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Stability and diffusion of surface clusters

T. Müller and W. Selke[a]

Institut für Theoretische Physik, Technische Hochschule, 52056 Aachen, Germany

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Abstract. Using kinetic Monte Carlo simulations and a bond–counting ansatz, thermal stability and diffusion of an adatom island on a crystal surface are studied. At low temperatures, the diffusion constant D is found to decrease for a wide range of island sizes like $D \propto N^{-\alpha}$, where α is close to one, N being the number of adatoms in the cluster. By heating up the surface, the system undergoes a phase transition above which the island disappears. Characteristics of that transition are discussed.

PACS. 68.35.Fx Diffusion; interface formation – 82.20.Wt Computational modeling; simulation – 36.40.Sx Diffusion and dynamics of clusters

1 Introduction

Stability and dynamics of adatom as well as vacancy islands of monoatomic height on crystal surfaces have been studied intensively during the last years, both experimentally and theoretically [1–12]. In particular, the equilibrium island size at low temperatures [10] as well as the decay of clusters in the presence of surface steps or larger islands ("Ostwald ripening") [9,11,12] have been analysed. Different microscopic mechanisms have been discussed to explain the size dependence of the diffusion constant D characterising the motion of the center of mass of an equilibrated island. Typically, D decreases with the number of adatoms N in the cluster in the form of a power–law, $D \propto N^{-\alpha}$, with α depending on the mechanism driving the island motion [1–8].

In this article, we consider adatom islands on a (100) surface of a simple cubic crystal with energy barriers for jumps of the adatoms to neighbouring surface sites given by isotropic nearest–neighbour bond energies. Equilibrium and dynamic properties are computed by using kinetic Monte Carlo techniques [13]. Specifically, for a single island in equilibrium with the "gas" of adatoms on the surrounding terrace a phase transition is observed at a critical temperature T_c, above which the island tends to disappear. This aspect seems to have been overlooked in previous investigations. A study on the equilibrium cluster size in a related Ising model had been performed already several years ago [14], but it had been limited to low temperatures. Quite recently, the thermal disintegration of a cluster was discussed [15], however, for systems without conservation of the number of particles. In addition, we monitor the motion of the equilibrated adatom island well below T_c, to estimate the value of α in the nearest neighbour isotropic bond–counting case.

[a] e-mail: selke@physik.rwth-aachen.de

The article is organized accordingly. In the next section, we introduce model and method. We then present results on the characteristics of the phase transition at which the island disappears, followed by a discussion of the diffusive motion of the cluster at low temperatures. We conclude with a short summary.

2 Model and method

Adatoms on a square lattice may be constrained to a single layer, with the occupation variable n_i at surface site i being either 1 or 0. To jump to an empty neighbouring site, the adatom has to overcome an energy barrier E_a. Using a bond–counting ansatz, that energy may be written in the form

$$E_a = E_0 + nE_b \tag{1}$$

where E_0 is the activation energy for free diffusion of the adatom on a locally perfect surface, n is the number of occupied neighbouring sites, $n = 0$, 1, 2, or 3, and E_b is the bond energy. Of course, the ansatz is not expected to give a realistic description of a specific material. However, it is useful in identifying generic properties of islands, as will be discussed below.

The energy barrier (1) corresponds to the Hamiltonian (apart from a constant)

$$\mathcal{H} = -E_b \sum_{i,j} n_i n_j \tag{2}$$

where the sum runs over neighbouring sites i and j. It is interesting to note that the Hamiltonian may be transcribed to a nearest–neighbour Ising model [11],

$$\mathcal{H}_{\mathcal{I}} = -E_b/4 \sum_{i,j} S_i S_j + \text{constant} \tag{3}$$

