Due to the peculiar directional elastic properties of the PbTe layers, the PbSe tetraeder islands create three elastic energy minima for subsequent nucleation in the PbTe layer covering them. Choosing the proper growth temperature (i.e. initial spacing) and the right spacer layer thickness, an fcc stacking of quantum dots results as shown in Figs. 6.18 and 6.19

6.3 Kinetic effects in growth

All our considerations up to now are considerations for a situation close to thermodynamic equilibrium, also the growth modes discussed above are growth modes close to thermodynamic equilibrium. However, usually thin film growth takes far from thermodynamic equilibrium. To gain insight into kinetic effects in thin film growth we will consider homoepitaxy. For homoepitaxy the expected growth mode is Frank-van der Merwe growth (close to equilibrium). However we envision also other growth modes:

     - high T : step flow - due to substrate steps
   - intermediate T : layer-by-layer growth (F-vdM)
      low T : mound formation due to step barrier
    very low T : self affine growth - atoms incorporate
        where they arrive.   See Fig. 6.20

The example of Pt on Pt (111) shows that nature is often even more complex (See Fig 6.21).

We now briefly discuss a number of kinetic effects.

- condensation: In order to stick to the surface, an atom has to loose its kinetic energy upon impact. This loss of energy is very efficient for metal atoms arriving on metal surfaces and takes place on the time scale of
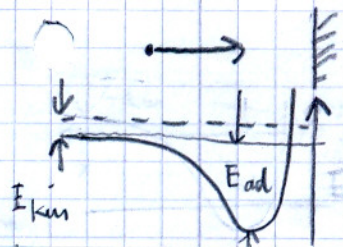
of a period of a lattice vibration, i.e. within a ps. For metals,
condensation is efficient and the sticking coefficient $S = 1$.
But for molecules it may be low: O_2 on $Al(111)$: $S = 0.02$ at 300k
Efficient sticking on a metal may be intuitively understood in a
two particle - spring model, where momentum and energy are
exchanged efficiently.
Once the adatom is bound, still it might have enough energy
to move parallel to the surface, i.e. use some of its condensation
energy for athermal diffusion. For metal atoms this kind of
transient mobility is absent, but for instance for Xe on $Pt(111)$
it takes place.
– steering The attractive potential in front of the surface diffracts the
arriving particle towards the surface normal :
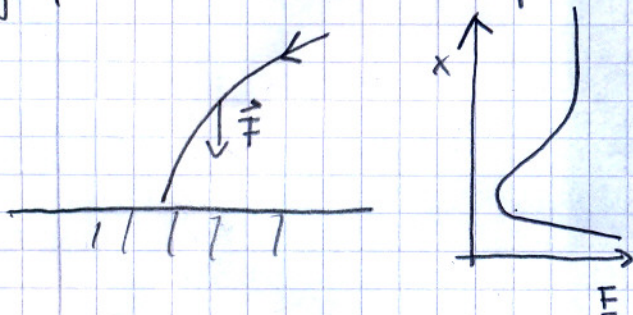
This effect has important
consequences. Consider a thin
film with mounds. The mounds
will receive an enhanced

atom supply and thus will develop.
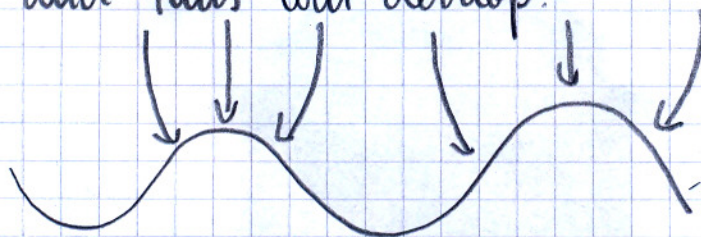
This effect amplifies roughness and prevents self affine growth.
Example: Pt growth on Pt (111) at 50 k   Fig 6.22
– diffusion and random walk
Consider a particle performing a one dimensional random walk,
i.e. an adatom in a furrow of an fcc (110) surface jumping
with equal probability to the left or to the right a lattice
distance ℓ. After N jumps the mean square displacement is

$$\langle (x(N) - x(0))^2 \rangle = N \cdot \ell^2.$$ This result follows immediately from the properties of the Binomial distribution. The result is also valid in two dimensions (relevant for us) or three dimensions

$$\langle (\vec{r}(N) - \vec{r}(0))^2 \rangle = N \cdot \ell^2$$

With the average hopping rate v we have $N = v \cdot t$ and

$$\langle (\vec{r}(t) - \vec{r}(0))^2 \rangle = \langle (\Delta \vec{r})^2 \rangle = v \cdot t \, \ell^2 =: 4Dt \qquad (*)$$

The quantity $D = \frac{1}{4} \ell^2 v$ is named tracer diffusion coefficient.

