

# Repetition: Nucleation Rates

Simple nucleation theory of the isolated nucleus as well as rate equations yield nucleation rates  $I$  of the form:

$$I[\text{m}^{-2}\text{s}^{-1}] \cong A \cdot R^p e^{-\frac{E}{k_B T_S}}$$

**Droplet-model:**

$E=E(\Delta G^*) \Rightarrow$  unambiguous

**Particle-model:**

$E=E(i, E_i) \Rightarrow$  ambiguous

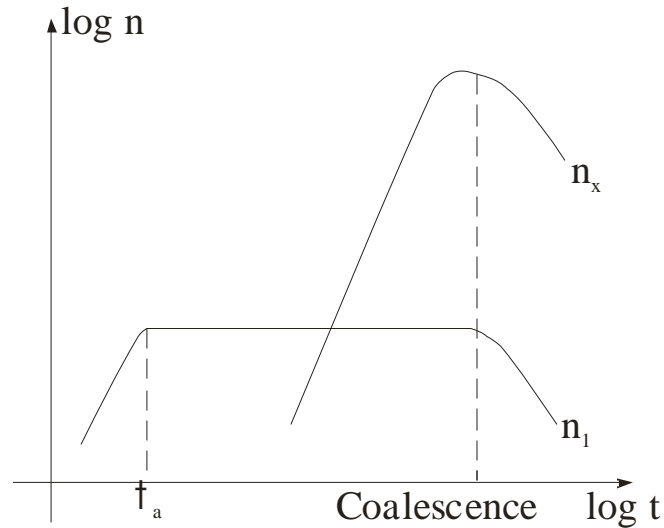
The exponent  $p$  can have integer or non-integer values.

# Repetition: Rate Equations General

## Incomplete condensation

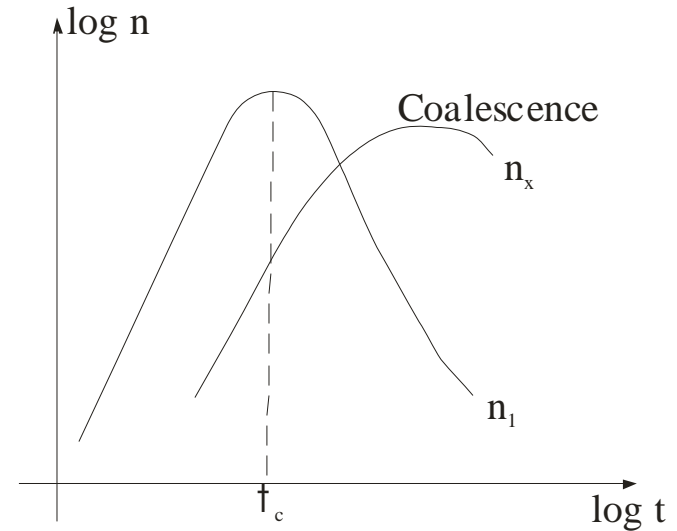
$$\frac{dn_1}{dt} = 0 = R - \frac{n_1}{\tau_a}$$

$$\frac{d(n_x w_x)}{dt} \cong 0$$



## Complete condensation

$$\frac{dn_1}{dt} = R - \frac{d(n_x w_x)}{dt}$$



# Repetition: KMC Simulation

**Kinetic Monte Carlo (KMC) simulations allow the determination of**

- **the shape of the stable islands**
- **the size distribution of stable islands**
- **the influence of defects on nucleation**

**they only use the elementary processes of film growth (deposition, surface diffusion, desorption, particle bonding) as input for the simulation of film growth.**

# Repetition: KMC - Principle

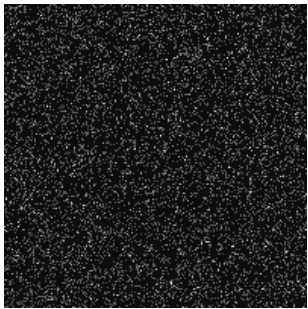
- **Definition of event types**
- **Definition of relative event probabilities ("conditional probabilities")**
- **Choice of a particle for the execution of the event**
- **Determination of the time interval between specific events**

**Advantage:** each chosen event changes the system

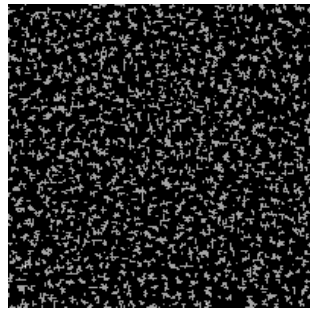
**Disadvantage:** not all event types are known a priori; algorithm is memory consuming

# Repetition: KMC – Results and Trends

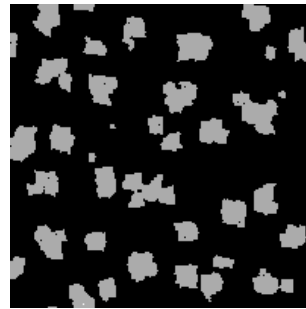
## Variation of substrate temperature $T_s$



$T_s=10K$



300K



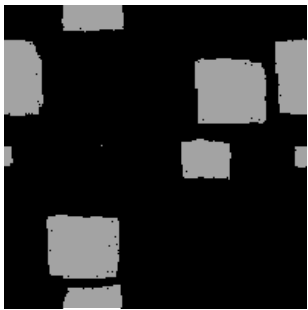
600K



700K

$R=1ML/s$   
 $E_{Diff}=0.5 eV$   
 $E_{Des}=1 eV$   
 $E_b=0.5 eV$

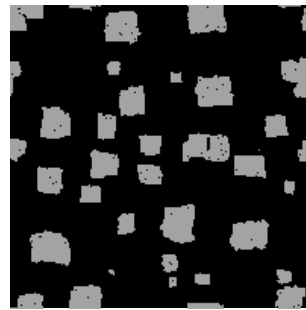
## Variation of deposition rate $R$



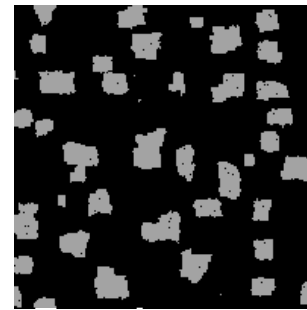
$R=0.5 ML/s$



1ML/s



5 ML/s



10 ML/s

$T_s=700 K$   
 $E_{Diff}=0.5 eV$   
 $E_{Des}=1 eV$   
 $E_b=0.5 eV$

# Epitaxy

**Epitaxy is the deposition of layers, which are monocrystalline in large regions**

- **Homoepitaxy:**

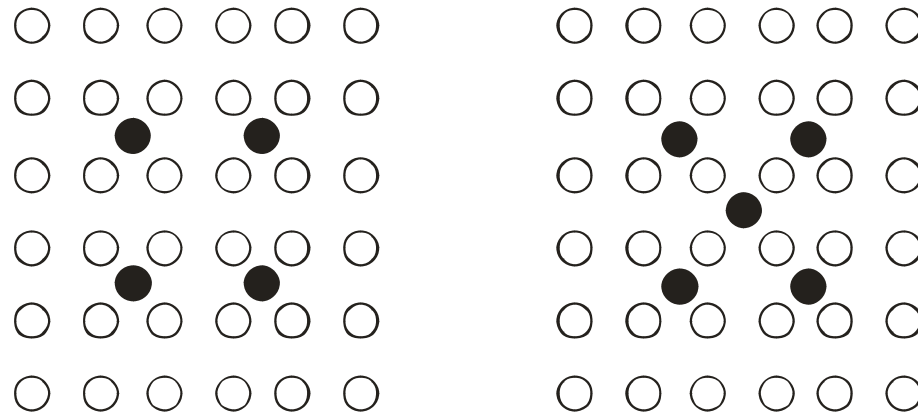
**Substrate material = film material**

- **Heteroepitaxy:**

**Substrate material  $\neq$  film material**

# Heteroepitaxy I

## Epitactic relation:



- Substrate material
- Film material

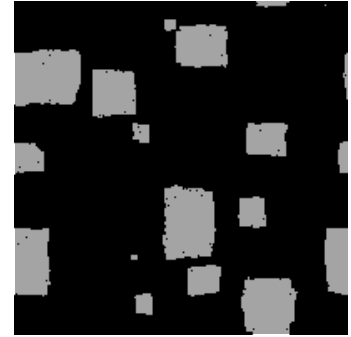
## Van-der-Waals epitaxy:

**The interaction between substrate material and film material is so weak, that film atoms can arrange themselves in a crystallographically favorable manner.**

# Heteroepitaxy II

## High temperature epitaxy:

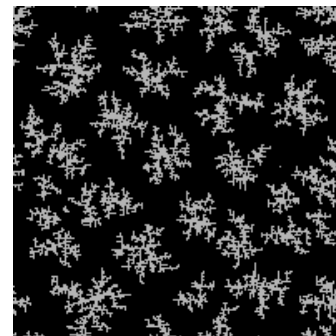
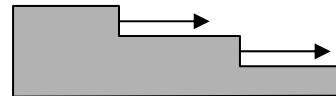
The crystallographically favorable arrangement of the atoms is reached by a high substrate temperature.



