Wiederholung

Photoemission: Grundlagen (XAS, XPS, UPS etc.)

Photonenquellen

ESCA / XPS chemische Information: Spin Bahn Aufspaltung / Chemical Shift / Depth Profiling

Electronic Interaction in XPS

Beam Damage, Imagig XPS

UPS / Molekuele Wechselwirkung von Elektronenzustaenden und Chemische Reaktionen / Porphyrinen

Repetition V

- Near Edge X-ray Absorption Fine Structure
- reflects density of unoccupied states
- Absorption processes and decay (soft X-rays)
- Sampling depths (total electron yield, secondary, Auger, Fluorescence)
- Multiplet structure (chemical, electronic sensitivity)
- XMCD (sum rules)
- XMLD
- Magnetism (spin and orbital moment, magnetocrystalline anisotropy)
- PEEM

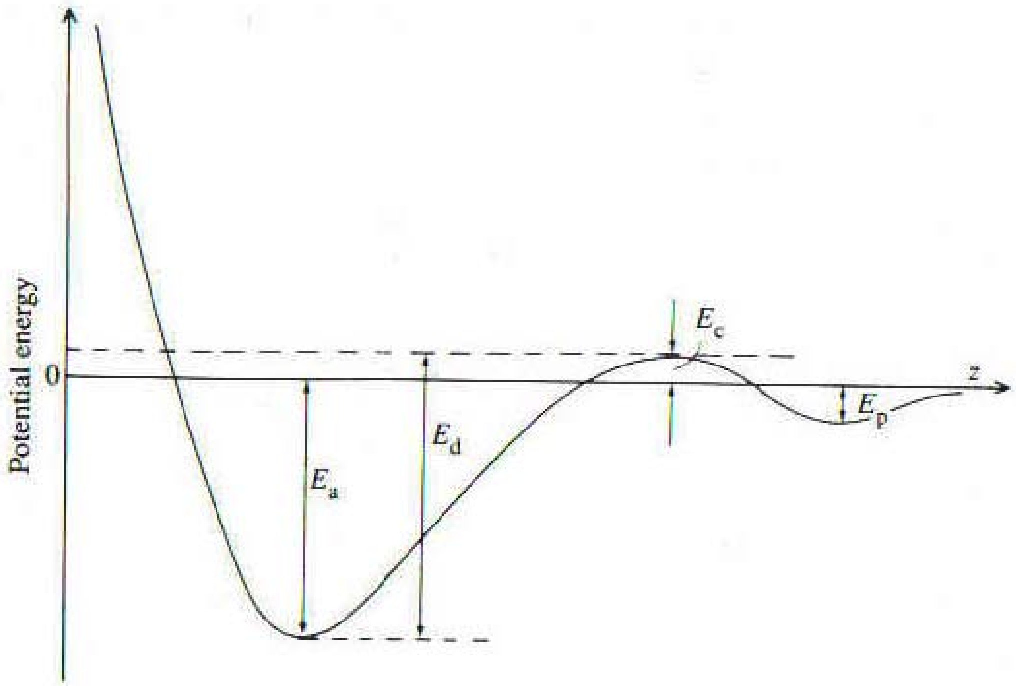
Wiederholung II

- Ionenstreuung → Rekonstruktionen und Relaxationen
- Dampfdruck / Verdampfung (Quelle und Vakuumproblem)
- Adsorption / Desorption

  a) Physisorption – VdW / Lennart Jones

  b) Chemisorption

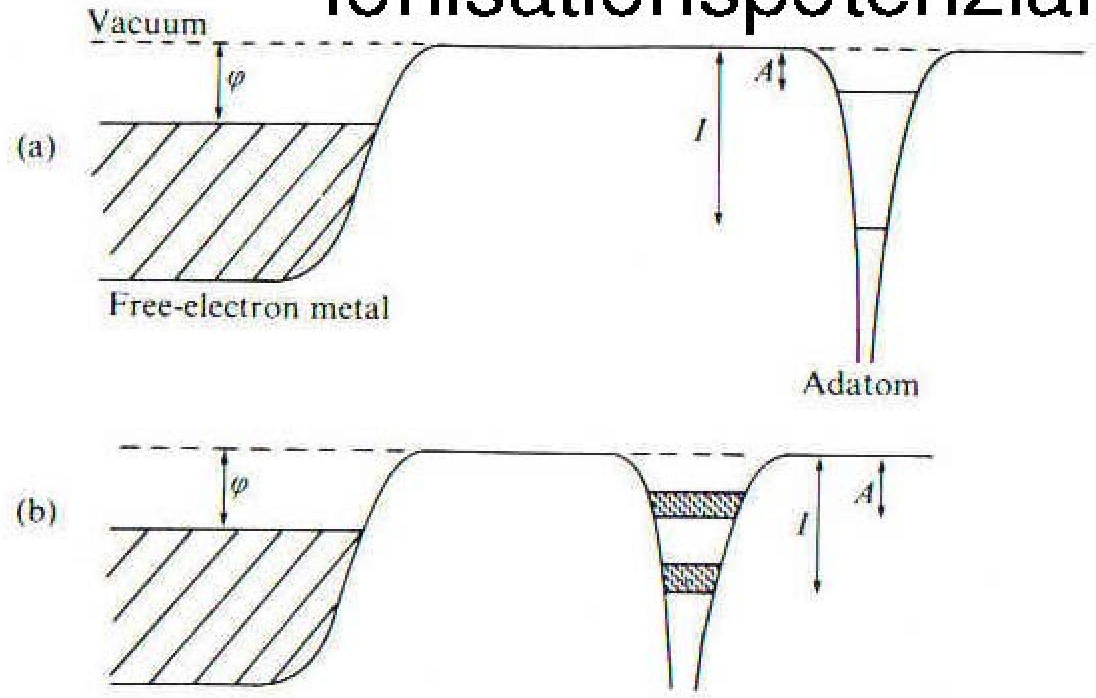
Chemisorption



Precursor-Zustand:
Zuerst schwach adsorpiert
Adatom kann über der Oberfläche
herumdiffundieren bis es
in den chemisorpierten Zustand
Wechselt.

Chemisorption: $E_A > 0.25$eV
Bindung ist mit Ladungstransfer verbunden (kovalente oder ionische Bindungen)
Es gibt auch dissoziative Chemisorption.