In the limit of low coverage (or low concentration) it agrees with the collective diffusion coefficient defined by Fick's first law :

$$\vec{j} = - D \, \nabla u \qquad\qquad j = \text{particle current}$$
$$u = \text{concentration of particles}$$

Using the Arrhenius law $v = v_{\partial} \, e^{-E_a/kT}$ with $(*)$

$$\langle (\Delta r)^2 \rangle = v_0 \cdot e^{-E_a/kT} \cdot t \cdot \ell^2 \qquad or$$

$$\ln \frac{\langle (\Delta r)^2 \rangle}{t} = - \frac{E_a}{kT} + \ln(v_0 \cdot \ell^2)$$

Plotting the quantity $\frac{\langle (\Delta r)^2 \rangle}{t}$ vs $\frac{1}{T}$ allows one to obtain the activation energy E_a from the slope and the attempt frequency from the intercept of the plot.

Figs. 6.23 and 6.24 give an example for Ir adatoms on Ir (111). For each temperature T, many heating intervalls t followed by determination of the induced displacement Δr allow one to obtain the average values $\frac{\langle (\Delta r)^2 \rangle}{t}$ and thus E_a and v_0 (or D_0).

The movie gives an alternative way of data aquisiton by STM
for Pt monomers moving on Pt(110).

— <u>nucleation for from equilibrium</u>

To understand, how the concentration of stable islands n_x results
from the adatom concentration n_1 and the deposition rate F
The situation is complex as shown in Fig 6.25. The most important
quantity is the size of the critical nucleus i^*. In metal homoepitaxy
at room temperature it is frequently just 1. The critical nucleus is
the one, which transforms into a stable island by the addition of one
atom. To solve the problem we may set up a set of coupled
differential equations:

$$\frac{dn_1}{dt} = F(1-z) - \frac{n_1}{\tau} - 2U_1 - \sum U_j$$

$$\frac{dn_j}{dt} = U_{j-1} - U_j \qquad i^* \geq j \geq 2$$

$$\frac{dn_x}{dt} = U_{i^*} - U_c \qquad x \geq i^*+1$$

Here
F = deposition rate
z = fraction of surface covered by stable cluster
τ = characteristic life time of an adatom before reevaporation
U_1 = net rate of capture of adatoms by adatoms
U_j = net rate of capture of adatoms by a cluster of size j
n_x = concentration of stable clusters with sizes $x \geq i^*+1$
U_c = rate of coalescence of stable clusters

The number of stable islands n_x shows a broad maximum

as a function of the deposited amount in the range between
0.2 and 0.6 ML. This value is named saturated island density $n_{x,sat}$

Assuming a local equilibrium of subcritical clusters of various sizes j,
we obtain that all $U_j = 0$
The remaining two differential equations are coupled, because

$$U_{ix} = \sigma_{i*} \cdot D \cdot n_1 \cdot n_{ix} \qquad (+) \qquad \text{see also Fig. 6.25}$$

Here $D = \frac{1}{4} \ell^2 \cdot \nu$ is the adatom diffusion coefficient and σ_i^* is the capture number, characterizing how efficiently an adatom is incorporated into a cluster of size i^*. The two equations may be solved under reasonable assumptions (see Krug / Michely : Islands, Mounds and Atoms) and yield a scaling relation

$$n_{x,sat} \sim \left(\frac{F}{\nu}\right)^\chi \qquad \chi = \frac{i^*}{i^* + 2}$$

Thus from the dependence of $n_{x,sat}$ on F the size of the critical nucleus is obtained and from the temperature dependence of $n_{x,sat}$ the activation energy E_{ad} for the adatom migration, since $\nu = \nu_0 e^{-E_{ad}/kT}$.
As shown in Figs. 6.26 and 6.27, from quantitative STM analysis one thus obtains the atomistic parameters of adatom diffusion.

