3. Condensation and Thin Film Growth

3.1. Introduction

If atoms hit the surface of a solid they are either reflected within a time of one or two lattice vibrations (approx. $10^{-12} - 10^{-13}$ s) or they transfer enough energy to the lattice to be weakly bound to the surface as so-called ad-atoms. As ad-atoms they diffuse along the surface until they either desorb again, a stable nucleus is formed or they attach to a stable island.

The surface mobility of ad-atoms is given by the substrate temperature, by their kinetic energy upon impingement and by the strength of interaction between a single atom and the substrate. If this interaction is strong one obtains a high nucleus density (nuclei per unit area). A weak interaction results in a low nucleus density. By the attachment of other ad-atoms the nuclei grow to islands (at constant nucleus density) which - depending on the given conditions - coalesce to a more or less connected film.

3.2. Theory

3.2.1. Elementary Processes at Surfaces

The first important atomistic elementary process is the approach of single atoms or molecules to a surface with the impingement rate $R$. In kinetic gas theory this is given by

$$R = \frac{\beta p_0}{\sqrt{2\pi mk_B T_0}} \left[ m^2 \text{s}^{-1} \right]$$

where $p_0$ is the vapor pressure at the substrate surface and $\beta$ is a proportionality factor. Additionally:
- $m = \text{atom or molecular mass [kg]}$
- $T_0 = \text{source temperature [K]}$

Upon approach to a crystalline surface the atoms or molecules begin to interact with the surface atoms. In a specific vertical distance from the surface an energetic minimum is existing for the system surface/approaching particle at any arbitrary lateral position. The absolute value of this minimum, however, depends on the lateral position. If one draws the variation of the energy minimum in dependence on the lateral position of the approaching atom one obtains the so-called Potential Energy Surface (PES).

The random position of impingement will not correspond to an energetic minimum of the PES in most cases. Within few lattice vibrations the loosely bound atom transfers its energy to the lattice and during this time finds a local minimum of the PES. For metal atoms on metallic surfaces the minima in the PES (these are the positions with maximum binding energy) are identical to positions with a high coordination number in most cases. For molecules on metallic and non-metallic surfaces the more complicated electronic structure does not allow for such general statements. The bonding of a deposition atom within a minimum of the PES is called adsorption. Typical adsorption energies $E_a$ are in the range from 1 to 2 eV.

The second elementary process which takes place at a surface right after impingement of an atom or molecule (the building blocks of a film will also be called "monomers" in the following) is the transfer of the energy of a monomer to the bulk.
lattice. This takes some lattice vibrations. The frequency $\nu_0$ of a lattice vibration is $10^{12} - 10^{13}$ Hz which means that within a time $\tau_0$ of $10^{-12} - 10^{-13}$ s the energy of the impinging monomer is dissipated and the free atom has become an adsorbate or "ad-atom". The frequency $\nu_0$ can be considered as the "clock rate" of the system. With this rate thermal energy from the phonon system of the bulk is supplied to the monomers adsorbed on the surface. Thisclocked energy supply influences all other atomistic atomic scale processes.

The adsorbed particles are confined within a two dimensional phase state. They are bound to the surface but can rather easily move along the surface due to the energy transfer by lattice vibrations described previously.

To perform such movements the ad-atoms have to cross the saddle ridges present within the PES. These crossing events occur with a frequency

$$v_d = v_0 e^{-E_d/(k_B T_S)}$$

$E_d$ = activation energy for surface diffusion [J], corresponds to the height of the saddle ridges in the PES

$T_S$ = substrate temperature [K].

Between two diffusion events the time

$$\tau_d = t / v_d = v_0^{-1} e^{-E_d/(k_B T_S)}$$

is passing. An uncorrelated sequence of jumps of a monomer from one PES minimum to another forms the third elementary process, the so called surface diffusion. An uncorrelated sequence of jumps is also called "random walk" or "Brownian motion" and is displayed in Fig. 3.1. for a regular quadratic lattice of adsorption sites.

![Fig. 3.1.: Surface diffusion as random walk on a quadratic lattice of adsorption sites](image)

- a ... lattice constant
- l ... effectively traveled distance

The essential quantity for thin film growth is the effectively traveled distance $l$ as it is displayed in Fig. 3.1. As it is visible from Fig. 3.1. $l$ is much shorter than the total distance $N a$ which is covered by the diffusing particle in $N$ jumps of length $a$. $l$ can be calculated as follows:

According to Pythagoras

$$l^2 = \left( \sum_{i=1}^{n} x_i \right)^2 + \left( \sum_{i=1}^{n} y_i \right)^2$$

$x_i, y_i = \pm a$

and
\[ l^2 = \left( \sum_{i=1}^{n_1} x_i \sum_{j=1}^{n_j} x_j \right) + \left( \sum_{i=1}^{n_1} y_i \sum_{j=1}^{n_j} y_j \right). \]

Calculating the expectation value of \( l^2 \) finally yields:

\[
\langle l^2 \rangle = \left( \sum x_i \sum x_j \right) + \left( \sum y_i \sum y_j \right) = \left( \sum x_i^2 \right) + \left( \sum y_i^2 \right) + \left( \sum x_i \sum x_j \right) + \left( \sum y_i \sum y_j \right) = \left( \sum x_i^2 \right) + \left( \sum y_i^2 \right) = (n_x + n_y) \cdot a^2 = N \cdot a^2.
\]

After extracting the root from \( \langle l^2 \rangle \) according to \( \sqrt{\langle l^2 \rangle} \equiv \sqrt{\langle l \rangle} \) (which is mathematically approximately valid) one obtains

\[
\langle l \rangle \equiv \sqrt{N} a.
\]