## Low temperature epitaxy :

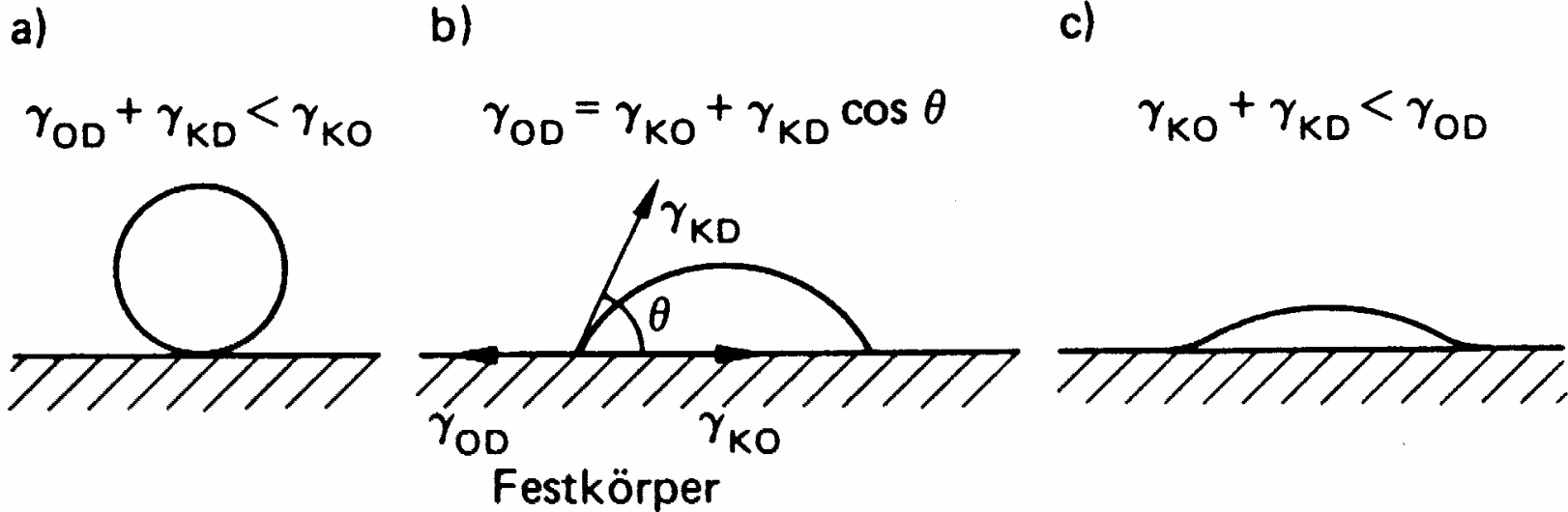
The crystallographically favorable arrangement of the atoms is reached by local defect structures

- Vicinal surfaces
- Dendritic Islands





# Film Growth: Nucleus Shape/Wetting



$\gamma$ ...Surface energy

O...Surface

D...Vapor

K...Nucleus

# Film Growth: Growth Modes

## Growth modes:

A: Substrate material  
B: Film material



Frank-Van der Merwe:  
layer by layer  $W_{AB} > W_{BB}$

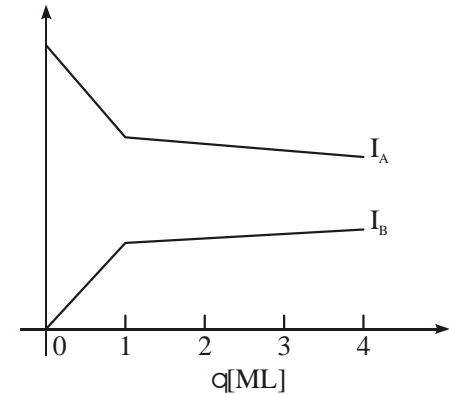
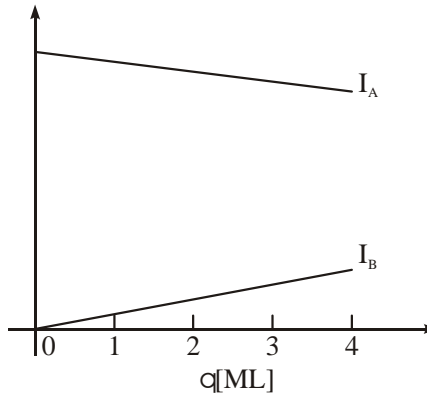
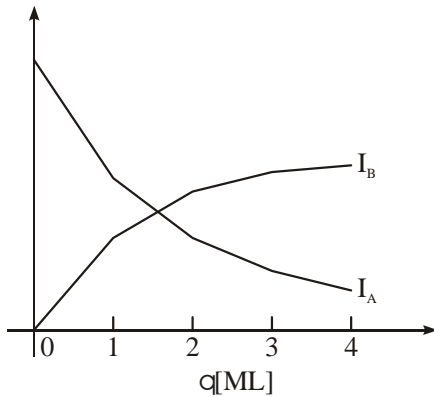


Volmer-Weber:  
islands,  $W_{AB} < W_{BB}$



Stranski-Krastanov:  
layer/island,  $W_{AB} > W_{BB}$   
stress relief by 3d islands

## Characterization: e. g.: Auger-electron spectroscopy



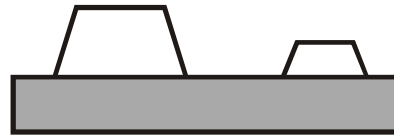
# Stress and Film Growth I

## Growth modes:

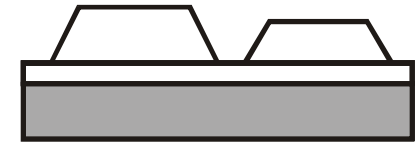
A: Substrate material  
B: Film material



Frank-Van der Merwe:  
layer by layer  $W_{AB} > W_{BB}$



Volmer-Weber:  
islands,  $W_{AB} < W_{BB}$



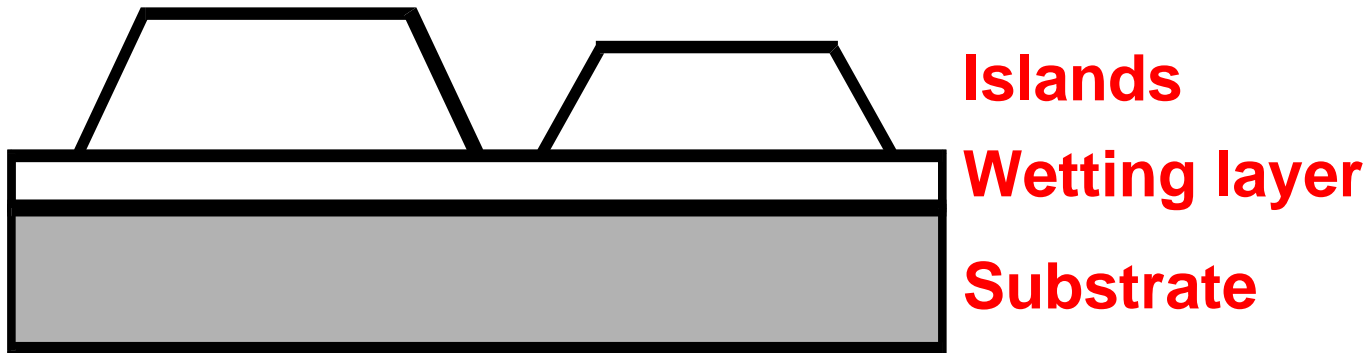
Stranski-Krastanov:  
layer/island,  $W_{AB} > W_{BB}$   
stress relief by 3d islands

**While the Frank-van der Merwe and Volmer-Weber Growth modes lead to mostly stress free films, in the Stranski-Krastanov-mode significant stresses are induced in the first growth phases.**

# Stress and Film Growth II

## Stranski-Krastanov-growth:

- + Lattice mismatch (misfit)
- + Misfit-dislocations
- + Islands

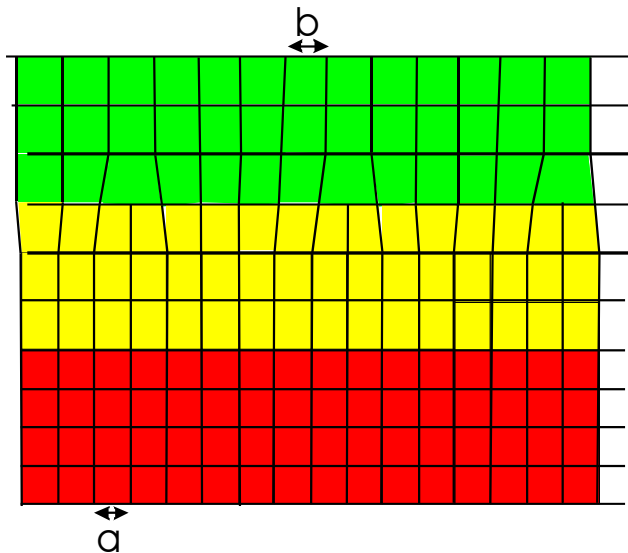


# Stress and Film Growth III

Detailed mechanism:

Lattice Mismatch  $\Delta$ :

$$\Delta = \frac{a - b}{a} \cdot 100[\%]$$



Film, lattice constant  $b$

Pseudomorphic transition zone

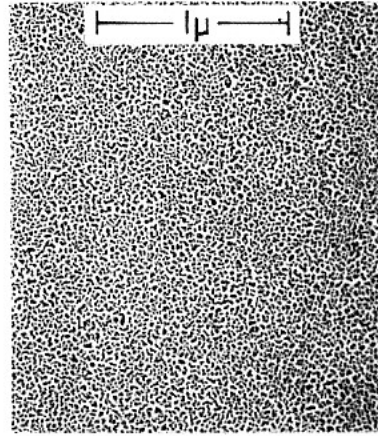
Substrate, lattice constant  $a$

# Film Growth: Experimental I

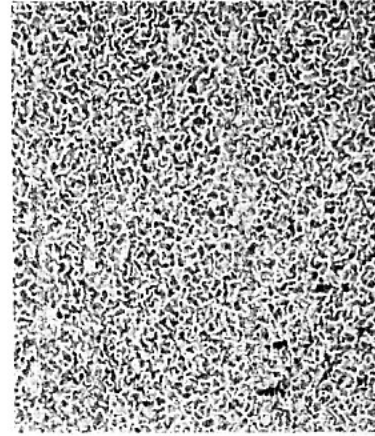
**Au on NaCl,  $R=0.1$  nm/s**



(a) 25°C 15Å

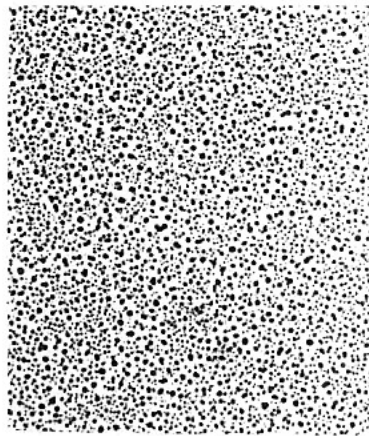


45Å

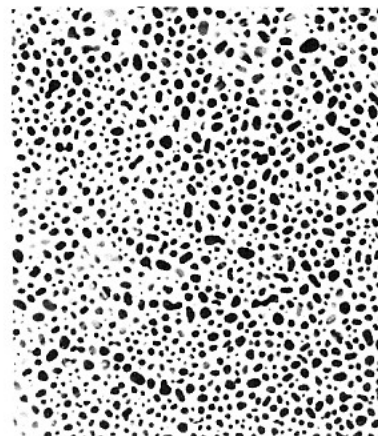


75Å

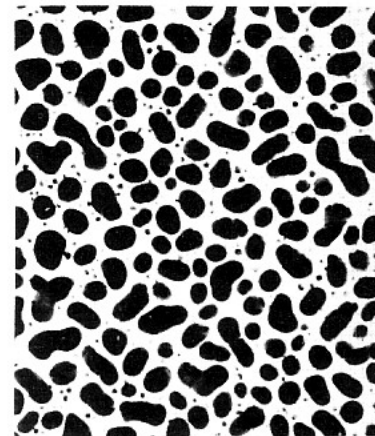
**Film  
thickness**



(b) 100Å 100°C



200°C



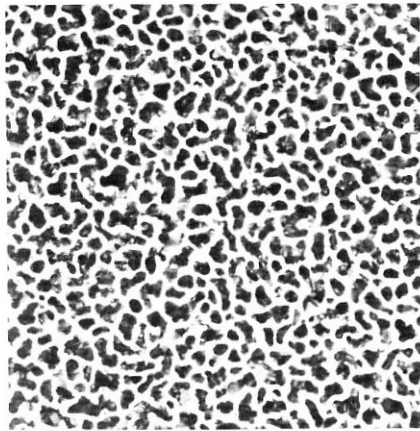
300°C

**Substrate-  
temperature**

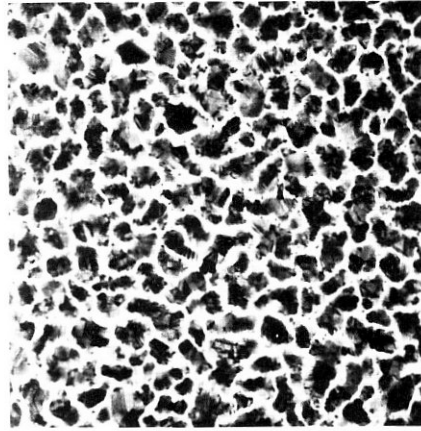


# Film Growth: Experimental II

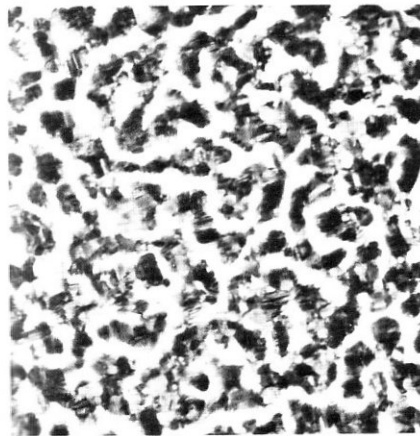
Ag on NaCl,  $R=0.1$  nm/s,  $T=100^\circ\text{C}$



(a)



(b)



(c)



(d)

**Coalescence:**

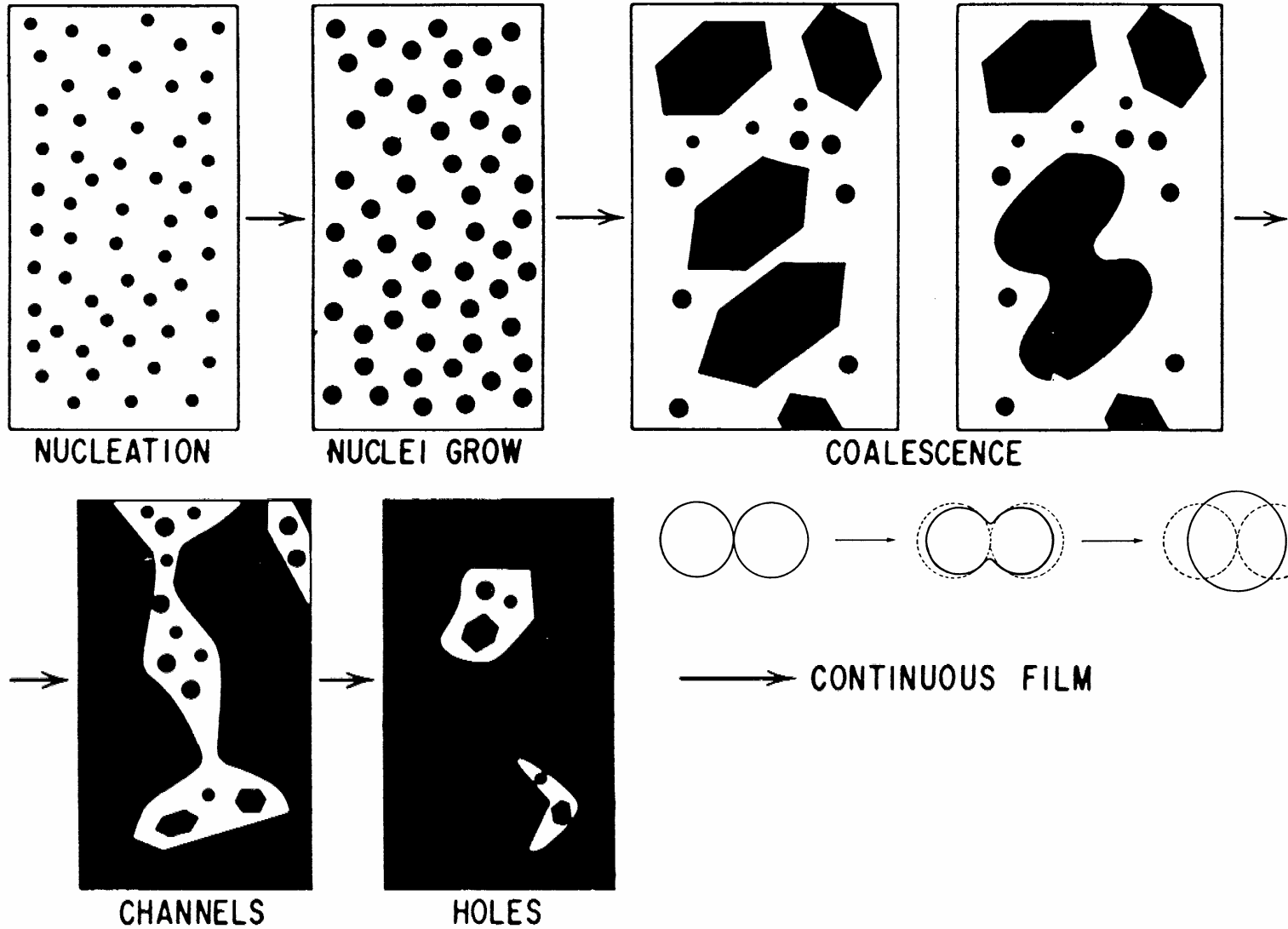
**(a)  $d=10$  nm**

**(b)  $d=10.5$  nm**

**(c)  $d=11$  nm**

**(d)  $d=11.5$  nm**

# Film Growth: Further Steps

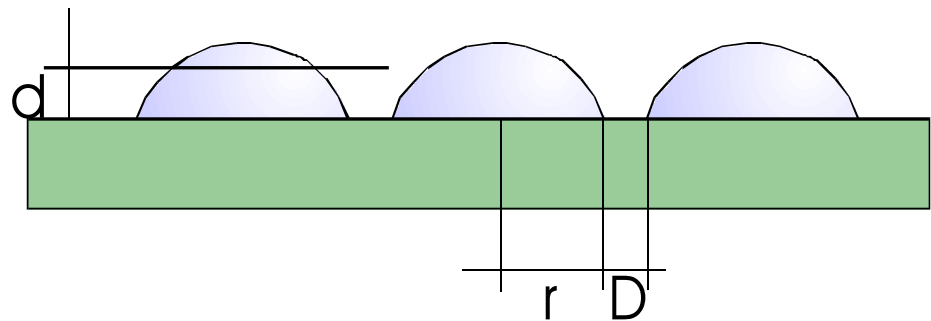




# Further Growth: Roughness/Film Structure

The film structure is determined by the roughness of the film growth front in the different growth phases to a high degree.