Elektronenaffinität und Ionisationspotenzial

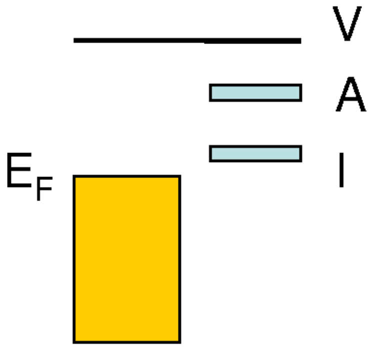


Durch Annähern des Adatoms verändern sich die Affinitäts- und Ionisations-Niveaus in Bänder. Ionisationspotenzial: Energie um Elektron abzugeben. Elektronenaffinität: Energie welche gewonnen wird wenn Elektron aufgenommen Wird.

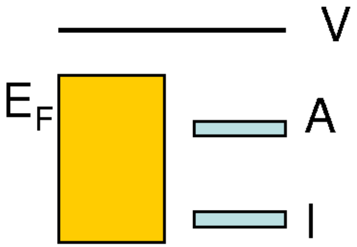
Die Elektronen beginnen zu wechselwirken:Zustaende → Baender

Chemisorption und Ladungstransfer

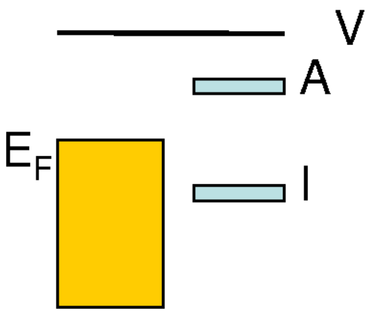
Fall 1:
Ionisationsenergie I des Adatoms ist kleiner wie die Austrittsarbeit φ des Metalls $\Rightarrow$ Adatom gibt Ladung ans Metall ab
Z.B. Cs (I=3.87eV) und Wolfram ($\varphi \approx 4.5$eV)



Fall 2:
Elektronenaffinität A des Adatoms ist grösser wie Austrittsarbeit φ eines Metallelektrons $\Rightarrow$ Adatom nimmt Ladung auf
Fluor (A=3.6eV,I=17.5eV) und Cs($\varphi \approx 1.8$eV). Es entsteht CsF.

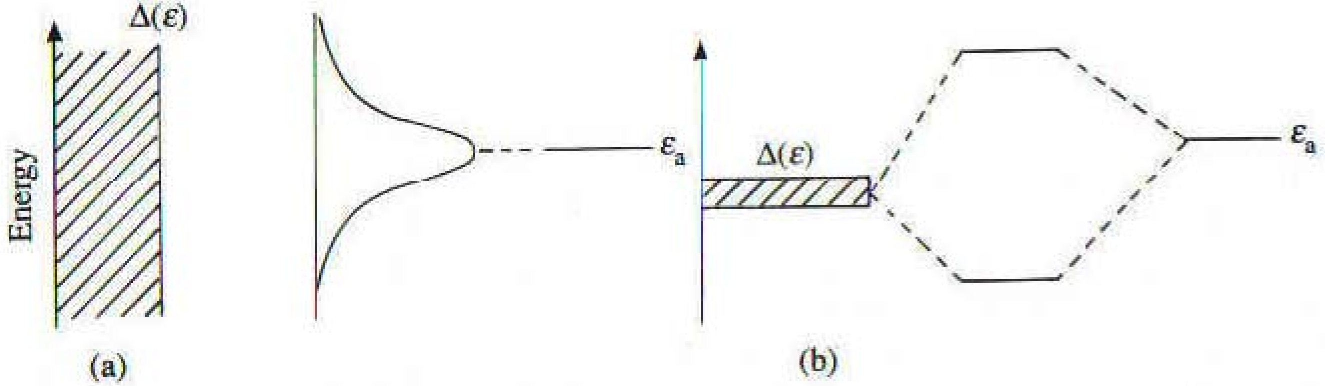


Fall 3:
I>φ>A
z.B. Wasserstoff: I=13.6eV und A=0.7eV. D.h. Wasserstoff wird auf denmeisten Metallen ($\varphi \approx 4$-6eV) neutral gebunden.



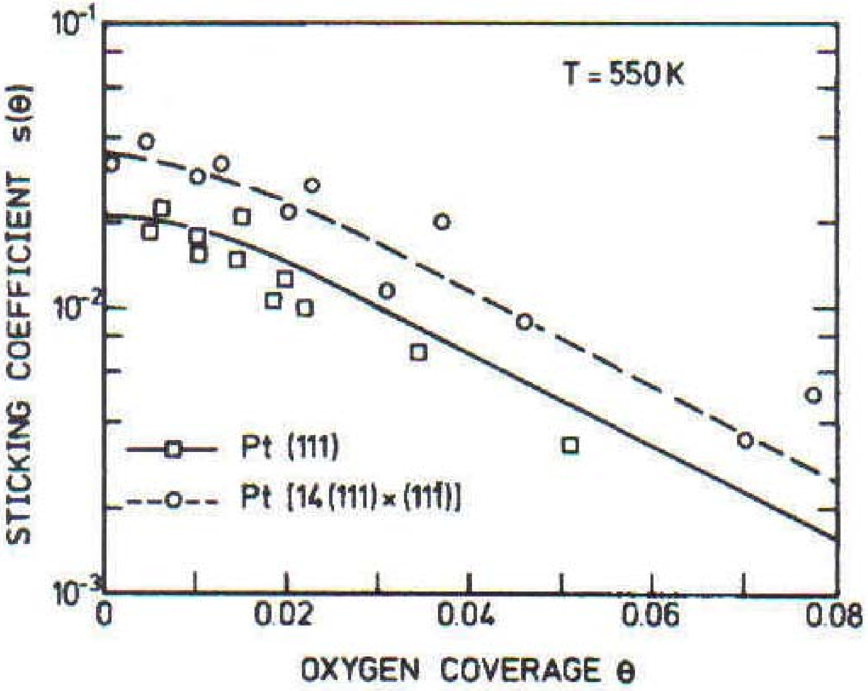
Theorie der Chemisorption

Durch den Überlapp der Wellenfunktionen von Adsorbat und Substrat, kommt es zur Bildung neuer Orbitale. Bei schwacher Bindung (im Vergleich zur Breite des Leitungsbandes) entspricht dies einer Verbreiterung der Adsorbat-orbitale. Bei starker Bindung entstehen bonding-antibonding Zustände.
D.h. Niveaus werden aufgespaltet.
Bsp.: schwache Chemisorption: Sauerstoff auf Aluminium
Starke Chemisorption: CO auf Ni(111)



Adsorptionswahrscheinlichkeit

Die Adsorptionswahrscheinlichkeit („sticking coefficient“) hängt stark von der Orientierung der Oberfläche und von der Rauhigkeit. Gestufte Oberflächen haben einen grosseren sticking coefficient.
⇒ Katalyse