The effective length \( l \) traveled by a monomer is only proportional to the square root of the number of jumps, \( N \), according to Eqn. (3.6). The relation given in Eqn. (3.6) can also be used to define the diffusion coefficient \( D \) for a single particle:

\[
D = a^2 \nu e^{E_d/(k_B T_k)} \ [m^2 s^{-1}] \quad (3.7)
\]

This exactly corresponds to Eqn. (3.6) if \( N \) is taken to be the number of jumps per second given by the diffusion frequency \( \nu = \nu_0 e^{E_d/(k_B T_k)} \). The distance a monomer travels on a surface within a time \( \tau \) is therefore intuitively given by the so-called "Einstein-relation"

\[
l = \sqrt{D} \tau. \quad (3.8)
\]

The fourth and last atomistic elementary process is the possibility of an adsorbed monomer to detach from the surface which is called desorption. As for surface diffusion the energy to accomplish this has to be taken from the thermal reservoir of the bulk. It is called desorption energy, \( E_{des} \) and has the same numerical value like the adsorption energy \( E_a \) but with opposite sign. Desorption processes happen with the frequency

\[
\nu_{des} = \nu_0 e^{-E_{des}/(k_B T_k)}. \quad (3.9)
\]

The mean time between two desorption events, \( \tau_{des} \) is given by

\[
\tau_{des} = \frac{1}{\nu_{des}} = \nu_0^{-1} e^{E_{des}/(k_B T_k)}. \quad (3.10)
\]

While the deposition rate \( R \) can be chosen independently from the situation on the substrate, \( \nu_d \) and \( \nu_s \) are strongly influenced by the substrate temperature \( T_S \) as table 3.1. shows for values of \( E_d = 0.2 \) eV and \( E_{des} = 2 \) eV.
Tab. 3.1.: Time scales of atomistic elementary events. $E_d = 0.2\, \text{eV}$, $E_{des} = 2\, \text{eV}$.

$\tau_d$ and $\tau_{des}$ were calculated for $\nu_0 = 5 \cdot 10^{12}\, \text{Hz}$

Table 3. 1. shows the extremely different time scales in which the single event types happen. The difference between $\tau_d$ and $\tau_{des}$ is very important because it allows to distinguish the two so-called "condensation regimes" which will be treated briefly in the following section.

3.2.2. Condensation Regimes

3.2.2.1. Complete Condensation

For low substrate temperatures $\tau_{des}$ can be very long while $\tau_d$ still is in the region of some ps or ns (see Tab. 2.2., $T_S = 300$ or 600 K). In this case all deposited monomers remain on the surface and diffuse until two or more monomers aggregate and form a so-called nucleus. There are basically no desorption events and the amount of deposited material increases linearly.

3.2.2.2. Incomplete Condensation

For high substrate temperatures $\tau_{des}$ is in the order of some tenths or hundredths of seconds. Although the diffusion frequency still is very high, monomers can desorb before a nucleus is formed. The average distance $l$ between the point of adsorption and the point of desorption is the diffusion length $l$ given by

$$l = \sqrt{D \tau_{des}} = a e^{(E_{des} - E_d)/2k_BT_S}.$$  \hspace{1cm} (3.11)

The mobility of the adsorbed atom is fully described by the quantities $D$, $\tau_{des}$ and $l$. The desorption rate $R_{des}$ of the ad-atoms is given by

$$R_{des} = n_1
\nu_0 e^{(-E_{des} / k_BT_S)} = n_1 / \tau_{des}$$  \hspace{1cm} (3.12)

with $n_1$, the surface concentration of the ad-atoms in $[\text{atoms}\cdot\text{m}^{-2}]$.

Before nucleation and at low nucleus density $n_1$ is constant because the frequent desorption events lead to the establishment of a so-called "adsorption/desorption equilibrium". Until the first nucleus is formed a rather long time may pass during which only monomers are located on the surface. This phenomenon is called "delayed nucleation".

The mechanisms of nucleation will be treated in the following section in more detail.
3.2.3. Nucleation

3.2.3.1. General Considerations

In the case of strict adsorption desorption equilibrium which corresponds to the establishment of the saturation vapor pressure $p_S$ above the substrate adsorption and desorption events are balanced. To enforce film growth, the number of adsorption events has to be higher than the one of desorption events. This can be achieved by supersaturating the vapor i.e. to establish a vapor pressure $p_0$ higher than $p_S$.

A certain part of the adsorbed atoms forms nuclei, i.e. many body aggregates which are energetically favorable compared to isolated monomers. These aggregates may still decay by the emission of single atoms. Only after a certain nucleus size is exceeded ("critical nucleus") it is energetically more favorable to attach atoms that to lose them.

For incorporating atoms into a solid surface the following scheme is valid:

Adsorption  
\[\text{Diffusion} \quad \text{Desorption} \]

Metastable nucleus  
Critical nucleus  
Attachment to steps or (screw) dislocations

According to this scheme the particles captured by the surface are going through the adsorbed state, which is a key issue for understanding film growth. Within the stock of adsorbed monomers three processes are triggered which generally occur simultaneously:

1.) Desorption
2.) Nucleation and growth of nuclei
3.) Step flow

For nucleation two cases can be distinguished: **homogeneous nucleation** means that only atoms of the condensing or crystallizing phase meet and form multi particle aggregates. **Heterogeneous nucleation** means the formation of nuclei at defects of the substrate as e.g. point defects, steps or chemically adsorbed impurities.

To quantitatively describe nucleation two models shall be discussed: the Droplet Model and the Particle Model.

3.2.2.2. Droplet Model

The foundations of nucleation theory were laid very early (1930 - 1940). For the droplet model it is assumed that the nuclei exhibit bulk properties, i.e. the values of surface tension and evaporation enthalpy correspond to those of the bulk.