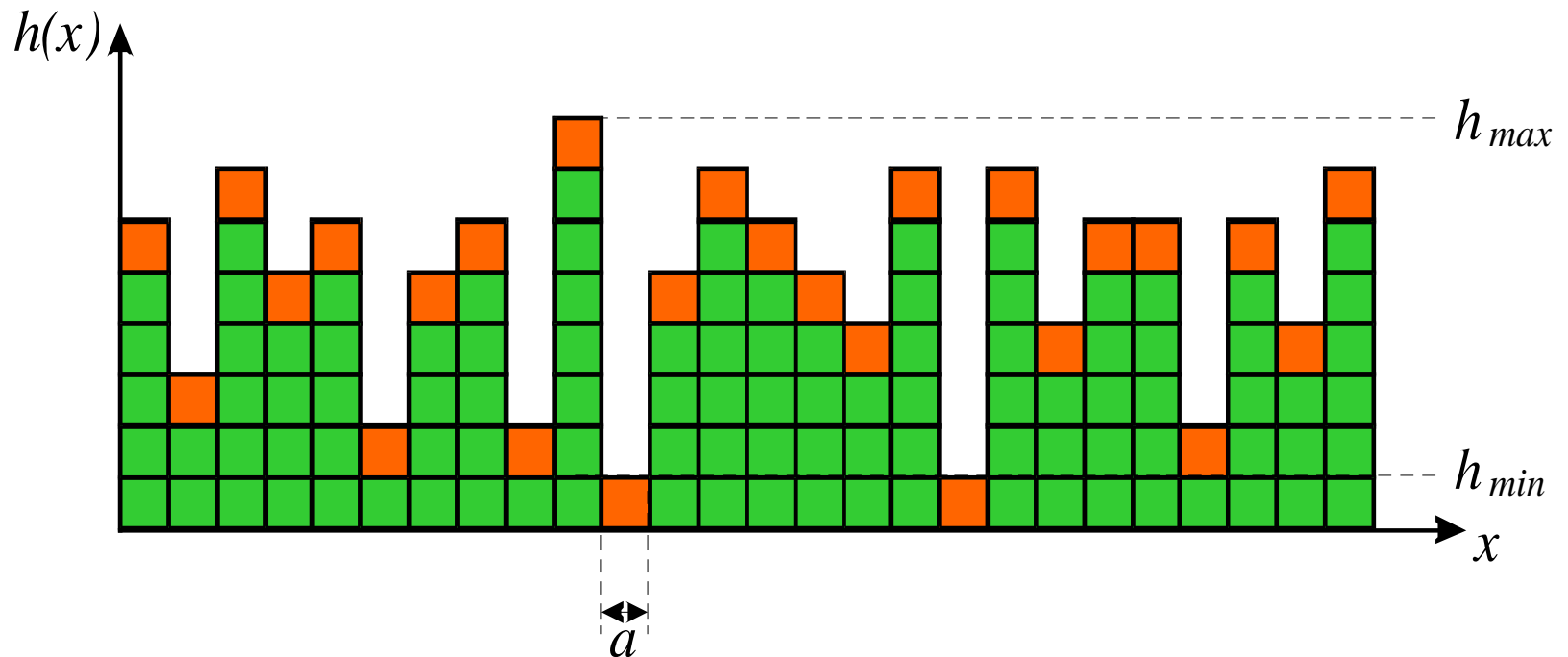
For very thin layers the roughness is in the order of the film thickness and can therefore be more important than the mean layer thickness.



# Roughness Types I

## Stochastic roughness – Solid on Solid (SOS) model

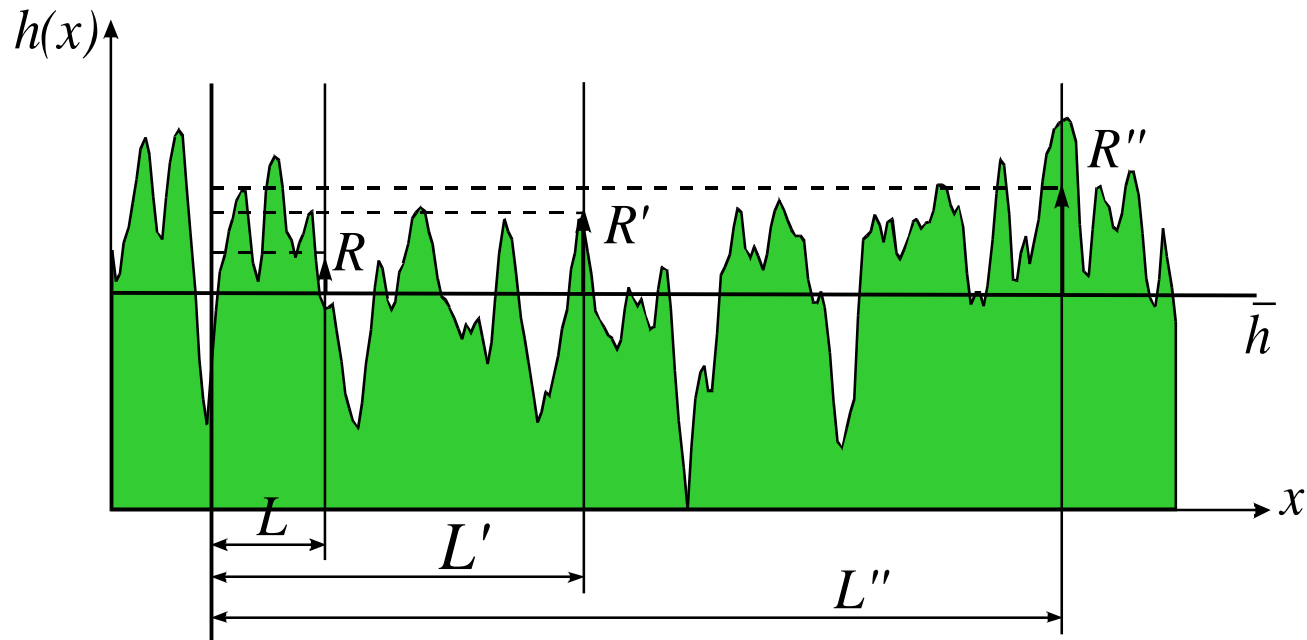
- + Particles have to have a below nearest neighbor (NN)
- + Particles stick where they land



# Roughness Types II

## Self similar surfaces – SOS model

- + Particles can reach energetically favorable positions (e. g. high coordination number)
- + Particle migration e. g. by surface diffusion