- the <u>roughness of the growth for from equilibrium</u> is decisively influenced by the existence of the step edge barrier for adatoms, also named Ehrlich – Schwoebel barrier. As schematically sketched in Fig 6.28, the extra energy ΔE_s results from the adatom being forced to move through a position of reduced coordination. Due to ΔE_s, an atom at the descending step is more likely to jump back to the terrace rather than to descent to become incorporated into the step. Consequently, the adatom concentration n_1 on top of an island will be enhanced if $\Delta E_s > 0$. Equation $(+)$ then tells us immediately, that the nucleation rate of island on top of islands is enhanced (think: $i^* = 1$). This effect causes mound formation in epitaxial growth. If the step edge barrier is infinitively high, i.e. if all atoms stay within their layer of deposition, a simple solution exists for the layer

distribution. Let Θ be the total deposited amount measured in ML and Θ_u be the coverage in the u-th layer.

Then the coverage in the u-th layer grows just from the atoms arriving in the exposed coverage $\varphi_{u-1} = \Theta_{u-1} - \Theta_u$ of the layer below:

$$\frac{d\Theta_u}{dt} = F \left(\Theta_{u-1} - \Theta_u \right) \qquad F \text{ measured in } ML/s$$

Using the boundary conditions $\Theta_0 = 1$ and $\Theta_{u \geq 1}(0) = 0$ this set of coupled differential equations has the solution

$$\Theta_u = 1 - e^{-\Theta} \sum_{k=0}^{u-1} \frac{\Theta^k}{k!} \qquad \qquad \Theta = \sum_{u=1}^{\infty} \Theta_u$$

This is straightforward to check and one just has to remember that $\frac{d\Theta}{dt} = F$. The exposed coverages $\varphi_u = \Theta_{u+1} - \Theta_u$ are then distributed according to a Poisson distribution:

$$\varphi_u = e^{-\Theta} \cdot \frac{\Theta^u}{u!}$$

Without going into detail, we note that the variance of the Poisson distribution is identical to the mean. Thus the standard deviation of the layer distribution or roughness is simply $\sigma_{rms} = \sqrt{\Theta}$

Fig 6.29 displays the typical „Zwiebeltürmchen" shape of mounds resulting from a 1D kinetic Monte-Carlo simulation.

In reality, a step edge barrier is never infinite, but finite. This implies a top terrace of finite size for the following reason. An adatom on the top terrace has a finite lifetime τ as it wanders around probes to descend and at one instance be successfull in descent. This may be prevented only if a second adatom arrives within τ such that the two may nucleate.

The average time interval between successive deposition events on the top terrace Δt decreases and the lifetime τ increases with the terrace size. Thus at a pretty well defined terrace size the nucleation takes place

From the average top terrace **diameter L'** one may obtain ΔE_S once E_{ad} is known. We have

see Fig. 6.30
$$\nu_0' \cdot e^{-(E_{ad} + \Delta E_S)/k_B T} = \gamma \cdot F \cdot L'^5 \qquad \gamma = \text{factor}$$

The overall shape of the mound however is not changed much. At the flanks of the mound it is not important whether an adatom could be reflected 10 times or one 1000 times: typically after one reflection it is incorporated to the ascending step. Therefore the precise value of ΔE_S is not relevant for the shape at the flanks. In conclusion, in homoepitaxy for from equilibrium one is able to read the fundamental atomistic parameters from the morphology: ν (and thus ν_0 and E_{ad}) from the mound separation and ν' (and thus ν_0' and ΔE_S) from the size of the top terrace. (Fig. 6.31)

There are many more interesting kinetic effects in growth (e.g. for island shapes) but at the end of this section we want to discuss the consequences of the step edge barrier for growth from a different viewpoint.
As pointed out in Fig. 6.32, a groove never closes (in the continuum approximation) as zero never reaches the turtle. As this is an effect at the flanks of the mounds, it is quite robust against the precise magnitude of ΔE_S. Therefore deep grooves are a typical problem in thin film growth. A number of examples from different growth situations are shown in Fig. 6.33

Growth manipulation

Based on our knowledge we may no define a simple criterion for layer-by-layer growth: If the average island separation $\lambda \propto \frac{1}{\sqrt{n_{x,sat}}}$ is smaller then the typical diameter L at which second layer nucleation takes place, we obtain layer-by-layer growth.

$$\text{l-b-l} \quad \text{if} \quad \lambda \leq L$$
$$\text{mounds} \quad \text{if} \quad \lambda > L$$