Sticking coefficients for oxygen on the flat Pt(111) and on the stepped Platinum surfaces as a function of oxygen coverage at 550 K. (After H. Hopster et al., J. Catal. 46, p. 32 (1977))

Sticking coefficients

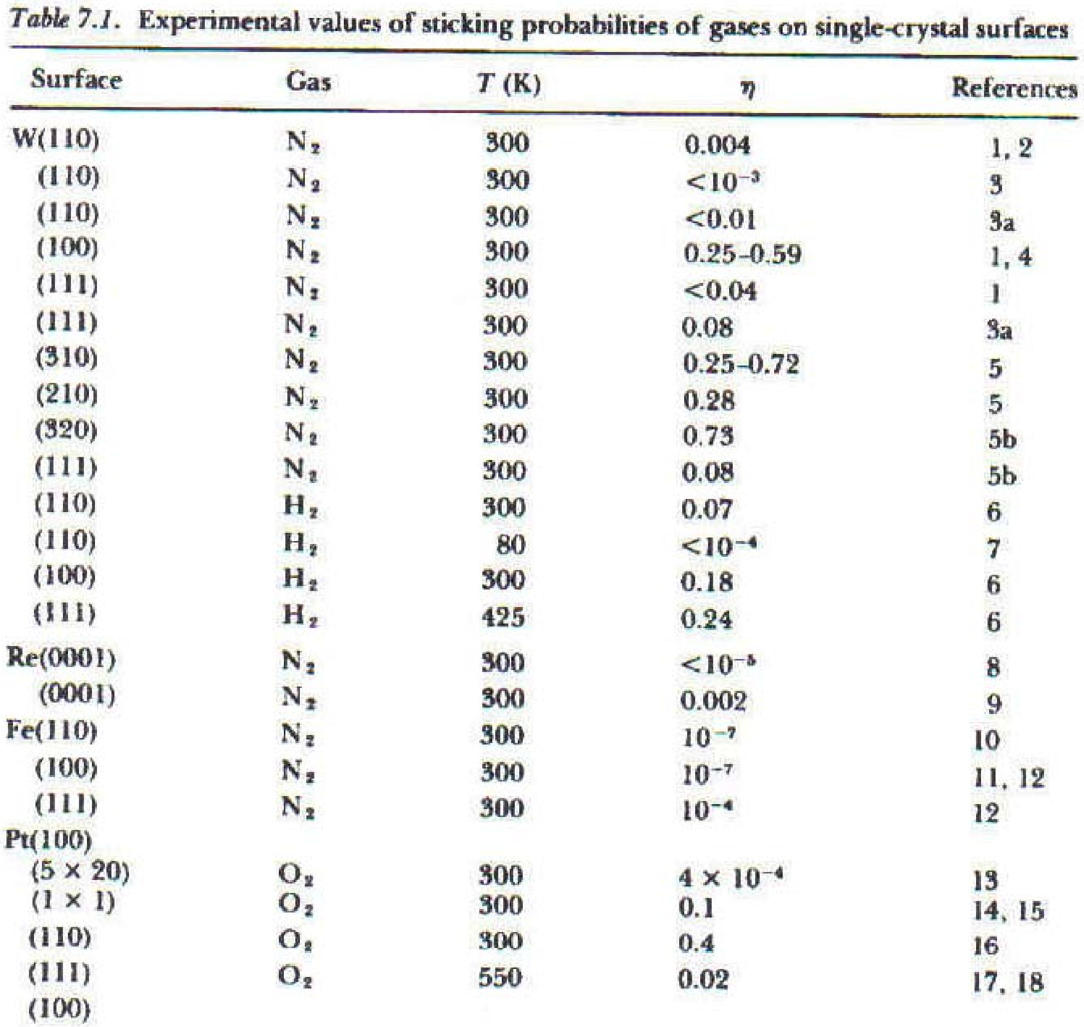


Table 7.1. Experimental values of sticking probabilities of gases on single-crystal surfaces

Surface	Gas	T (K)	η	References
W(110)	N_2	300	0.004	1, 2
(110)	N_2	300	$<10^{-3}$	3
(110)	N_2	300	<0.01	3a
(100)	N_2	300	0.25–0.59	1, 4
(111)	N_2	300	<0.04	1
(111)	N_2	300	0.08	3a
(310)	N_2	300	0.25–0.72	5
(210)	N_2	300	0.28	5
(320)	N_2	300	0.73	5b
(111)	N_2	300	0.08	5b
(110)	H_2	300	0.07	6
(110)	H_2	80	$<10^{-4}$	7
(100)	H_2	300	0.18	6
(111)	H_2	425	0.24	6
Re(0001)	N_2	300	$<10^{-5}$	8
(0001)	N_2	300	0.002	9
Fe(110)	N_2	300	10^{-7}	10
(100)	N_2	300	10^{-7}	11, 12
(111)	N_2	300	10^{-4}	12
Pt(100)				
(5 × 20)	O_2	300	4×10^{-4}	13
(1 × 1)	O_2	300	0.1	14, 15
(110)	O_2	300	0.4	16
(111)	O_2	550	0.02	17, 18
(100)				

Precursor-Zustand

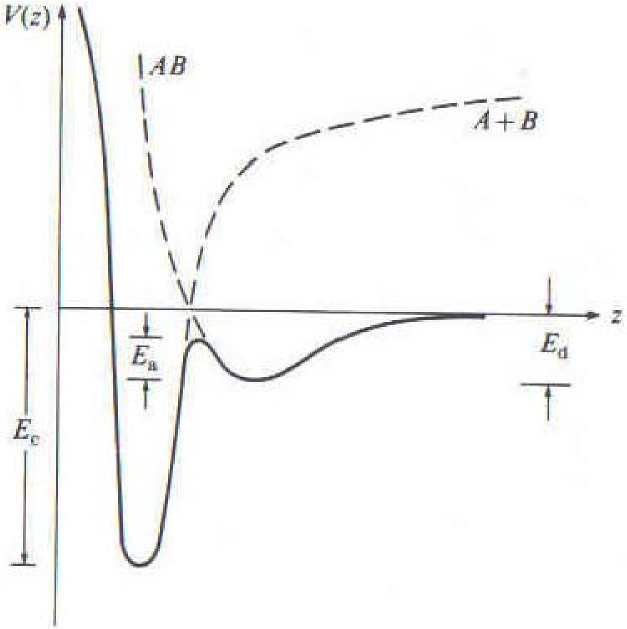
Adsorptionswahrscheinlichkeiten (sticking coefficients) sind erstaunlich klein.