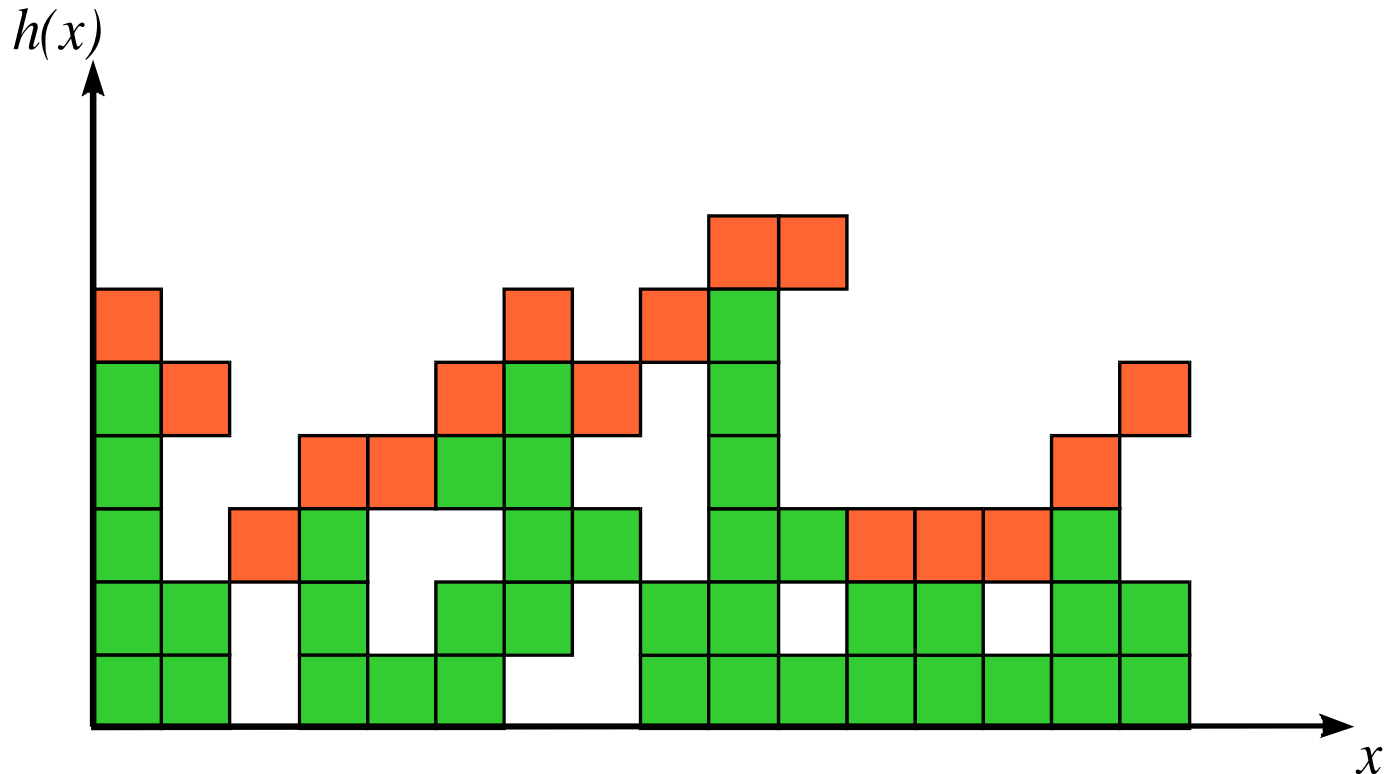


$$R=f(L), R''>R'>R$$

# Roughness Types III

## Ballistic aggregation – pore formation

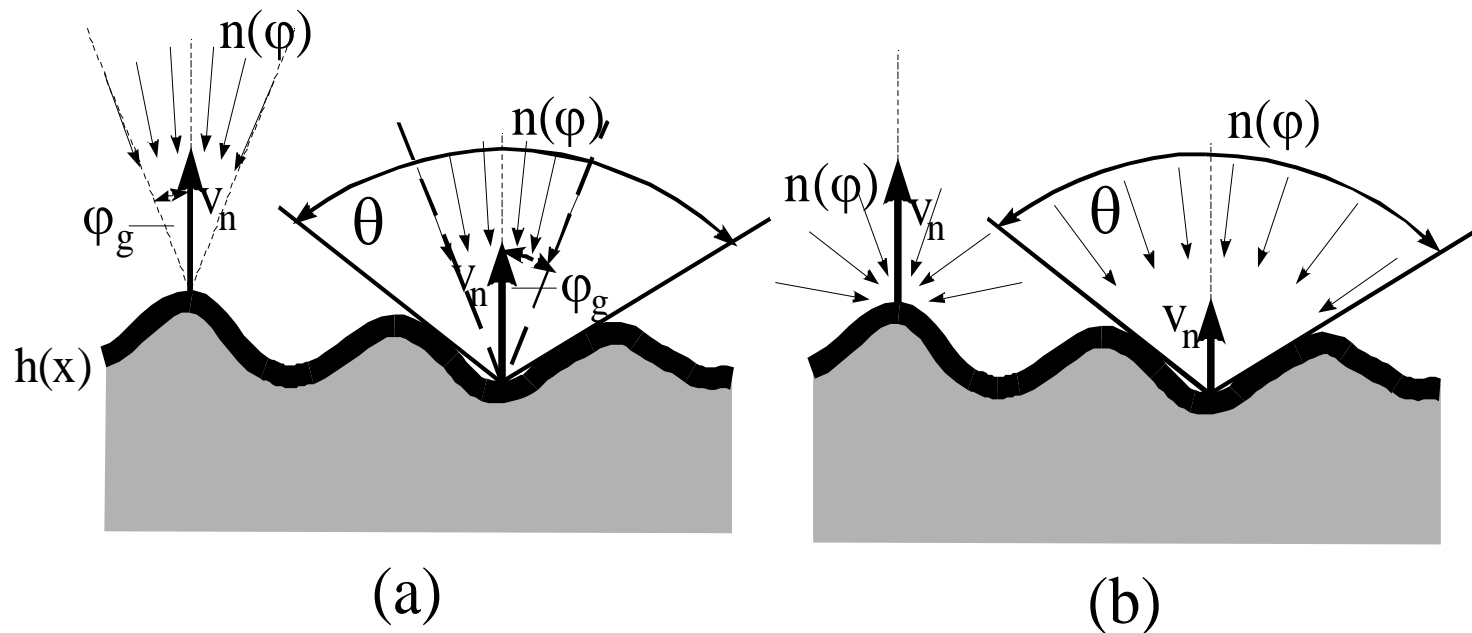
- + Particles stick where they land
- + Particles do not have to have a below NN



# Shadowing

Given initial profile and impingement angle distribution

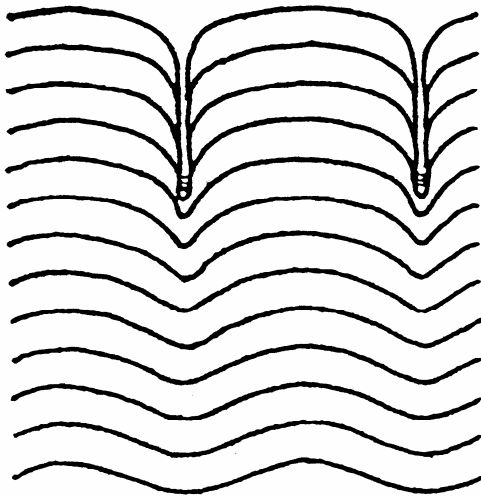
- + **Narrow impingement angle distribution:**  
peaks see the same particle flow as valleys (a)
- + **Wide impingement angle distribution:**  
peaks see larger particle flow than valleys (a)



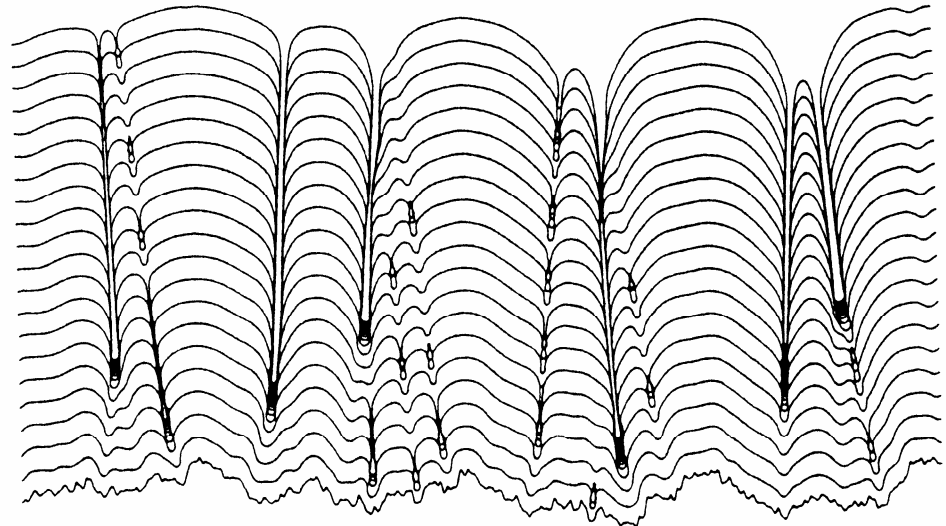
# Shadowing Dominated Growth

**Peaks grow faster than valleys**

- + **Formation of columnar structures (a)**
- + **Pore formation in combination with surface diffusion (b)**



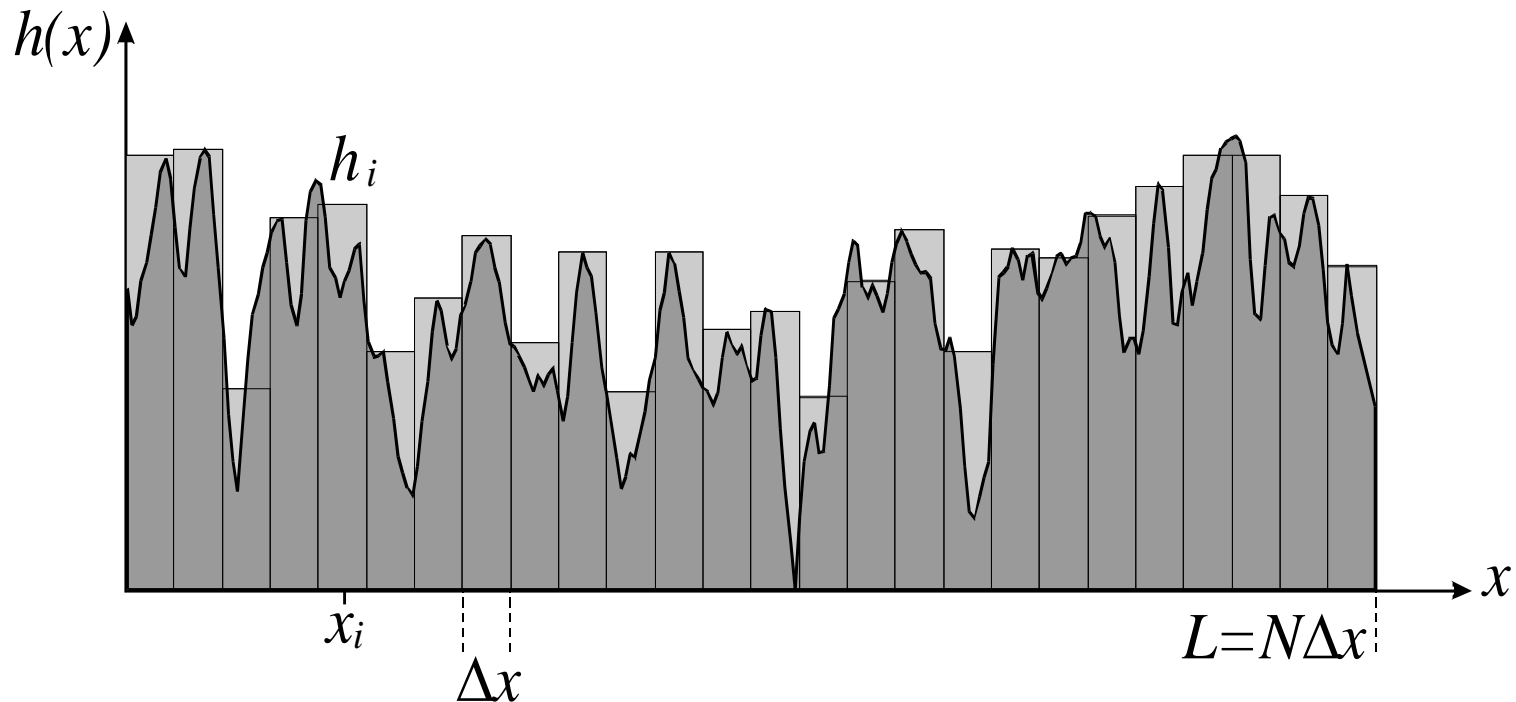
**(a)**



**(b)**

# Roughness Measurement in Real Space I

Conversion of a continuous height function to a set of discrete height values due to the finite lateral resolution of the measurement device.