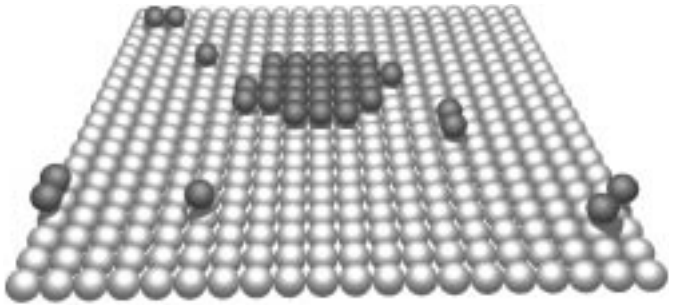

Fig. 1. Island of monoatomic height in equilibrium with the surrounding gas of adatoms.

with the Ising spin $S_i = \pm 1$ being related to the occupation variable n_i by $S_i = 2n_i - 1$. The conservation of the number of adatoms on the surface corresponds to the conservation of the magnetization in the Ising model.

We considered square surfaces with $L \times L$ sites and $M \times M$ adatoms, *i.e.* with a coverage $\theta = M^2/L^2$. Usually, full periodic boundary conditions were used, to reduce boundary effects. However, to compare with possible experiments, we also applied free boundary conditions as encountered for a terrace of L^2 sites with large reflecting energy barriers at the descending steps bordering the terrace (large Schwoebel–Ehrlich barriers).

In the simulations, L ranged from 50 to 1000, and M from 5 to 50, with the coverage θ varying between 4×10^{-4} and 4×10^{-2}. Obviously, at those coverages the adatoms form a compact island at low temperatures due to the attractive interactions, see (1). A typical configuration is shown in Figure 1.

The kinetic Monte Carlo simulations were performed in the standard way [13,16], based on jump probabilities for the adatoms to neighbouring sites $\propto \exp(-E_\mathrm{a}/k_\mathrm{B}T)$, with k_B being the Boltzmann constant and T the temperature. The time may be measured in units of trial jumps per adatom (MCA). Other commonly used time scales, invoking, *e.g.*, a microscopic attempt frequency ν, are linearly related to that unit. At low temperatures, the efficient algorithm of Bortz, Kalos, and Lebowitz [17], BKL, was implemented.

To study stability and dynamics of the island, several quantities were computed. Among others, we recorded the distribution of clusters (as usual, a s-cluster is formed by s adatoms connected by occupied neighbouring sites), especially the fraction of adatoms in the largest cluster, *i.e.* the "reduced island size",

$$n_\mathrm{max} = N_\mathrm{max}/M^2 \tag{4}$$

where N_max is the number of adatoms in the largest cluster. Furthermore, the fluctuations of that island size, the density of adatoms, the energy E, see (2), and the fluctuations of the energy were monitored. To analyse the motion of the island, we determined the time evolution of the position of its center of mass, see Section 4.

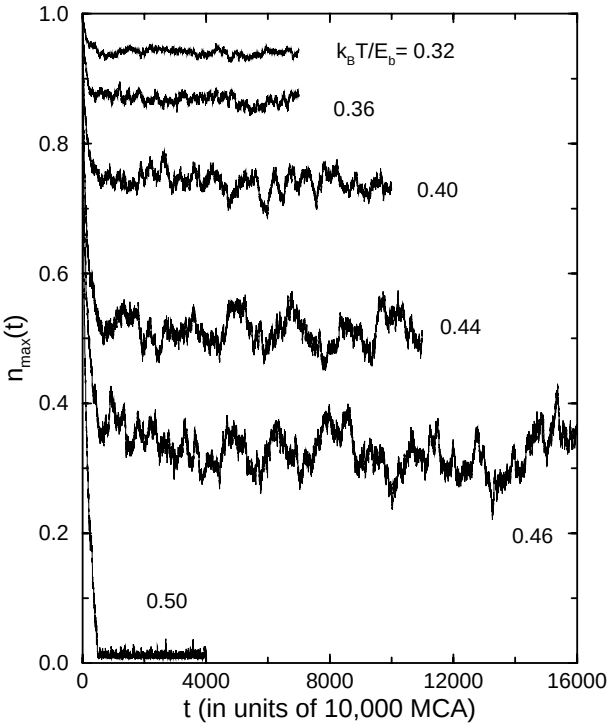

Fig. 2. Time dependence of the island size $n_\mathrm{max}(t)$ for $M = 50$ and $L = 250$, at various temperatures $k_\mathrm{B}T/E_\mathrm{b}$. The initial configuration of the simulations is a square cluster with M^2 adatoms. The time is measured in trial jumps per adatom (MCA).