Erklärung durch Lennard Jones: J. Lennard-Jones, Trans. Faraday. Soc. 28, 333 (1932).

Es wird angenommen, dass sich das Molekül zu Beginn in einem Precursor-Zustand befindet.

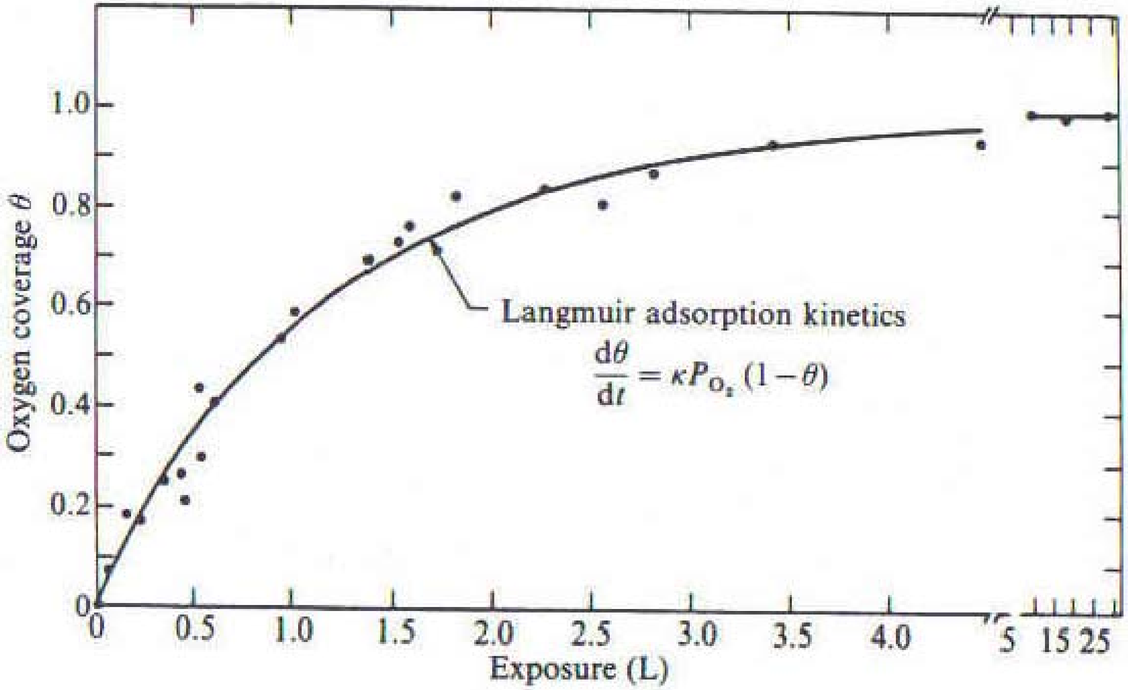
Es existiert somit eine Aktivierungsenergie. Da dieser Precursor-Zustand nur sehr schwach gebunden ist (schwache Physisorption) kann das Molekül leicht desorbiert werden, was zu den kleinen sticking coefficients führt.

Fig. 14.5. Schematic view of a one-dimensional gas–surface interaction potential which contains both a precursor physisorption well and a deeper chemisorption well.



Adsorptions-Kinetik

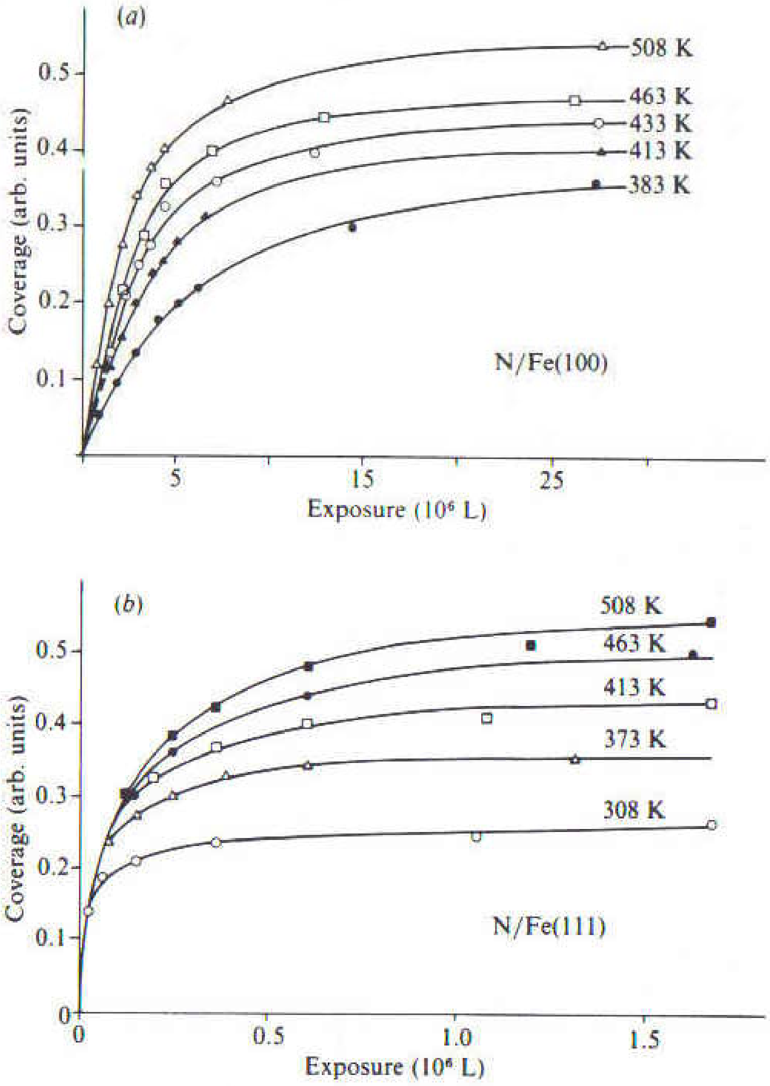
Fig. 14.2. O_2/Rh(111) adsorption kinetics at 335 K. The unit of exposure is 1 L = 10^{-6} Torr s (Yates, Thiel & Weinberg, 1979).



Einfache Langmuir-Kinetik: Adsorptionsrate $d\theta/dt$ ist proportional zum Partialdruck und zur Anzahl freie Plätze $\propto(1-\theta)$

Adsorptionskinetik

Fig. 14.3. Rate of nitrogen chemisorption on iron surfaces at different surface temperatures as a function of exposure: (*a*) Fe(100); (*b*) Fe(111). Note the change of scales for the abscissa (Bozso, Ertl, Grunze & Weiss, 1977).