***Roughness values (vertical) may depend on the lateral resolution of the measurement device.***

# Roughness Measurement in Real Space II

- + **Stylus profilometer:** **1d**
- + **Scanning tunneling microscope, STM:** **2d**
- + **Scanning force microscope, AFM:** **2d**
- + **Optical near field microscopy, SNOM:** **2d**

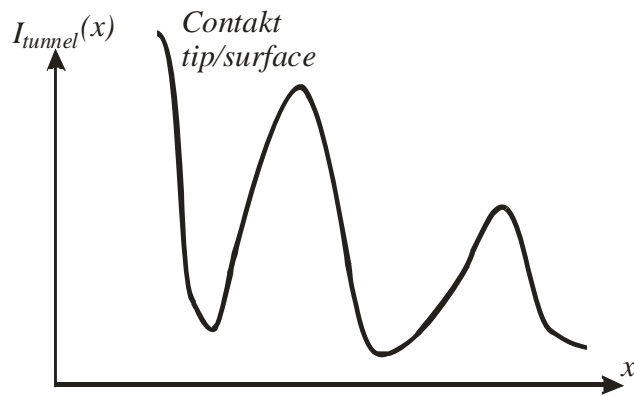
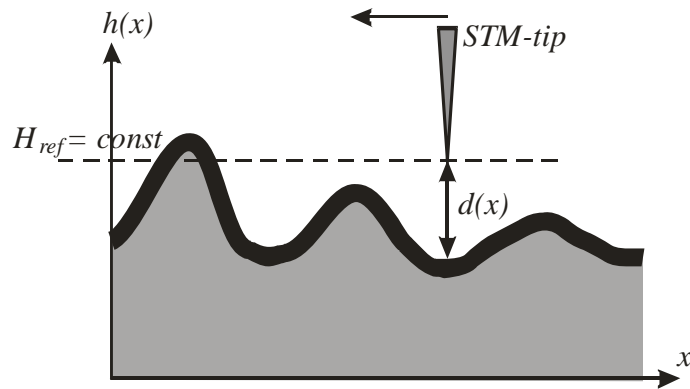


# The Feedback Principle

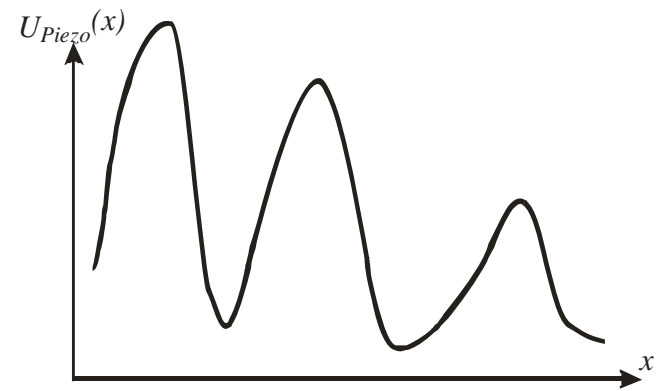
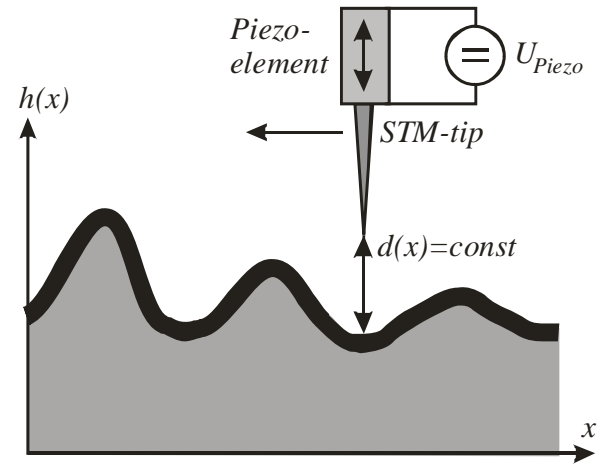
## Example: STM

(a) absolute tip position constant

(b) relative tip position constant



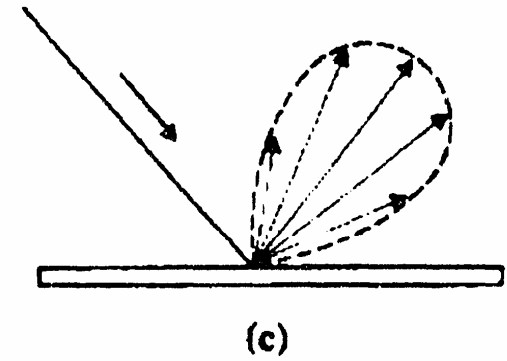
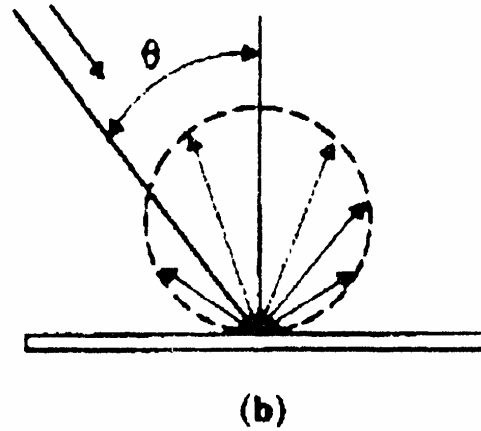
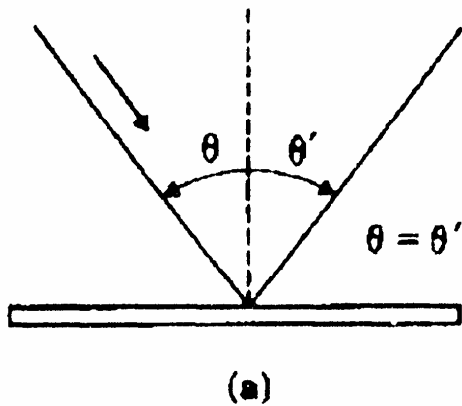
(a)



(b)

# Roughness Measurement in Fourier Space I

Scattering of visible light, X-rays or particles at outer or inner interfaces



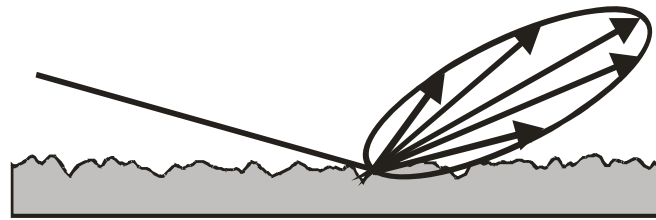
**(a) Specular reflexion**

**(b) Diffuse reflexion**

**(c) Signal combined from (a) and (b)**

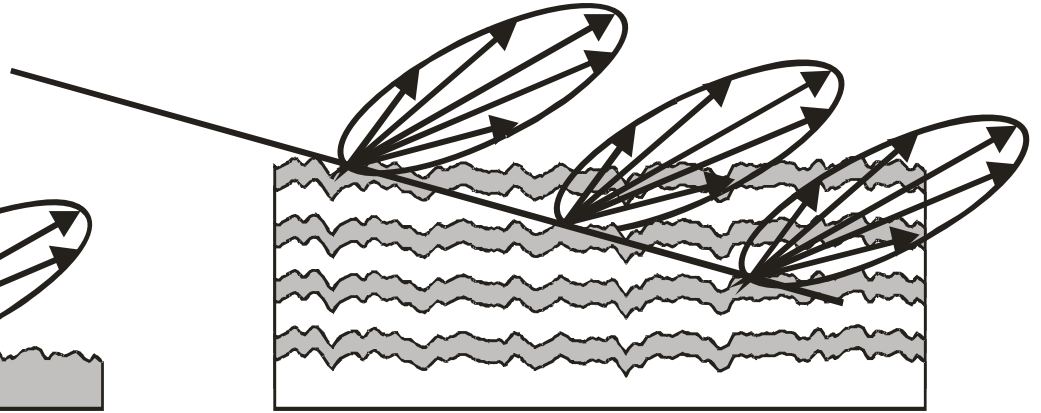
# Roughness Measurement in Fourier Space II