3 Thermal stability

In the ground state, $T = 0$, the M^2 adatoms form a compact square cluster, at sufficiently low coverage θ (otherwise, a stripe of adatoms will minimize the energy). At non–zero temperatures, adatoms may detach from the island, leading to a dynamic equilibrium of the rounded cluster and the "gas" of adatoms on the terrace, see Figure 1. Of course, the size of the island is expected to shrink as the temperature increases, as demonstrated in Figures 2 and 3.

For reasons of simplicity, we assume equal energy barriers in the bond–counting ansatz, (1), *i.e.* $E_0 = E_\mathrm{b}$. Starting the simulations with a square cluster of M^2 adatoms, the time evolution of the island size, $n_\mathrm{max}(t)$, at various temperatures $k_\mathrm{B}T/E_\mathrm{b}$, is shown in Figure 2. Obviously, equilibration may be rather slow, as observed before in the related Ising model [14]. Discarding the initial relaxation, the thermal equilibrium value for the reduced island size, $n_\mathrm{m}(T) = \langle n_\mathrm{max} \rangle$, is obtained by averaging over the subsequent, possibly strongly fluctuating, see Figure 2, simulational data. The resulting temperature dependent island size is depicted in Figure 3, at coverage $\theta = 0.04$ with $M = 25$ and 50 (hence, $L = 125$ and 250).

The drastic decrease of $n_\mathrm{m}(T)$, both for periodic and free boundary conditions, in a narrow range of temperatures suggests a phase transition at the critical temperature T_c in the thermodynamic limit, $L, M \longrightarrow \infty$, at constant coverage $\theta = M^2/L^2$. The reduced island size

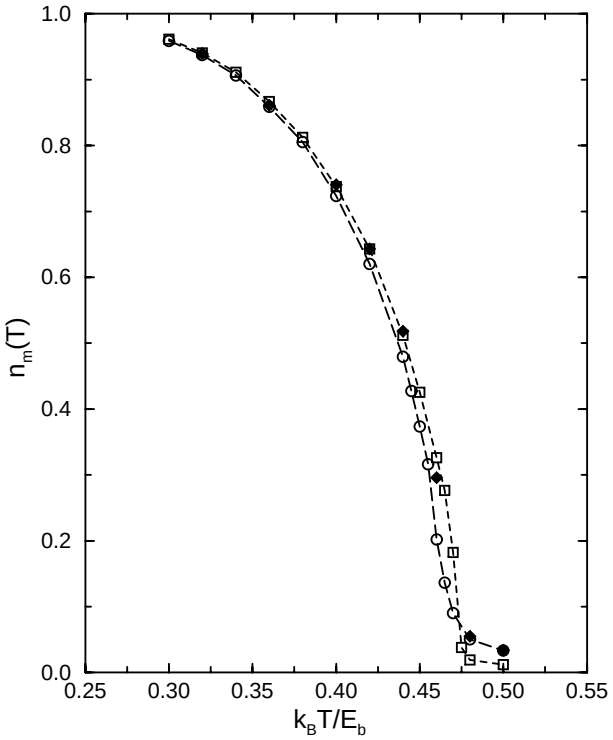

Fig. 3. Temperature dependence of the thermally averaged island size $n_{\rm m}(T)$ for surfaces with 125^2 sites and 25^2 adatoms (open circles: periodic boundary conditions; full diamonds: reflecting boundaries) as well as 250^2 sites and 50^2 adatoms (open squares: periodic boundary conditions). Error bars are smaller than symbol sizes.