To investigate the nucleation process in more detail at first a step free surface with $n_{\text{ads}}$ adsorbed atoms shall be considered. Sometimes two adsorbates meet and form adsorption complexes which are stronger bound to the surface than the isolated monomers. The two atoms form a so-called metastable, sub critical nucleus. To this sub critical nucleus other atoms may attach before it decays, until in some cases the critical nucleus size is reached and the nucleus becomes more stable with ongoing monomer attachment.
Critical Nucleus

For the determination of the radius $r^*$ of a critical nucleus the following assumptions have to be made:

$r = \text{mean linear dimension of the nucleus (spherical "droplet")}$
$a \cdot r^2 = \text{surface of the nucleus exposed to the vapor phase}$
$b \cdot r^2 = \text{contact area between nucleus and substrate}$
$c \cdot r^3 = \text{volume of the nucleus}$
$\sigma_1 = \text{surface tension (free energy) of the nucleus}$
$\sigma_2 = \text{free energy between nucleus and substrate}$
$\sigma_3 = \text{surface tension (free energy) of the substrate}$
$\Delta G_v = \text{condensation enthalpy of the coating material}$

The total free energy $\Delta G$ of a nucleus is then given by

$$\Delta G = cr^3 \Delta G_v + ar^2 \sigma_1 + br^2 \sigma_2 - br^2 \sigma_3 \quad [J]$$

with

$$\Delta G_v = \frac{kT}{V} \ln \frac{R_{\text{des}}}{R} = \frac{kT}{V} \ln \frac{p_S}{p_O} \quad [J \cdot m^{-3}]$$

$V = \text{volume of a film forming particle [m}^3\text{]}$
$R = \text{imingement rate of film forming particles}$
$R_{\text{des}} = \text{desorption rate}$
$p_S = \text{saturation vapor pressure}$
$p_O = \text{vapor pressure of coating material above the surface}$

Given the assumption that the shape and the free energy of the nuclei do not change with their size, taking the first derivative $\delta \Delta G / \delta r = 0$ and equating this to zero yields the radius $r^*$ and the free Energy $\Delta G^*$ of a critical nucleus:

$$r^* = -\frac{2(a \sigma_1 + b \sigma_2 - b \sigma_1)}{3c \Delta G_v}$$

$$\Delta G^* = \frac{4(a \sigma_1 + b \sigma_2 - b \sigma_1)^3}{27c^2(\Delta G_v)^2}$$

The dependence of the free energy $\Delta G$ of a nucleus on its size is schematically displayed in Fig. 3.2. The condition of maximum free energy is equivalent to the minimum stability of the nucleus and is given for the critical radius $r^*$. For values of $r > r^*$ the $r^3$ term (volume term) is dominant which leads to the formation of stable nuclei with big radii.

If an additional atom attaches to a critical nucleus the nucleus will gain stability (decrease its free energy) and the probability of dissociation into single atoms is reduced. If, on the other hand, a single atom detaches from the critical nucleus it will decay with high probability, since the reduction in $r$ leads to decreasing $\Delta G$. For the formation of a stable film therefore nuclei with $r > r^*$ have to be formed.
The further growth of critical nuclei can either be due to the direct capture of atoms from the vapor or because of the attachment of atoms from the diffusion field of adsorbed monomers. If only a small part of the substrate surface is covered by nuclei, the latter mechanism dominates.

The capture of ad-atoms by nuclei depends on the nucleus density and on the collision frequency between ad-atoms and nuclei. In the case of incomplete condensation the collision frequency can easily be estimated.

In adsorption/desorption equilibrium, where the number of monomers on the surface, \( n_1 \), is constant

\[
\frac{dn_1}{dt} = 0 = R - n_1 \cdot V_0 \exp \left[ - \frac{E_{\text{des}}}{k_B T_S} \right],
\]

(3.17)

\( R \) = deposition rate

is valid. Therefore the number of atoms adsorbed on the surface is:

\[
n_1 = \frac{R}{V_0} \exp \left[ - \frac{E_{\text{des}}}{k_B T_S} \right].
\]

(3.18)

If one neglects the direct impingement of atoms on the critical nuclei with radius \( r^* \), particles can only be attached to a critical nucleus by surface diffusion. The single atom which transforms the critical nucleus to a supercritical nucleus (also called "stable island") can only emerge from an annular zone of width \( a \) around the critical nucleus if the jump length in surface diffusion is restricted to one lattice constant, \( a \). This annulus is called "capture zone" (see Fig. 3.3.).
**Fig. 3.3.**: Schematic of the capture zone (dark grey) around a critical nucleus in the droplet model

- $a$ = Lattice constant
- $r^*$ = radius of the critical nucleus
- $U^*$ = circumference of the critical nucleus

The area of the capture zone is given by $U^* \cdot a = 2\pi r^* \cdot a$, and the impingement frequency of monomers onto the critical nucleus, $\nu$, is given by

$$\nu = n_i V_0 \exp\left[-\frac{E_d}{k_B T_S}\right]. \quad (3.19)$$

In equilibrium with the monomer field chemical kinetics yields the number of critical nuclei with radius $r^*$:

$$n(r^*) = n_i \exp\left[-\frac{\Delta G(r^*)}{k_B T_S}\right] = n_i \exp\left[-\frac{\Delta G^*}{k_B T_S}\right]. \quad (3.20)$$

The formation rate of supercritical nuclei, $I$, is therefore given by the product:

- Number of critical nuclei $\times$
- Impingement rate from the diffusion field $\times$
- Area of the capture zone,

which is:

$$I = \frac{R}{V_0} \exp\left[\frac{E_{des}}{k_B T_S}\right] \cdot \exp\left[-\frac{\Delta G^*}{k_B T_S}\right] \cdot n_i \cdot V_0 \exp\left[-\frac{E_d}{k_B T_S}\right] \cdot U^* \cdot a = U^* \cdot a \cdot R \cdot n_i \cdot \exp\left[\frac{E_{des} - E_d - \Delta G^*}{k_B T_S}\right]. \quad (3.21)$$

Eqn. (3.21) strongly depends on the nucleation kinetics (supersaturation) - and therefore on the deposition parameters - via $\Delta G^*$ (see Fig. 3.4.). An arbitrary limit for the onset of film formation can be drawn at a value of one nucleus per cm$^2$s.