Anfangs-Steigung ergibt $s(\theta)/s_0$

N/Fe(100) ist T-abhängig
⇒ Precursor ergibt aktivierten Prozess

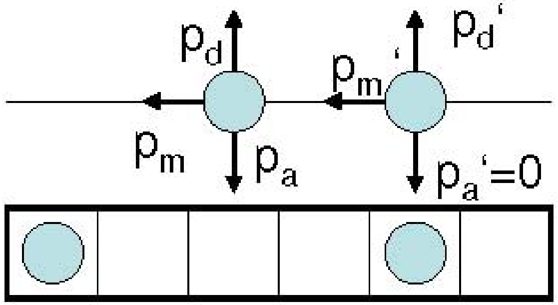
N/Fe(111) ist nicht T-abhängig

Kinetik mit Precursor

$$\frac{s}{s_0} = \left(1 + \frac{K\theta}{1-\theta}\right)^{-1}$$

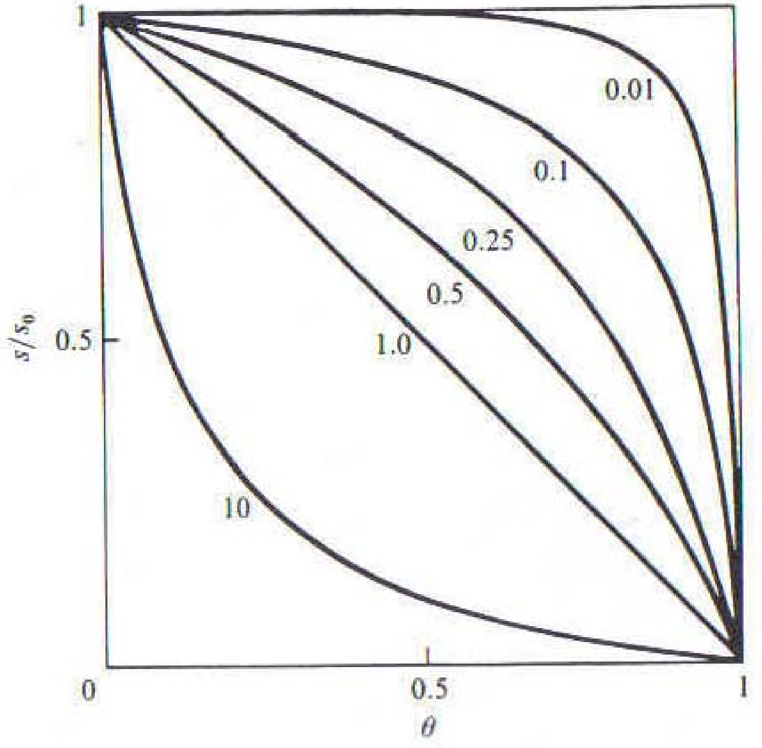
$$K = \frac{p'_d}{p_a + p_d}$$

typisch K<1



Langmuir: $s/s_0 = k\,(1 - \theta)$

Fig. 14.6 Plot of s/s_0 as a function of the parameter K in the precursor model of adsorption (Kisliuk, 1957).



$P_a \sim 1 - \Theta$: chemisorption

P_m : migration

P_d : desorption

Ann: physisorption unabh. von Bedeckung

K: Konstante

adsorption / desorption kinetics / dynamics

- Adsorption can be treated like a chemical reaction:

  A(gas)+S → S:A(ads) *atomic adsorption*

  2S:A(ads) → 2S + A_2(gas)

  recombinative molecular desorption

  → gesamter thermodynamischer Apparat der Chemie ist anwendbar (Oberflaechenreaktionen / Katalyse)

adsorption / desorption
‘take home’ message

- Complex multi – stage process
- T variation affects relaxation
- Important for the formation of interfaces and thin films
- Important for catalysis
- Important for the analysis of interface bonding
- Adsorption can be treated like a chemical reaction:

Surface Physics 2010

Surface Diffusion

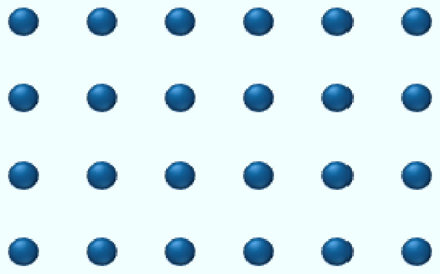
UNI
BASEL

Lecturer: Dr. Enrico Gnecco

NCCR Nanoscale Science

Random-Walk Motion

- Thermal motion of an adatom on an ideal crystal surface:



- Thermal excitation → the adatom can hop from one adsorption site to the next

- Mean square displacement at time *t*:

$$\boxed{\left\langle \Delta r^2 \right\rangle = \nu a^2 t}$$

a = jump distance; ν = hopping frequency

(Note that νt = number of hops!)