$n_{\rm m}(T)$ may then be interpreted as the "order parameter", vanishing at $T \geq T_{\rm c}$. In the high–temperature phase, the island disappears in the gas of adatoms. Indeed, finite–size analyses of the Monte Carlo data, at fixed coverages, allow to locate the phase transition: For example, at $\theta = 0.01$, the turning point, $T_{\rm m}(M)$, of the temperature dependent island size $n_{\rm m}(T)$, see Figure 3, is found to shift for large values of M approximately like $T_{\rm c} - T_{\rm m}(M) \propto 1/M$, and at temperatures above $T_{\rm c}$, $n_{\rm m}(T)$ goes to zero inversely proportional to M^2 (for details, see Ref. [18]). Moreover, the transition is signalled by a pronounced maximum in the temperature derivative of the energy close to $T_{\rm m}$, similarly to that of the fluctuations in the island size and the energy. All these quantities seem to show singular behaviour in the thermodynamic limit.

In general, a phase diagram in the temperature–coverage $(k_{\rm B}T/E_{\rm b}, \theta)$ plane may be determined, with a single large cluster or, at $\theta \geq 1/4$, a stripe of adatoms characterising the low–temperature phase. Because of the transcription to the Ising model, (3), $T_{\rm c}$ is known exactly at $\theta = 1/2$, namely $k_{\rm B}T/E_{\rm b} = 1/(2\ln(\sqrt{2}+1))$. Certainly, the transition temperature tends to decrease with decreasing coverage. For instance, we estimated, at $\theta = 0.04, 0.01$, and 0.0016 the critical temperatures $k_{\rm B}T/E_{\rm b} \approx 0.49, 0.38$, and 0.28, respectively.

Approaching the phase transition from below, the largest cluster becomes more and more ramified and may dissociate quite easily, while other groups of adatoms may coalesce forming a new largest cluster, as one may readily observe in the simulations. Accordingly, the island size $n_{\rm m}(T)$ as well as the energy may fluctuate strongly, and good statistics is needed to get reliable equilibrium values in the critical region, and to quantify the asymptotics. In particular, we analysed the "order parameter" $n_{\rm m}(T)$, as $T \longrightarrow T_{\rm c}$. Fitting the simulational data to a power–law

$$n_{\rm m}(T) \propto (T_{\rm c} - T)^{\beta} \tag{5}$$

we obtained, from extensive simulations at coverages $0.0016 \leq \theta \leq 0.04$, $\beta = 0.45 \pm 0.01$, being (if at all) only fairly weakly dependent on the coverage. The rather large error bar reflects, especially, uncertainties in extrapolating the estimates to the thermodynamic limit. Actually, we computed an effective exponent $\beta_{\rm eff} = {\rm d}\ln(n_{\rm m})/{\rm d}\ln(t)$, where $t = |T_{\rm c} - T|$ or $|T_{\rm m} - T|$, leading to upper and lower bounds for the critical exponent β, which is approached in the limit $L, M \longrightarrow \infty$ and $t \longrightarrow 0$.

The standard description of a cluster in equilibrium with a gas is based on the Gibbs–Thomson formula [19]. The equilibrium density ρ of the gas of adatoms in coexistence with a circular island of radius R is then [11,12]

$$\rho(R) = \rho_{\rm s} \exp[\gamma/(R\rho_{\rm i}k_{\rm B}T)] \tag{6}$$

where γ is the free energy per unit length of the island edge, $\rho_{\rm i}$ is the density of the island, and $\rho_{\rm s}(T)$ denotes the density of a gas of adatoms in the presence of a straight step. Modified formulae have been discussed [11–14] to include, *e.g.*, interactions between the adatoms on the terrace. However, no attempt is known to us to extend the description into the critical region, where the island tends to disappear, $\rho \approx \rho_{\rm i}$.

In our simulations, we confirmed that the density of adatoms ρ is, indeed, constant, when exceeding a critical distance from the center of the island. Moreover, at low temperatures and coverages, the Gibbs–Thomson formula (6) predicts an approximately logarithmic dependence of the characteristic temperature T_x, with $n_{\rm m}(T_x) = x$, on the coverage θ

$$k_{\rm B}T_x \propto -1/\ln[\theta(1-x)] \tag{7}$$

fixing the number of adatoms M^2 and varying the surface size L^2. To derive (7), one may use the low–temperature relation [12] $\rho_{\rm s} \propto \exp(-E_{\rm ad}/k_{\rm B}T)$, where $E_{\rm ad}$ is the energy to detach an atom from the step. Indeed, for example, our simulational data at $M = 10$, $100 \leq L \leq 1000$, and $x = 1/2$ agree well with (7) [18].