**Fig. 3.4.**: Nucleation rate in dependence on the supersaturation (droplet model)
Experimental results, on the other hand, show that a critical nucleus may consist of only very few particles. In the extreme case one particle may be the critical nucleus size. In this case the assumptions of the droplet model are no longer valid.

### 3.2.3.3. Particle Model

The principal difference between the particle model and the droplet model is the introduction of an energy $E_i$ which is the dissociation energy needed to transform a nucleus consisting of $i$ monomers into $i$ single atoms. This energy corresponds to $\Delta G$ in the droplet model which describes the free energy needed to form a nucleus from the vapor phase.

Also in the case of the atomistic particle model adsorption desorption equilibrium is assumed, the expression for $n_1$ therefore remains the same. The transformation of $i$ single atoms adsorbed on the surface to a $i$-atom aggregate is described by the law of mass action. For dilute concentrations (which corresponds to a low monomer density at the surface) the law of mass action shall briefly be deduced:

One considers a general reaction of the form

$$ A + B \leftrightarrow C + D $$

(3.22)

The reaction velocities $v_1$ and $v_2$ then are:

$$v_1 = k_1 c_A c_B \quad \text{and}$$

$$v_2 = k_2 c_C c_D$$

(3.23)

(3.24)

$k_{1,2} =$ velocity constants

$c_{A,B,C,D} =$ concentrations

In equilibrium $v_1=v_2$, is valid, therefore

$$ k_1 c_A c_B = k_2 c_C c_D \quad \text{or} $$

$$ \frac{k_1}{k_2} = K_c = \frac{c_C c_D}{c_A c_B}.$$ 

(3.25)

In the case of a stochiometric reaction of the form

$$ aA + bB \leftrightarrow cC + dD $$

(3.26)

$$v_1 = k_1 \underbrace{c_A \cdots c_A}_{a} c_B \cdots c_B \quad \text{and}$$

$$v_2 = k_2 \underbrace{c_C \cdots c_C}_{c} c_D \cdots c_D, \quad \text{therefore}$$

$$ \frac{k_1}{k_2} = K_c = \frac{c_C c_D}{c_A c_B}.$$ 

(3.29)

is valid.
The reaction constant $K_c$ is connected to the energy consumed or set free during the reaction by the thermodynamic relation

$$\Delta E = -k_B T \ln K_c \quad (3.30)$$

In the case of island formation during film growth the law of mass action can therefore be formulated according to:

Reaction equation:

$$i \cdot n_i \leftrightarrow l \cdot n_l, \quad (3.31)$$

i. e. $i$ monomers aggregate to a Cluster consisting of $l$ atoms.

Concentrations:

$$c_i = \frac{n_i}{N_0}, \quad (3.32)$$

$$c_l = \frac{n_l}{N_0}, \quad (3.33)$$

with: $N_0 =$ number of possible adsorption sites.

Mass action law:

$$\frac{n_i}{N_0} \approx \left( \frac{n_l}{N_0} \right) = K_c = \exp \left[ -\frac{\Delta E}{k_B T} \right]. \quad (3.34)$$

For $i$ monomers it is always energetically more favorable to form an $i$-particle aggregate because free valences are saturated. Therefore $\Delta E$ can be set negative and $-\Delta E = E_i$ is valid. $E_i$ is the energy gained at the formation of an $i$ particle aggregate. The further approach for the determination of the rate of nucleus formation is completely analogous to the droplet model. First, a capture zone of width $a$ (lattice constant) is constructed around the $i$ particle aggregate ($i$ is considered to be the size of the critical nucleus), see Fig. 3.5.: 

Fig. 3.5.: Schematic of the caprure zone (dark grey) around a critical nucleus in the particle model

$a =\ $lattice constant

$U_i =\ $circumference of the critical nucleus consisting of $i$ monomers

Again, the formation rate of supercritical nuclei, $I$, is given by the product:

\[
\text{Number of critical nuclei } \times \\
\text{Impingement rate from the diffusion field } \times \\
\text{Area of the capture zone,}
\]

where the number of critical nuclei is now given by the mass action law and amounts with
\[ n_i = \frac{R}{v_0} \exp \left[ \frac{E_{\text{des}}}{k_B T_S} \right] \] (3.35)

to
\[ n_i = N_0 \left( \frac{n_i}{N_0} \right)^i \cdot \exp \left[ \frac{E_i}{k_B T_S} \right] = \frac{I}{N_0^{i-1}} \left( \frac{R}{v_0} \right)^i \cdot \exp \left[ \frac{i \cdot E_{\text{des}} + E_i}{k_B T_S} \right]. \] (3.36)

The nucleus formation rate \( I \) is then
\[
I = U_i \cdot a \cdot n_i \cdot n_i \cdot v_0 \exp \left[ -\frac{E_d}{k_B T_S} \right] = \\
= U_i \cdot a \cdot \frac{I}{N_0^{i-1}} \left( \frac{R}{v_0} \right)^i \cdot \exp \left[ i \cdot E_{\text{des}} + E_i \right] \cdot \frac{R}{v_0} \exp \left[ \frac{E_{\text{des}}}{k_B T_S} \right] \cdot v_0 \exp \left[ -\frac{E_d}{k_B T_S} \right] = \\
= U_i \cdot a \cdot N_0 \cdot R \left( \frac{R}{N_0 v_0} \right)^i \exp \left[ \frac{(i+1) \cdot E_{\text{des}} + E_i - E_d}{k_B T_S} \right] \] (3.37)

for the particle model.

