4 \times 10^{-2 \pm 0.3}$	$7 \times 10^{13 \pm 0.3}$	STM	[24]
Pt/Pt(111)	260 ± 10	$1 \times 10^{-3 \pm 0.5}$	$5 \times 10^{12 \pm 0.5}$	STM	[20]
	260 ± 3	$2.0 \times 10^{-3 \pm 0.15}$	$1.0 \times 10^{13 \pm 0.15}$	FIM	[28]
Ir/Ir(111)	289 ± 3	$3.5 \times 10^{-4 \pm 0.15}$	$2.1 \times 10^{12 \pm 0.15}$	FIM	[28]
Cu/Ni(001)	350 ± 20	$6 \times 10^{-5 \pm 0.3}$	$4 \times 10^{11 \pm 0.3}$	STM	[30]
Pt/Pt(001)	470 ± 10	1×10^{-3}	5×10^{12}	FIM	[31]
Pt/Pt(110) in [001]	690 ± 70	6×10^{-4}	2×10^{12}	FIM	[32]
in [110]	720 ± 70	3×10^{-4}	8×10^{11}	FIM	[32]
Ir/Ir(110) in [001]	710 ± 20	6×10^{-2}	2×10^{14}	FIM	[33]
in [110]	800 ± 40	4×10^{-3}	2×10^{13}	FIM	[33]
Rh/Rh(001)	880 ± 70	1×10^{-3}	6×10^{12}	FIM	[29]
Pt/Rh(001)	920 ± 130	2×10^{-3}	1×10^{13}	FIM	[34]

the system Xe/Ni(111) [40]. In all cases, extraordinarily small preexponential factors were encountered.

In conclusion, we investigated surface migration in the weak corrugation regime, where activation barriers approach the thermal and typical phonon excitation energies. It was found that the dynamics of such systems are characterized by increasingly reduced effective preexponential factors the smaller the migration energy barriers encountered. Further theoretical investigations are strongly suggested to clarify the origins of this anomalous diffusion behavior. The universal nature of the underlying physics suggests that such effects may be of general importance for low barrier rate processes driven by thermal activation.

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