4 Diffusion

The exchange of adatoms between the island and the surrounding terrace gas leads to a diffusive motion of the equilibrated island. The corresponding diffusion constant

D follows from the fluctuations in the position of the center of mass of the cluster, $\mathbf{r}_{\rm cm}(t)$,

$$D = \langle(\mathbf{r}_{\rm cm}(t) - \mathbf{r}_{\rm cm}(0))^2\rangle/(4t) \tag{8}$$

where the brackets denote the equilibrium average.

From previous studies [1–8], one expects that D depends on the number of adatoms in the island, $N = \langle N_{\rm max}\rangle$, at least asymptotically for large values of N, as

$$D \propto N^{-\alpha} \tag{9}$$

with the value of α characterising the dominat mechanism of exchange between the cluster and the gas, discriminating, *e.g.*, island-edge or periphery diffusion, terrace diffusion and evaporation–condensation kinetics (a similar classification holds for step fluctuations [20,21]), see below.

To check the diffusive character of the island motion, (8), and to determine the characteristic exponent α, we performed kinetic Monte Carlo simulations, using the bond–counting ansatz, (1), with $E_0 = 0$, thereby speeding up the dynamic processes. The time may be measured in units of seconds. Invoking the microscopic attempt frequency ν, one trial jump per adatom, 1 MCA, corresponds then to $1/(4\nu)$ seconds [13,16]. We chose $\nu = 10^{11}$ Hz. The lattice constant of the square surface was set equal to one. To compute the fluctuations in the position of the center of mass of the island, (8), we first equilibrated the system, before averaging over an ensemble of initial times as well as an ensemble of (up to 1000) realizations. The simulations were done at low temperatures, well below $T_{\rm c}$, namely $k_{\rm B}T/E_{\rm b} = 0.2$ and 0.28, for islands of sizes N ranging from about 20 to about 700. The coverage was fixed, $\theta = 0.01$. We applied here the BKL algorithm in our extensive simulations.

The positional fluctuations, $\langle(\mathbf{r}_{\rm cm}(t) - \mathbf{r}_{\rm cm}(0))^2\rangle$, are found to increase, indeed, linearly in time, even at early times. The diffusion constant D is then readily obtained from linear regression. The resulting size dependent $D(N)$ at $k_{\rm B}T/E_{\rm b} = 0.28$ is shown in Figure 4. Discarding the smallest island size, the characteristic exponent α is estimated to be, on average, $\alpha = 1.02 \pm 0.03$. At $k_{\rm B}T/E_{\rm b} = 0.2$, the value of α seems to be consistent with $\alpha = 1$ as well ($\alpha = 1.04 \pm 0.04$), for island sizes N ranging from 20 to 700.

From elementary geometry and energy considerations [14] and from a Langevin theory [2], $\alpha = 1$ may be argued to correspond to an island motion driven by terrace diffusion, where the adatom emitted by the island diffuses as a random walker on the terrace before attaching again (or a vacancy may diffuse through the island).

In principle, other mechanisms may compete, in particular, random detachments and attachments of adatoms at the island edge (evaporation–condensation kinetics) or diffusion of the atoms along the island edge (periphery diffusion), leading to $\alpha = 1/2$ and $3/2$, respectively [2,14]. In addition, periphery diffusion may be hindered by corners and kinks, modifying, possibly, the value of α [4,6]. Among others, details of the shape of the islands as well as the activation energies are expected to determine which mechanism dominates. In general, it is reasonable to consider an effective characteristic exponent $\alpha_{\rm eff} = -{\rm d}\ln D/{\rm d}\ln N$, which may depend on island size N and temperature T, as observed in experiments and simulations.