For very high supersaturations the critical nucleus may contain only one atom and \( E_i = 0 \) (i.e., a two-atom aggregate is the smallest stable island) From Eqn. (3.37) the temperature \( T_i \) can be found at which \( i \) atoms are contained in the stable nucleus (see also Fig. 3.6.).

![Fig. 3.6. Nucleation rate as function of the inverse temperature](image-url)
3.2.4. Film Growth

From the theories of nucleation and film formation as well as from extensive observations made during in-situ experiments in a Transmission Electron Microscope (TEM) the stages passed until the formation of a continuous film are as follows:

1. Monomer adsorption
2. Formation of sub-critical nuclei ("embryos") of different sizes
3. Formation of critical nuclei (nucleation phase)
4. Growth of the critical nuclei to supercritical nuclei (accompanied by a decreasing number of monomers in the capture zone)
5. In concurrence to point 4 nucleation of critical nuclei happens where monomers are still present with full density
6. Stable islands touch and coalescence sets in (the island resulting from the coalescing two islands may change form and cover less area; nucleation points become available again)
7. Monomers adsorb at positions uncovered by coalescence ("secondary nucleation")
8. Large islands grow together (holes and channels form)
9. Holes and channels are filled by secondary nucleation until a continuous film is formed

Some of these steps are schematically displayed in Fig. 3.7.

Fig. 3.7.: Phases of film growth (schematic)

Fig. 3.8. shows the coalescence of two supercritical nuclei.

Fig. 3.8.: Shape change during coalescence
At high activation energies nucleus formation at low supersaturations is a rare event. On the other hand, at extremely high supersaturations the number of atoms within the critical nucleus may drop below one, i.e. each adsorbed monomer is a nucleus. In these cases a subdivision of particle attachment to the surface in adsorption and nucleation is not viable any more. Surface impurities may also significantly change the shape of the nucleus. This can qualitatively be studied even for the droplet model. The nucleus is considered as liquid a droplet located on the substrate. The contact angle to the substrate \( \Theta \) is given by the surface energies \( E_{OD}, E_{KO} \) and \( E_{KD} \) (see Fig. 3.9.).

It is

\[
E_{OD} = E_{KO} + E_{KD} \cos \Theta 
\] (3.38)

where O, D und K are the indices for surface, vapor and nucleus, respectively.

\[
\gamma_{OD} + \gamma_{KD} < \gamma_{KO} \\
\gamma_{OD} = \gamma_{KO} + \gamma_{KD} \cos \Theta \\
\gamma_{KO} + \gamma_{KD} < \gamma_{OD}
\]

**Fig. 3.9.:** Wetting characteristics of substrate surfaces
- **a** no wetting (\( \Theta = 180^\circ \))
- **b** partial wetting (\( 0^\circ < \Theta < 180^\circ \))
- **c** total wetting (\( \Theta = 0^\circ \))

In the case of ideal nucleus formation \( E_{OD} = E_{KD}, E_{KO} = 0 \) and \( \Theta = 0^\circ \), i.e. the surface of the forming film is parallel to the substrate.

Impurities at a real surface surface often lead to a lower \( E_{OD} \) and therefore yield contact angles \( \Theta > 0 \). The nucleus obtains the shape of a spherical cap if the surface energy is isotropic.

### 3.2.4.1. Growth Modes

Growth via the flow of monoatomic steps is called two dimensional growth (Frank-van-der-Merwe growth mode), while growth in the form of droplet shaped nuclei is called three dimensional growth (Volmer-Weber growth mode). These two growth modes are displayed in Fig. 3.10. Between these two extremes a multitude of transitions exist which are collectively summarized under the terminus Stranski-Krastanov growth mode.

**Fig. 3.10.:** Growth modes:
- **a** Two dimensional growth (layer by layer)
- **b** Three dimensional growth (islands)
3.3. Advanced Concepts of Thin Film Formation

3.3.1. Rate Equations

Previously the aggregation of single adsorbed atoms, nucleation and growth were, strictly taken, considered only for one isolated multi-particle aggregate. This simplification could be justified by limiting all calculations to the regime of incomplete condensation. In the case of a real deposition process, however, the ensemble of all forming and growing aggregates has to be considered to obtain statements about nucleation rates, island densities and other global quantities describing the system.

One possible method to obtain these quantities is the formalism if the so-called rate equations. Within the framework of a mean field theory they describe the temporal and spatial evolution of a forming coating. The terminus "Mean Field Theory" has to be understood as follows: All quantities describing a given system are given by their mean values. In the case of a growing film these are the monomer density as well as the density of all multi particle aggregates. Local variations within these quantities, as e. g. fluctuations in the monomer density or local clustering of many body aggregates are neglected.