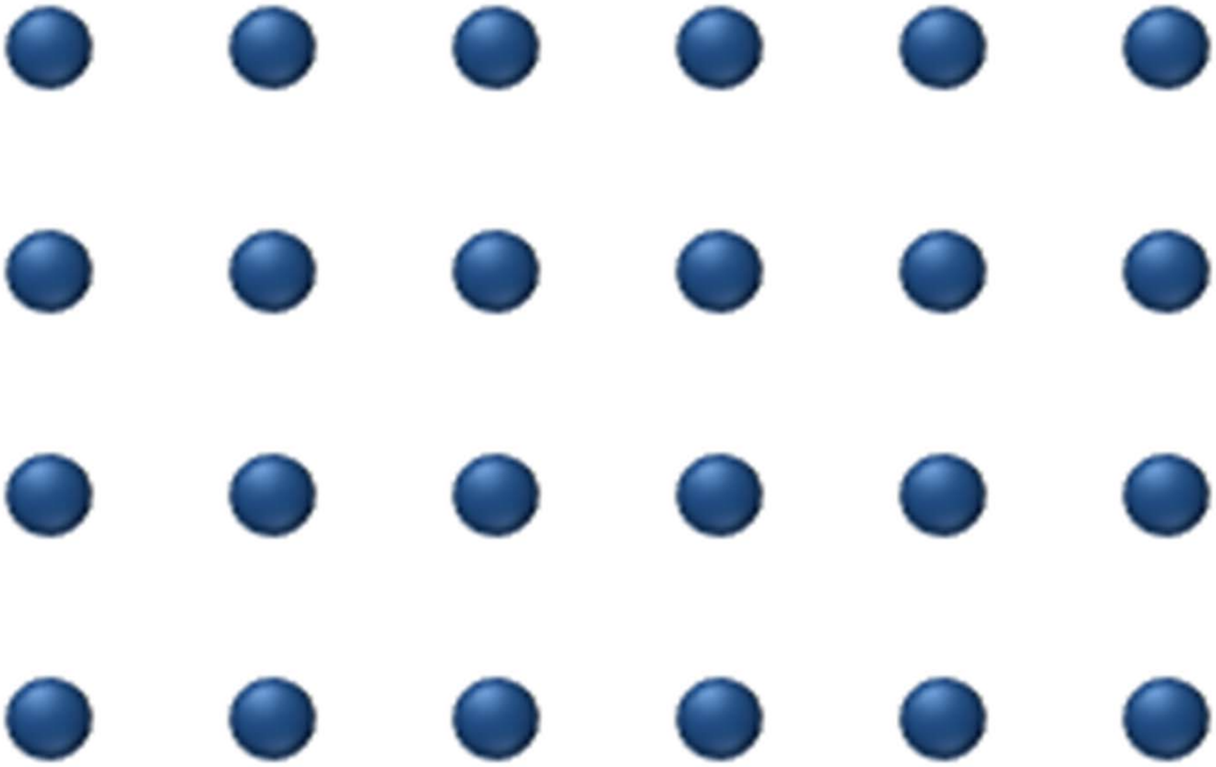
$$< \Delta^2 r(t) >= \frac{1}{N} \sum_{i=1}^{N} < [\underline{R}_i(t) - \underline{R}_i(0)]^2 >$$

- **Diffusion coefficient**:

$$\boxed{D = \frac{\left\langle \Delta r^2 \right\rangle}{zt} = \frac{\nu a^2}{z}}$$

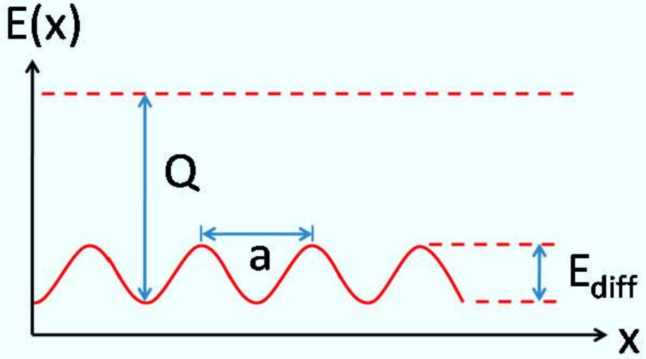
z = number of first neighbors = $\left[\begin{array}{l} \text{2 in 1D diffusion} \\ \text{4 on a square lattice} \\ \text{6 on a hexagonal lattice} \end{array} \right.$

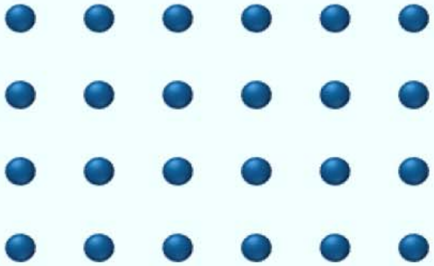
Diffusion



Random-Walk Motion

- Hopping → surmounting a potential barrier





- **Arrhenius law**:

$$\boxed{\nu = \nu_0 \exp\left(-\frac{E_{diff}}{k_B T}\right)}$$

ν_0 = oscillation frequency of the atom in the well;

E_{diff} = barrier height

Tipically E_{diff} ~ 5-20% of Q (heat of desorption)

- For chemisorbed species: $E_{diff} >> k_B T$
- If $E_{diff} < k_B T$: 2D gas (only a few physisorbed species)

Fick’s Laws

- **Fick’s First Law** (for 1D diffusion):

$$\boxed{J = -D\frac{\partial c}{\partial x}}$$

diffusion flux

concentration gradient

(flux → region of lower concentration)

- **Fick’s Second Law** (for 1D diffusion):

$$\boxed{\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}}$$

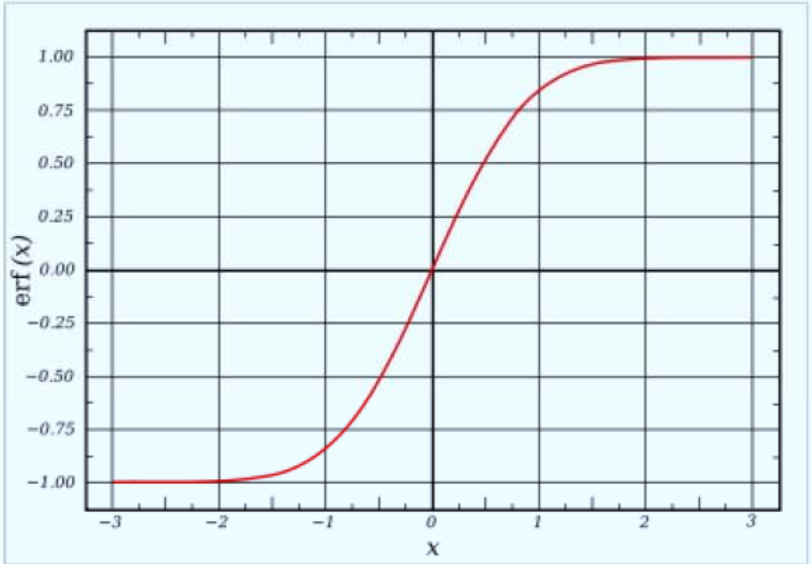
← from equation of continuity

- Analytical solutions can be found for specific initial and boundary conditions!