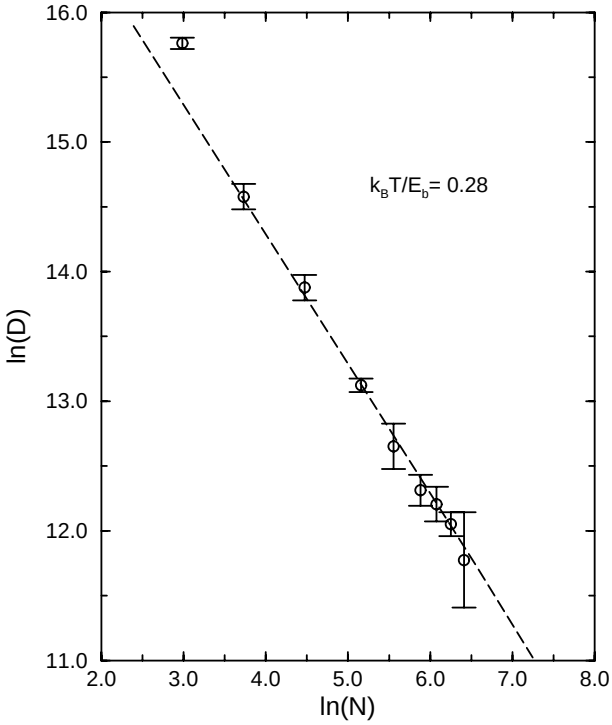

Fig. 4. Logarithm of the diffusion constant D *vs.* logarithm of number of adatoms in the largest cluster N at coverage $\theta = 0.01$ and temperature $k_{\rm B}T/E_{\rm b} = 0.28$. The dashed line corresponds to $\alpha = 1$. The size of the surfaces (L^2) ranged from 50^2 to 280^2 in the simulations.

In our case, Figure 4 indicates an increase of $\alpha_{\rm eff}$ from higher values at small island sizes towards $\alpha \approx 1$ at $Ni \approx 30 - 40$. Of course, another crossover at cluster sizes exceeding those we studied, $N \approx 700$, cannot be excluded. Actually, simulations on a related Ising model, applying Kawasaki dynamics, were interpreted as providing evidence for a crossover from periphery diffusion to evaporation–condensation kinetics, studying somewhat smaller cluster sizes, $N \leq 500$, and higher coverages, with an average exponent α not far from one [14]. In contrast to the previous study, we determined $D(N)$ at fixed coverage. Obviously, our data do not show clearly such a crossover, but it cannot be ruled out.

It seems interesting to note that $\alpha \approx 1$ has been found in experiments on Ag(111), using scanning tunneling microscopy [1], but other values of α have been reported for different surfaces, reflecting the above mentioned competing mechanisms.

5 Summary

Thermal stability and diffusion of an adatom island of monoatomic height on a square surface have been

studied, using a standard bond–counting ansatz for the energy barriers and performing kinetic Monte Carlo simulations.

A phase transition has been identified, with the fraction of adatoms in the largest cluster n_{m} being the "order parameter". $n_{\mathrm{m}}(T)$ vanishes on approach to the transition temperature T_{c} as $n_{\mathrm{m}} \propto |T_{\mathrm{c}} - T|^{\beta}$ with $\beta = 0.45 \pm 0.10$ at various small coverages θ. In addition, the energy as well as fluctuations in the island size and in the energy exhibit singular behaviour at T_{c}. Experimentally, such phenomena may be observed on a terrace bordered by descending steps with large Schwoebel–Ehrlich barriers to allow for equilibration of the island with the surrounding gas of adatoms on the terrace.

The diffusion constant D, describing the island motion, decreases with the number of adatoms in the island N like $D \propto N^{-\alpha}$, with α being close to one for an extended range of island sizes at temperatures well below T_{c} at $\theta = 0.01$. $\alpha = 1$ corresponds to the case where the dominant mechanism driving the motion of the island is terrace diffusion. An alternative interpretation invokes a crossover from periphery diffusion to evaporation–condensation kinetics.

Of course, it would be interesting to investigate the robustness of our findings against varying, especially, the activation energies in a systematic way.

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Note added in proof

Attention is drawn to related recent work on island diffusion [22,23].

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