Given the case that only monomers are mobile on the surface the rate equations in their most general form consist of the following system of an infinite number of coupled differential equations of first order:

\[
\frac{dn_1}{dt} = R - \frac{n_1}{\tau_{des}} - 2U_1 - \sum_{j=2}^{\infty} U_j \\
\frac{dn_j}{dt} = U_{j-1} - U_j
\]

(3.39) (3.40)

\( R \) = deposition rate
\( \tau_{des} \) = reevaporation time of a monomer
\( n_1 \) = number of monomers/unit area (monomer concentration)
\( n_j \) = number of aggregates consisting of \( j \) monomers/unit area
\( U_j \) = capture rates of aggregates with containing \( j \) monomers

A reduction to a finite number of equations can be achieved by sub deviding the aggregate species to sub critical nuclei (\( j \leq i \)) and stable islands (\( j > i \)). Stable islands are considered as one species and

\[
n_x = \sum_{j=i+1}^{\infty} n_j
\]

(3.41)

is valid. So a system of \( i+1 \) differential equations of first order is obtained and only the first one and the last one are coupled to each other:
\[
\frac{dn_i}{dt} = R - \frac{n_i}{\tau_{\text{des}}} - \frac{d(n_i \omega_x)}{dt} \tag{3.42}
\]
\[
\frac{dn_j}{dt} = 0 \quad (2 \leq j \leq i) \tag{3.43}
\]
\[
\frac{dn_x}{dt} = U_i - U_c - U_m \tag{3.44}
\]

\(w_x\) = mean number of atoms in stable islands
\(U_i\) = increase in the number of stable islands due to capture of a monomer by an i-nucleus
\(U_c\) = loss term due to growth coalescence
\(U_m\) = loss term due to mobility coalescence

From the first equation it is possible to instantly draw some qualitative conclusions concerning the monomer concentration \(n_1\):

* High substrate temperature: \(\tau_{\text{des}}\) is small and the term \(n_1/\tau_{\text{des}}\) limits the monomer concentration due to the fast achievement of adsorption/desorption equilibrium which is valid for \(n_1=R\ \tau_{\text{des}}\). The capture of monomers by stable nuclei plays a minor role and happens mostly by direct impingement onto stable islands.

* Low substrate temperature: \(\tau_{\text{des}}\) is large. The limiting term is \(d(n_x w_x)/dt\). The monomer concentration is limited by the capture of ad-atoms by stable islands. Monomer transport to the islands happens by surface diffusion.

Also the system of equations treating the sub-critical nuclei can be solved. Due to microreversibility (as many j-nuclei form as decay) their number in each size class j is constant and the Walton relation is valid:

\[
\frac{n_j}{N_0} = \left(\frac{n_j}{N_0}\right)^j \sum_m C_j(m) e^{-\beta E_j(m)} \tag{3.45}
\]

\(N_0\) = total number of available adsorption sites
\(\beta = 1/(k_B T_S)\)

The \(C_j(m)\) are configuration dependent contributions to the entropy of the aggregate. At low temperature only the aggregate with the highest binding energy \(E_j\) will yield an important contribution to the above sum which will therefore contain only one term. It is then identical to the solution of the chemical reaction equation for the reversible transition of \(j\) monomers to a \(j\)-particle aggregate described via the mass action law:

\[
\frac{n_j}{N_0} \propto \frac{n_j}{N_0} = k_c = e^{-\beta E_j} \tag{3.46}
\]

For a detailed treatment of the temporal behavior of the concentration of stable islands \(n_x\) additional assumptions about the island shape (2d discs or 3d spherical caps) and about the capture mechanism of the monomers by the critical i-nuclei have to be made. Generally, independent of the condensation regime, solutions of the following type can be found which are valid until the onset of coalescence:

\(n_x \propto R^p, \ p \in N \) : "fractional power law"-dependence of the island density on the deposition rate

\(n_x \propto \exp\{E/(k_BT_S)\} \) : exponential "Arrhenius"-dependence of the island concentration on the inverse substrate temperature

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Dependent on the condensation regime and on the assumptions on the island shape are only the specific values of the parameters $E$ and $p$ as shown below.

The most general functional form of the dependence of the island concentration $n_x$ on the coverage $Z$ (i.e., the projected area of all aggregates on the substrate) is given by:

$$\frac{n_x(Z)}{N_0} \equiv \eta(Z) \left( \frac{R}{N_0 V} \right)^p e^{R E}$$

(3.47)

$\eta(Z)$ is a dimensionless function which depends on the condensation regime and describes several global properties of the distribution of stable islands as e.g., island sizes or island distances. The choice of the coverage $Z$ instead of the deposition time $t$ is due to the fact that it is easier to express assumptions about the island shape in terms of the substrate coverage.

**High substrate temperature, "extremely incomplete" condensation:**

3d-islands:

$$p = \frac{2i}{3}$$

$$E = \frac{2(E_i + (i+1)E_{des} - E_d)}{3}$$

2d-islands:

$$p = i$$

$$E = E_i + (i+1)E_{des} - E_d$$

**Low substrate temperature, "complete" condensation:**

3d-islands:

$$p = \frac{1}{i + 2.5}$$

$$E = \frac{E_i + iE_d}{i + 2.5}$$

2d-islands:

$$p = \frac{i}{i + 2}$$

$$E = \frac{E_i + iE_d}{i + 2}$$

$E_i$ = total binding energy of an $i$-island  
$E_{des} =$ desorption energy of a monomer  
$E_d =$ activation energy of monomer surface diffusion
From the above relations it is visible that from the behavior of the island density with progressing substrate coverage limited conclusions can be drawn on microscopic parameters such as activation energies for desorption and surface diffusion as well as on the size of the critical nucleus $i$. A significant uncertainty, however, is given by the island binding energy $E_i$ which can only be determined by ad-hoc assumptions about the specific shape of the critical nucleus.

Fig. 3.11. shows the qualitative behavior of the monomer and island concentration $n_1$ and $n_x$ in dependence on the deposition time $t$:

![Fig. 3.11.: Qualitative behavior of the monomer and island concentration](image)

**Fig. 3.11.:** Qualitative behavior of the monomer and island concentration

- **a** "extreme incomplete" condensation, $T_S$ high
- **b** "complete" condensation, $T_S$ low

The above dependencies have been experimentally observed and are the most exact description of a deposition process possible within a mean field approach.