Outer interfaces



Light  
Electrons  
Ions

Inner interfaces



X-rays  
Synchrotron radiation

## Advantages:

- + Damage free
- + not necessarily vacuum based

## Disadvantage:

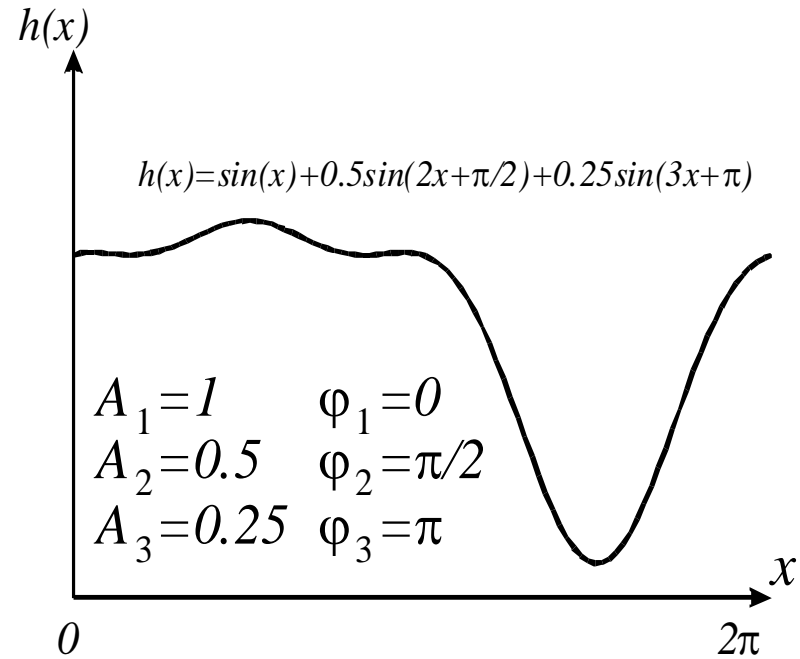
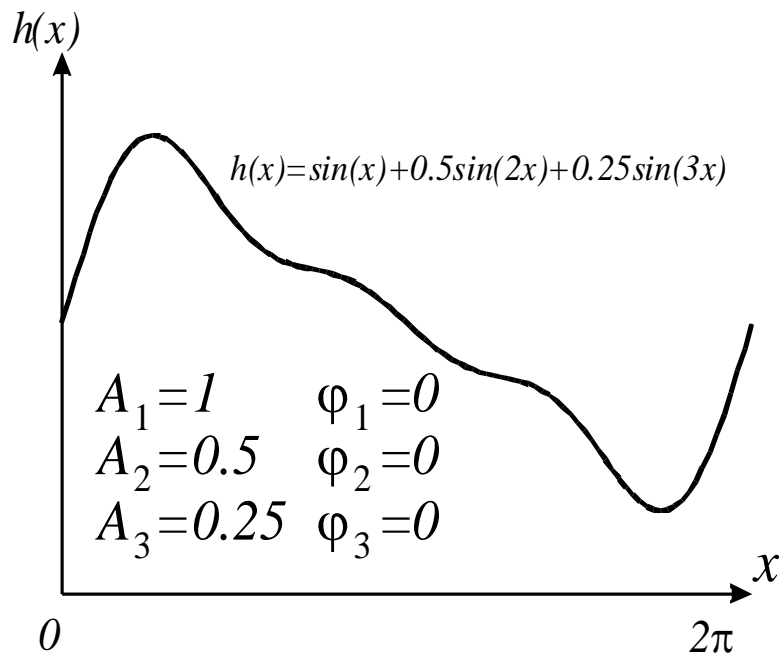
- + Surface profile not unambiguously reconstructible

# Loss of Phase Information

Scattering basically yields the Fourier Transform of a surface  $\Rightarrow$  loss of phase information

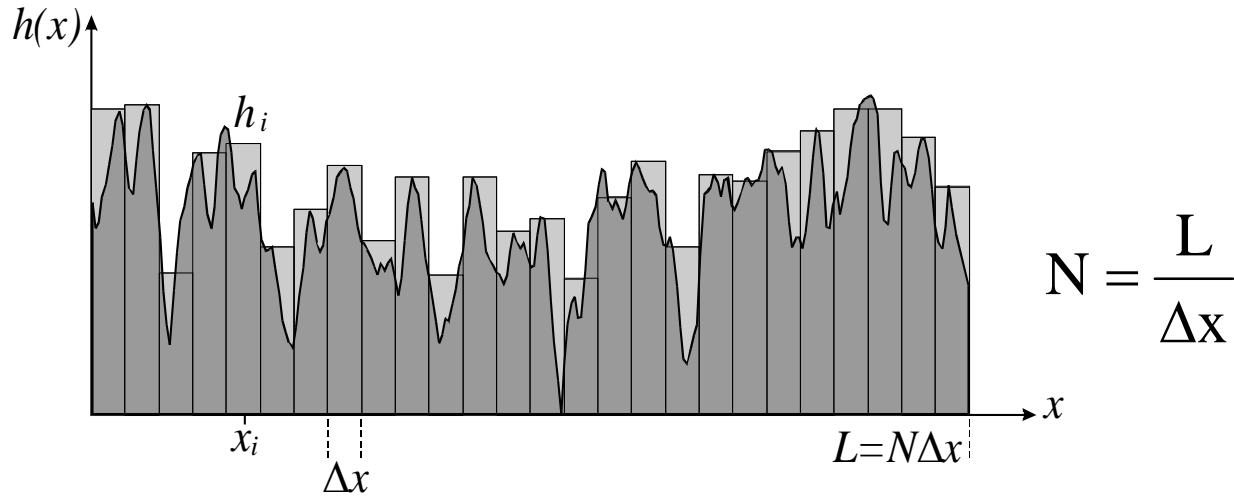
$\Rightarrow$  no unambiguous reconstruction of the profile possible

$$h(x) = \sum_{k=0}^N \underbrace{A_k}_{\text{known}} \sin(kx + \underbrace{\varphi_k}_{\text{unknown}})$$



# Quantification of Roughness I

## Linear profile, Sampling Interval $\Delta x$



## Quadratic scan

$$N = \left( \frac{L}{\Delta x} \right)^2$$

$$L_x = L_y \equiv L$$

$$\Delta x = \Delta y \equiv \Delta x$$

## Mean film thickness

$$\bar{h} = \frac{1}{N} \sum_{i=1}^N h_i$$

# Quantification of Roughness II

**$R_a$ -value: mean absolute deviation**

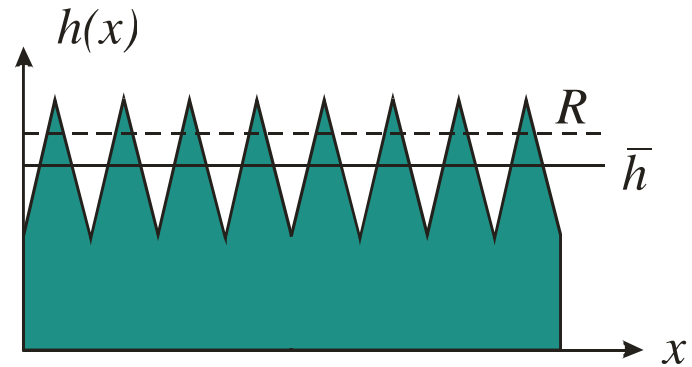
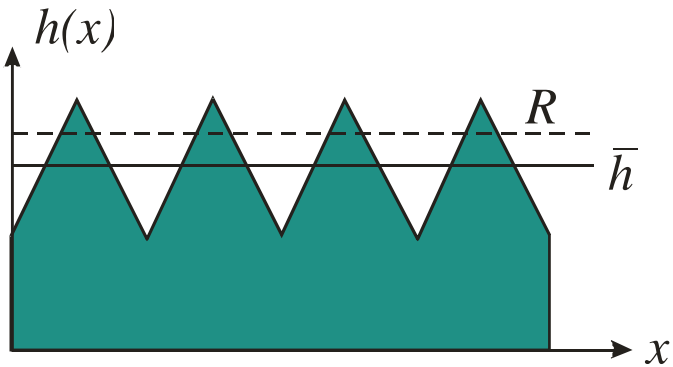
$$R_a = \frac{1}{N} \sum_{i=1}^N |\bar{h} - h_i|$$

**$R_q$ - or RMS-value:  
mean quadratic deviation**

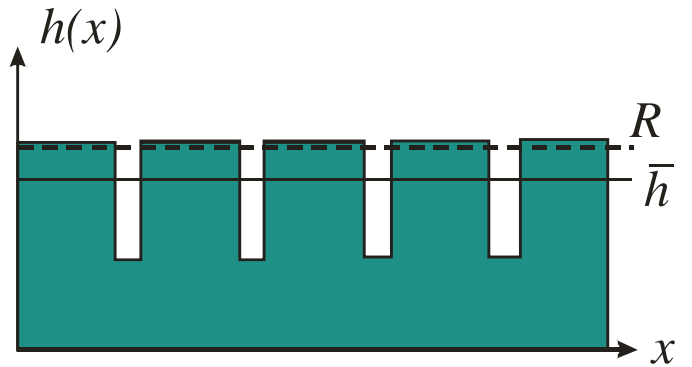
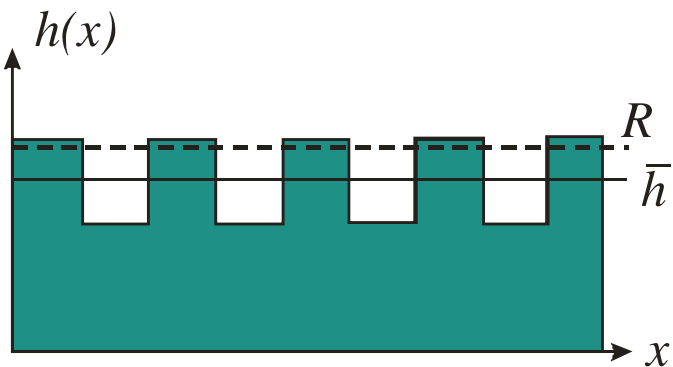
$$R_q = R_{\text{RMS}} = \text{RMS} = \sqrt{\frac{1}{N} \sum_{i=1}^N (\bar{h} - h_i)^2}$$