### 3.3.2. Kinetic Monte-Carlo-Simulations: Local Effects and Surface Defects

The mean field theory of the rate equations yields information about global quantities like island densities and mean monomer concentrations. Local influences like an irregular distribution of the stable islands or the existence of defects are not considered.

Local conditions can be incorporated into a detailed model of the deposition process. To obtain such a model the elementary events of a deposition process (deposition, surface diffusion, re-evaporation, formation of lateral bonds etc.) are performed according to their frequency within a simulation algorithm. Especially the wide range in time- and length scales ($10^{-10}$ s for single diffusion jumps, $10^3$ s for the total duration of the deposition run; $10^{-10}$ m as length of a diffusion jump, $10^{-3}$ m for the total film thickness) which exists within a deposition cycle is a big challenge to the efficiency of the algorithm.

In the following the most important points of modeling are sketched. As low substrate temperature is assumed the desorption of monomers is neglected. The material transport along the surface is solely due to thermally activated surface diffusion and the surface is considered as a quadratic lattice. All lengths are measured in units of it’s lattice constant $a$.

1) **Choice of the elementary time-steps:**

**Time between two deposition events:**

- **given:** deposition rate $R = 1$ nm/s, i. e. approx. 3 particles/lattice site/s
- **wanted:** time interval between two 2 deposition events on a lattice with variable total side length $L$
To achieve this deposition rate all adsorption sites of the LxL lattice have to be occupied approximately 3 times per second. The temporal offset between two single deposition events is therefore given by:

$$\Delta t_{\text{depos}} = \frac{1}{L^2 R^3}.$$  \hspace{1cm} (3.48)

<table>
<thead>
<tr>
<th>LxL [a²]</th>
<th>$\Delta t_{\text{depos}}$ [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>100x100</td>
<td>$3.3 \times 10^{-5}$</td>
</tr>
<tr>
<td>500x500</td>
<td>$1.3 \times 10^{-6}$</td>
</tr>
<tr>
<td>1000x1000</td>
<td>$3.10^{-7}$</td>
</tr>
</tbody>
</table>

Tab. 3.2.: $\Delta t_{\text{depos}}$ in dependence on the system size

Time between two diffusion events of a monomer:

Surface diffusion is a thermally activated process. For substrate temperatures up to approx. ¾ of the melting point of a given material the diffusion frequency is dependent on the activation energy and the substrate temperature according to:

$$v_{\text{d}} = v_0 \exp[-E_d/(k_B T_s)]$$  \hspace{1cm} (3.49)

$v_0$ = phonon frequency, approx. $5 \times 10^{12}$ s$^{-1}$
$E_d$ = activation energy for surface diffusion, approx. 0.2 - 0.7 eV
$T_s$ = substrate temperature, value in example: 600 K

The diffusion process itself is a sequence of uncorrelated jumps from one binding position to one of the four neighboring ones ("random walk"). The thermal reservoir of the substrate has to deliver the energy to overcome the energy barrier $E_d$ between the binding positions.

<table>
<thead>
<tr>
<th>$E_d$ [eV]</th>
<th>$v_{\text{Diff}}$ [s$^{-1}$]</th>
<th>$\Delta t = v_{\text{Diff}}^{-1}$ [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>$1.5\times 10^9$</td>
<td>$6.6\times 10^{11}$</td>
</tr>
<tr>
<td>0.4</td>
<td>$2.2\times 10^9$</td>
<td>$4.5\times 10^{10}$</td>
</tr>
<tr>
<td>0.5</td>
<td>$3.1\times 10^8$</td>
<td>$3.2\times 10^9$</td>
</tr>
<tr>
<td>0.6</td>
<td>$4.5\times 10^7$</td>
<td>$2.2\times 10^8$</td>
</tr>
</tbody>
</table>

Tab. 3.3.: Monomer diffusion frequencies at 600 K in dependence on the activation energy

Number of diffusion jumps of an adsorbed monomer between two deposition events:

According to the above values, on a 1000x1000 lattice each adsorbed monomer performs the number of diffusion jumps between two deposition events given in Tab. 3.4.

<table>
<thead>
<tr>
<th>$E_d$ [eV]</th>
<th>$\Delta t_{\text{Depos}} / \Delta t_{\text{Diff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>4545.5</td>
</tr>
<tr>
<td>0.4</td>
<td>666,667</td>
</tr>
<tr>
<td>0.5</td>
<td>93.8</td>
</tr>
<tr>
<td>0.6</td>
<td>13.6</td>
</tr>
</tbody>
</table>

Tab. 3.4.: Number of diffusion jumps between two deposition events for a 1000x1000 lattice
2) Bonding and modification of diffusion rates - method of conditional probabilities:

The aggregation of two monomers leads to a change in the jump frequencies of the adsorbed single particles due to the formation of lateral bonds, as it is shown in Fig. 3.12. The lateral bond strength was assumed to be $E_b = 0.2 \text{ eV}$.

$$v_i = v_0 \exp\left[-\frac{E_i}{kT}\right] \equiv 1$$

$$v_2 = v_0 \exp\left[-\frac{E_i + E_b}{kT}\right] \equiv 0.02v_1$$

$$v_3 = v_0 \exp\left[-\frac{E_i + 2E_b}{kT}\right] \equiv 4.10^{-4}v_1$$

$$v_4 = v_0 \exp\left[-\frac{E_i + 3E_b}{kT}\right] \equiv 9.10^{-6}v_1$$

$$v_5 = v_0 \exp\left[-\frac{E_i + 4E_b}{kT}\right] \equiv 2.10^{-7}v_1$$

**Fig. 3.12.**: Particle configurations together with the associated modifications in jump frequency caused by the formation of lateral bonds; $E_d = 0.4 \text{ eV}, E_b = 0.2 \text{ eV}$

According to Fig. 3.12. the modified jump frequency $v'$ in dependence on the number of nearest neighbors, $n$, is given by

$$v' = v \cdot \exp\left[-\frac{nE_b}{k_B T}\right] . \quad (3.50)$$

Additionally, Fig. 3.12 shows that even one nearest neighbor leads to a reduction in the jump frequency of a particle which is part of a dimer by a factor of 50. A conventional Monte Carlo (MC) algorithm which randomly chooses a particle and then determines whether it performs a jump or not by a random number would therefore be highly inefficient.

A possibility to circumvent this fact is the method of conditional probabilities. Particles within a given system are incorporated into certain particle groups. Jump rates are assigned to these groups according to the bonding situation of the selected particle. In addition also the rate of deposition events has to be taken into account. For the particle configuration displayed in Fig. 3.13. the following groups and event rates are obtained:

**Fig. 3.13.**: Example of a simple particle configuration

Total number of possible events: 7

<table>
<thead>
<tr>
<th>Event group</th>
<th>Relative Rate (normalized to monomer jump frequency)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1x deposition (D)</td>
<td>1x1,5.10^-3</td>
</tr>
<tr>
<td>1x diffusion monomer (M)</td>
<td>1x1</td>
</tr>
<tr>
<td>4x diffusion dimer (Di)</td>
<td>4x0,02</td>
</tr>
<tr>
<td>1x diffusion central particle pentamer (P)</td>
<td>1x10^-7</td>
</tr>
</tbody>
</table>
To chose an event with the right weight from this grouped list, the sum of all rates has to be normalized to one. By doing this, to the product of the number of particles within a group times the respective rate a probability is assigned. The following event can therefore be determined by a simple MC step, i.e. the generation of a random number \( \varepsilon \) within the interval \([0,1]\), as Fig. 3.14 shows.

\[
\begin{array}{c|c|c|c|c|c}
0 & D & M & \varepsilon & Di & P \\
\end{array}
\]

Abb. 3.14.: Determination of the following event for the particle configuration displayed in Fig. 3.13.

Once the event is determined, a random particle has to be selected from the event group and the event (e.g. diffusion jump or deposition) has to be executed. Then the group list is updated because the actual particle configuration has changed.

3) Determination of the time interval between two subsequent events:

The advantage of the previously described procedure is that each event really leads to a change in the system. This means that the simulation times are significantly reduced. Additionally the simulation also yields real time scales since the time interval between two subsequent events \( \Delta t_{\text{event}} \) can be determined by

\[
\Delta t_{\text{event}} = -\left( R_{\text{depot}} + \nu \left( \sum_n n_n \exp\left[\frac{-(E_d + nE_r)}{(k_B T_S)}\right] \right) \right)^{-1} \ln R. \quad (3.51)
\]

\( R = \text{random number } \in [0,1] \)
\( n_n = \text{number of particles in event group } n \)

This is not the case for conventional MC procedures which solely try to determine the equilibrium state of a system by energy minimization. A disadvantage, however, is the dynamic management of the particle lists which can become rather involved for multi component systems or three dimensional particle aggregates because of the large number of particle configurations.

3.3.3. Concluding Remarks

Rate equations and kinetic Monte Carlo simulations are of course only a small segment of the analytical and numerical procedures used for the description of thin film processes. The ongoing increase of computer power and the refinement of mathematical methods and tools creates also the possibility to link calculation methods and simulation techniques which cover different spatial and temporal ranges to an ever increasing extent. The bundling of different models to describe a process which covers several orders of magnitude in time or space is called "multiscale modelling" of hybride method. These hybrid methods will gain importance for all aspects of thin film technology in special and for material science in general. The aim of this approach is the complete description of a material starting from the single atom and ending in macroscopic dimensions. A brief summary of several involved techniques and their respective input and output parameters is given in Tab. 3.5.
<table>
<thead>
<tr>
<th>Simulation method/ mathem. technique</th>
<th>Input quantities</th>
<th>Output quantities</th>
<th>Time/length scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ab initio methods</td>
<td>Schrödinger-equation</td>
<td>Electronic states of the multi particle system; multi particle potentials; potential energy surfaces</td>
<td>Atomic length scales; up to $10^{10}$ s</td>
</tr>
<tr>
<td>Molecular dynamics</td>
<td>Interatomic multi-particle potentials and potential energy surfaces</td>
<td>Adsorbate trajectories, mechanisms and rates of diffusion processes, binding energies, critical nucleus sizes</td>
<td>nm to (in extreme cases) µm; 1-10 ns</td>
</tr>
<tr>
<td>Kinetic Monte-Carlo-Simulation</td>
<td>Elementary diffusion mechanisms and their rates</td>
<td>Island size distributions and island morphologies, microscopic capture numbers</td>
<td>nm - 100 µm; µs - s</td>
</tr>
<tr>
<td>Rate equations</td>
<td>Island shapes, capture numbers, island energies, critical nucleus sizes</td>
<td>Island density, percolation thresholds, coverages</td>
<td>Arbitrary lengths; ns - min</td>
</tr>
<tr>
<td>Models of crystal growth</td>
<td>Island densities and island size distributions</td>
<td>Texture evolution, crystallinity</td>
<td>nm - mm; s - min</td>
</tr>
<tr>
<td>Finite element simulations</td>
<td>Material properties of crystallites, elastic constants, size distributions</td>
<td>Mechanic behavior (static and dynamic)</td>
<td>mm - m s - h</td>
</tr>
</tbody>
</table>

**Tab. 3.5.:** Some analytical methods and simulation techniques and their application fields

On the one hand, Table 3.5. shows that for the description of a complete deposition process no single model is available up till now. On the other hand the interfaces between the single methods can be tuned in a way that the results of one technique may serve as input for the next model.