# Quantification of Roughness III

**Different profiles may have the same  $R_a$  or RMS-values:**



different periodicities



different symmetries

# Shape Specific Parameters

Allow limited statements about profile shape:

**Skewness  $S_k$ :**

$$S_k = \frac{1}{NR_q^3} \sum_{i=1}^N (h_i - \bar{h})^3$$

**$S_k < 0$ :**  
many height values  $< \bar{h}$

**$S_k > 0$ :**  
many height values  $> \bar{h}$

**Kurtosis  $K$ :**

$$K = \frac{1}{NR_q^4} \sum_{i=1}^N (h_i - \bar{h})^4$$

**$K$ : Measure of mean flank steepness**

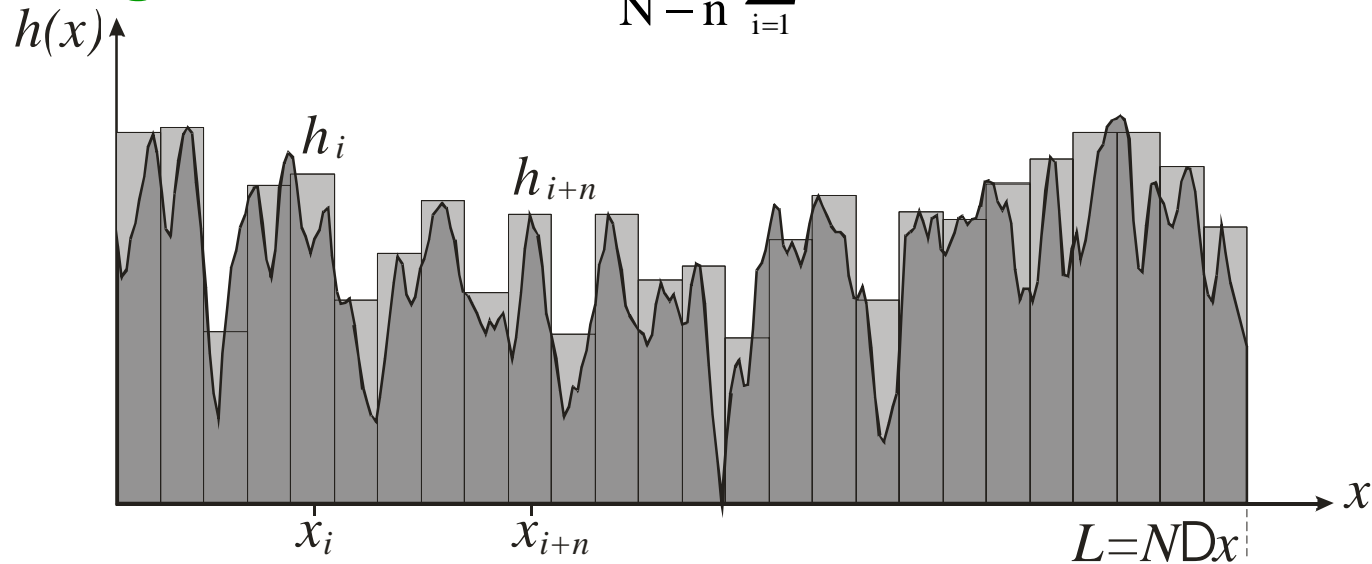


# Correlation Functions

Allow detailed statements about vertical and lateral profile properties:

**Point-point correlations for a discretized profile:**

**e. g.:**  $R(X) = R(n \cdot \Delta x) = \frac{1}{N-n} \sum_{i=1}^{N-n} (h_i - \bar{h}) \cdot (h_{i+n} - \bar{h})$



$n=0 \Rightarrow N$  point pairs

$n=1 \Rightarrow N-1$  point pairs

$n=2 \Rightarrow N-2$  point pairs

Therefore always  $N-n$  point pairs can be correlated within the interval

# Auto Covariance Function

## Discrete

$$R(X) = R(n \cdot \Delta x) = \frac{1}{N-n} \sum_{i=1}^{N-n} (h_i - \bar{h}) \cdot (h_{i+n} - \bar{h})$$

## Continuum

$$R(\tau) = \frac{1}{L-\tau} \int_0^{L-\tau} (h(x) - \bar{h}) \cdot (h(x + \tau) - \bar{h}) dx$$

# Structure Function

## Discrete

$$S(X) = S(n \cdot \Delta x) = \frac{1}{N - n} \sum_{i=1}^{N-n} [(h_i - \bar{h}) - (h_{i+n} - \bar{h})]^2$$

## Continuum

$$S(\tau) = \frac{1}{L - \tau} \int_0^{L-\tau} [(h(x) - \bar{h}) - (h(x + \tau) - \bar{h})]^2 dx$$

# Connection Between $R(\tau)$ and $S(\tau)$

**Normalized Autocovariance function  
(Autocorrelation function):**

$$\rho(X) = R(X) / R(0) \quad \text{or} \quad \rho(\tau) = R(\tau) / R(0)$$

**It is:**

$$R(0) = R_q^2$$
$$S(\tau) = 2R_q^2 [1 - \rho(\tau)]$$

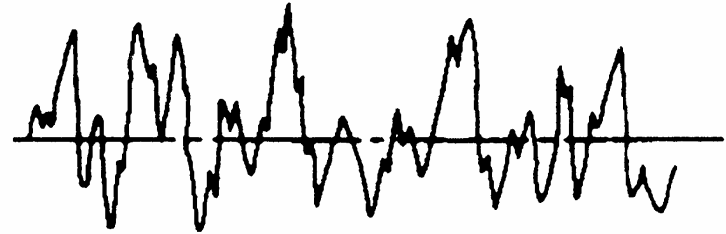
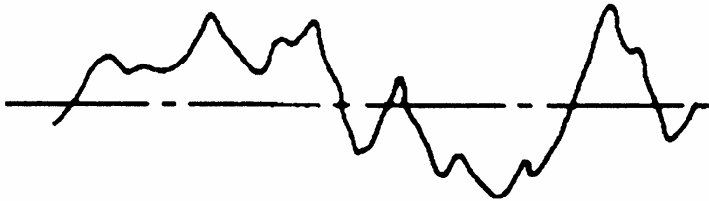
# Summary Correlation Functions

<b>Non normalized quantities</b>	<b>Normalized quantities</b>
<b>Autocovariance function</b> $R(\tau) = \langle h(x) \cdot h(x + \tau) \rangle dx$	<b>Autocorrelation function</b> $\rho(\tau) = R(\tau) / R(0)$
<b>Structure function</b> $S(\tau) = \langle [h(x) - h(x + \tau)]^2 \rangle$ $S(\tau) = 2R_q^2 [1 - \rho(\tau)]$	

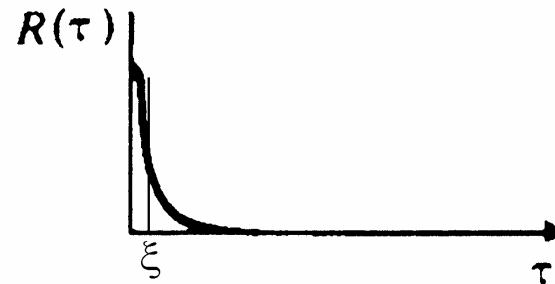
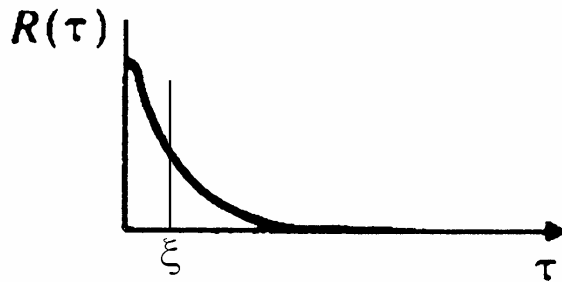
**Note: All height values are measured from the mean height  $\bar{h}$ .**

# Correlation Length $\xi$

## Surface profile



## Autocovariance function



***Within  $\xi$  the profile exhibits similar height values.***

***Periodicities are present, if  $R(\tau)$  exhibits maxima at  $\tau \neq 0$ .***

# Correlation Functions and Fourier Spectra

**Result of a scattering experiment:  
"Power Spectral Density"**

$$P(k) = \lim_{L \rightarrow \infty} \frac{1}{L \cdot (2\pi)^2} \left| \int_{-\infty}^{\infty} h(r) e^{ikr} dr \right|^2$$

$$k = \frac{2\pi}{\lambda}$$

$\lambda$  ... **Wavelength of a characteristic surface feature**

**P(k) ist the fourier transformed of the Autocovariance function R( $\tau$ ).**

$$P(k) = \frac{1}{(2\pi)^2} \int_{-\infty}^{\infty} R(r) e^{ikr} dr$$

***A scattering experiment therefore basically yields the Autocovariance function with all related statistical quantities ( $\xi$ ,  $R_q$ ).***