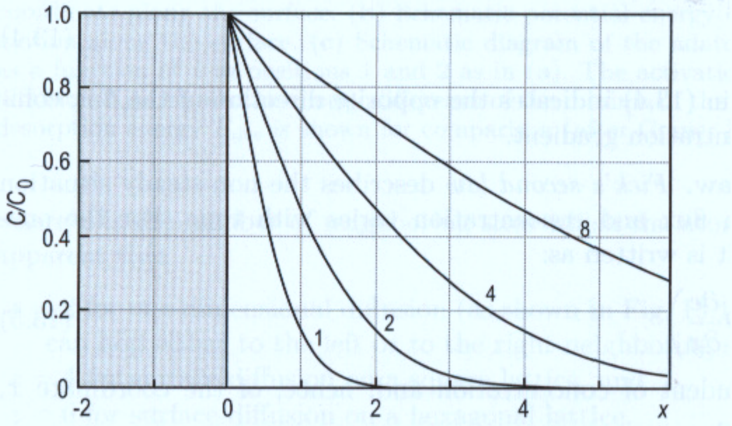
Analytical Solutions of Fick's Laws

- We introduce the **error function**

$$\boxed{\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-t^2)\, dt}$$



- Source of constant concentration:



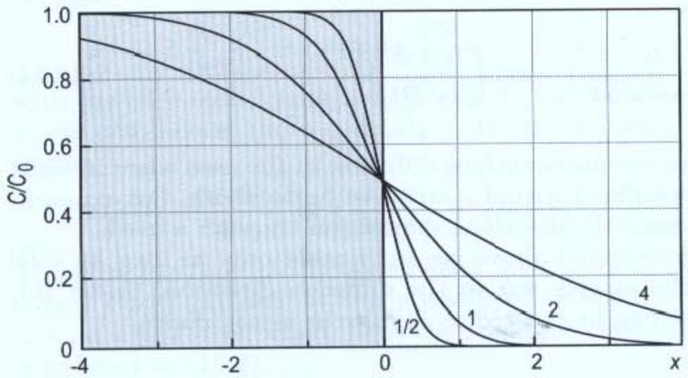
$$c(x,t) = c_0\left[1-\operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right]$$

$2\sqrt{Dt}$: **diffusion length**

  - Example: Submonolayer film with 3D islands supplying mobile adatoms

Analytical Solutions of Fick's Laws

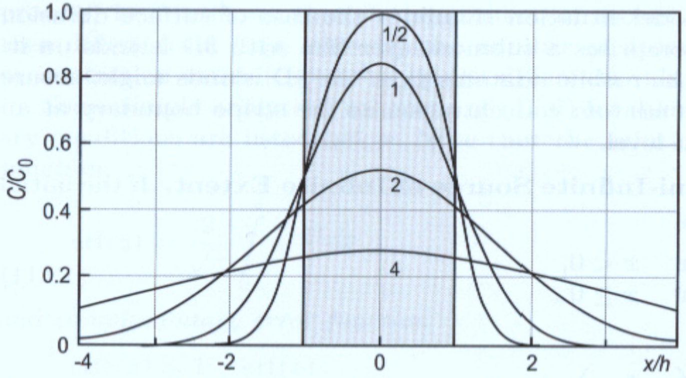
- Source of infinite extent:



$$c(x,t)=\frac{c_0}{2}\left[1-\operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right]$$

- Example: Submonolayer film

- Source of limited extent:



$$c(x,t)=\frac{c_0}{2}\left[\operatorname{erf}\left(\frac{h-x}{2\sqrt{Dt}}\right)+\operatorname{erf}\left(\frac{h+x}{2\sqrt{Dt}}\right)\right]$$

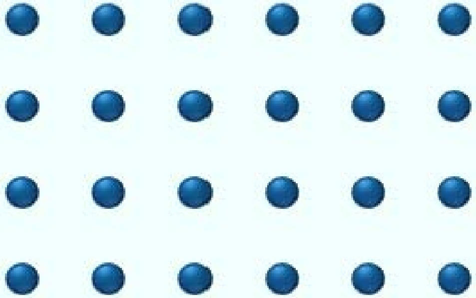
- Example: Submonolayer film confined in a stripe of finite width

Diffusion Mechanisms

- Depending on the <u>coverage</u> Θ:
  - Tracer diffusion (low Θ)
  - Chemical diffusion (intermediate to high Θ)

Tracer Diffusion

- **Tracer Diffusion:**
  - Low coverage (<0.01 ML)
  - Individual adparticles



- Fick's first law is valid:

$$D = \frac{\langle \Delta r^2 \rangle}{zt}$$

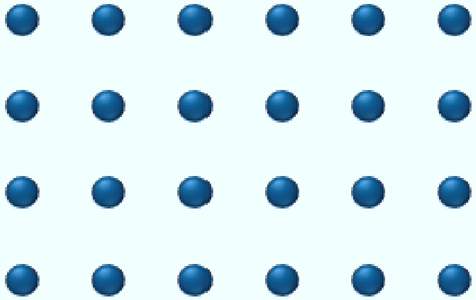
- For an ensemble of many particles:

$$D = \frac{1}{zNt} \sum_i \langle \Delta r_i^2 \rangle$$

(no relation to radioactive tracers!)

Chemical Diffusion

- **Chemical Diffusion:** - Higher coverage
  - Attraction or repulsion between adatoms



- Fick's first law can be generalized:

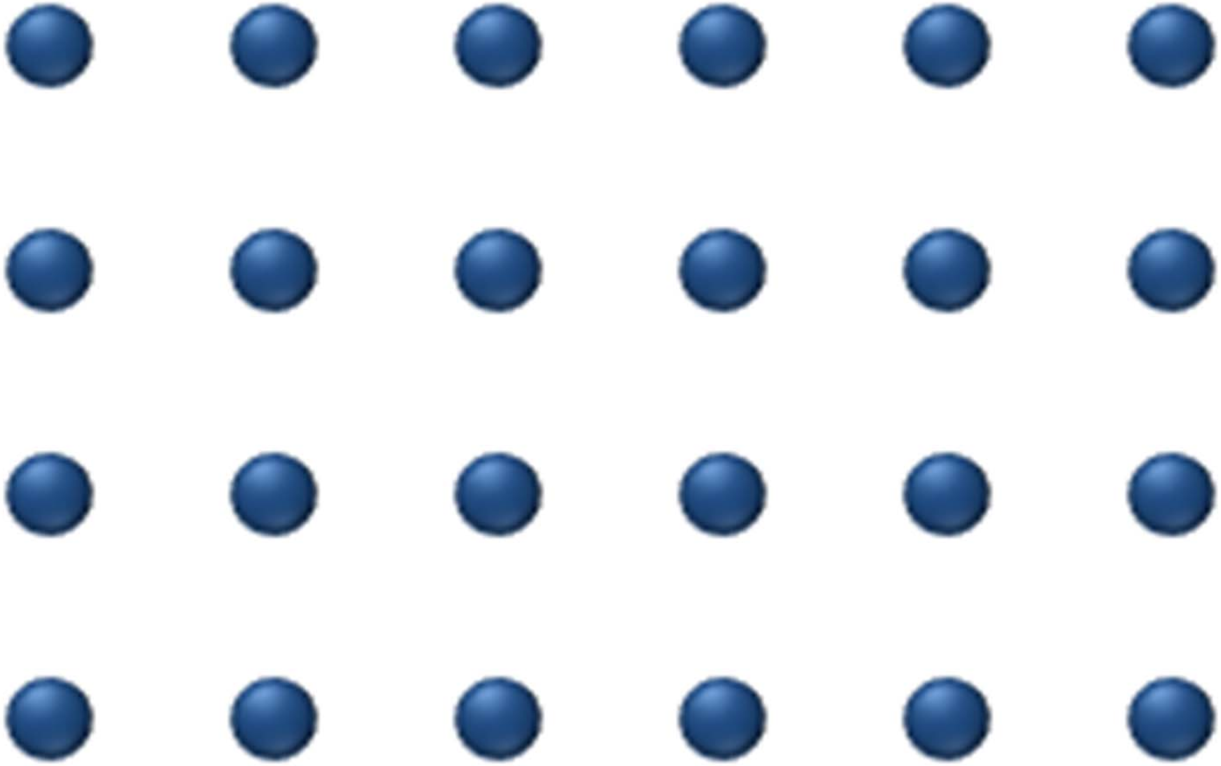
coverage

$$J = -D_c(\Theta)\frac{\partial \Theta}{\partial x}$$

chem. diff. coefficient

- Strong dependence on adsorbate coverage is expected, especially when ordered phases are formed (Naumovets-Vedula, 1986)

‘Chemical Diffusion’



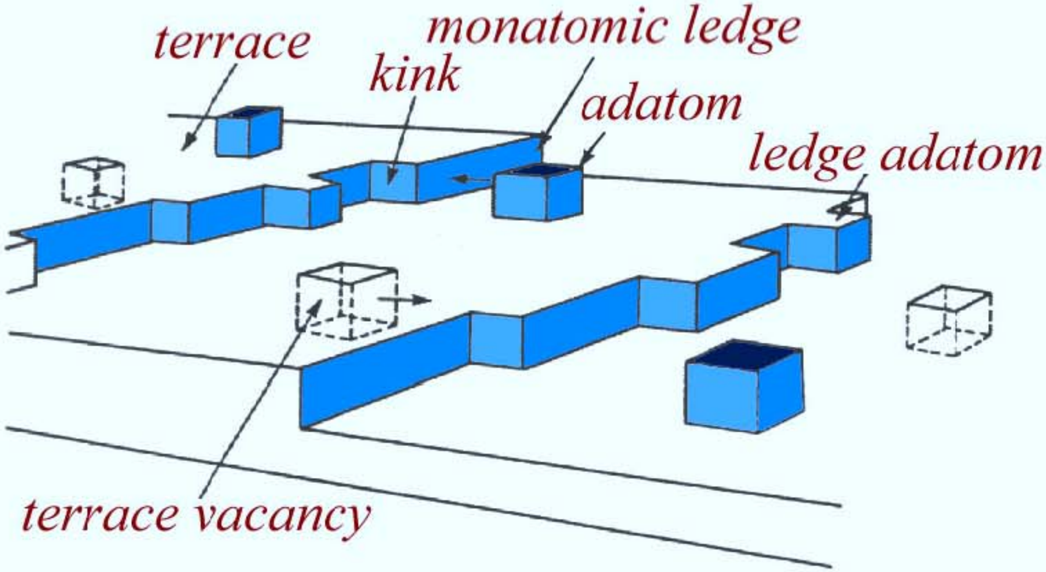
Diffusion Mechanisms

- Depending on the landscape:
  - Intrinsic diffusion (no sources and traps)
  - Mass transfer diffusion (generation and/or trapping)

Intrinsic Diffusion

- Adparticle motion is monitored within a single terrace → Spatial limit ~ 100 nm

- In practice: no strong distinction from tracer diffusion



Mass Transfer Diffusion

- Real surfaces contain defects (steps, kinks, adatoms or vacancy clusters, etc.)

- If average separation between defects < diffusion length → number of mobile particles (and diffusion) become strongly temperature dependent

- If adatoms and substrate are the same chemical species:

$$D = \frac{\nu_0 a^2}{z} \exp\left(-\frac{\boxed{\Delta G} + E_{diff}}{k_B T} \right)$$

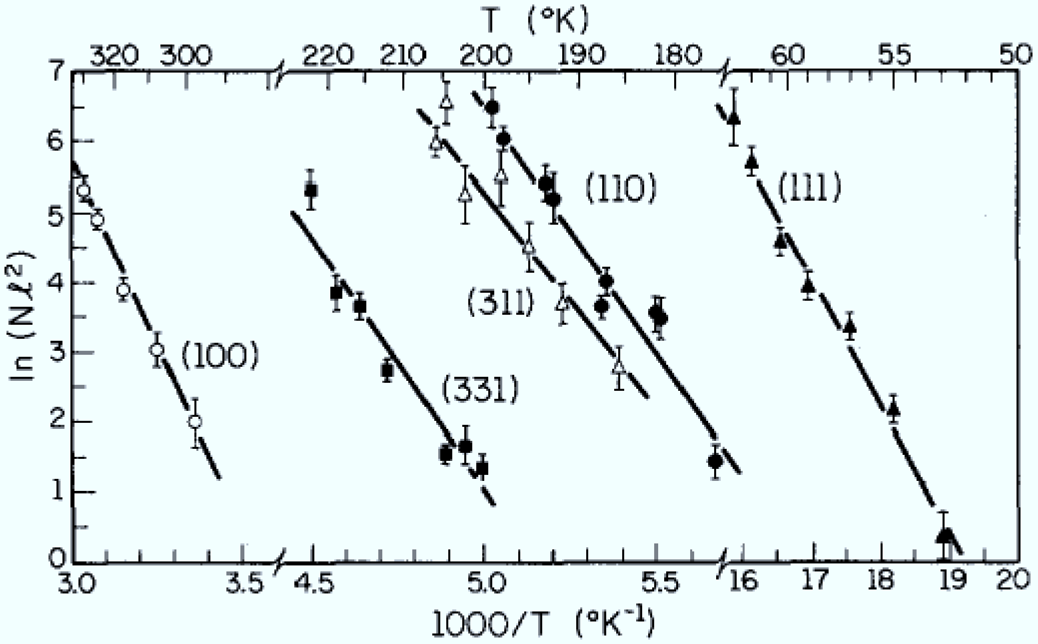
ΔG = energy of adatom formation

(→ two types of energy barriers!)

Anisotropy of Surface Diffusion

- **Orientational Anisotropy:** the diffusion coefficient depends on the <u>orientation of the surface</u>

- Example: Rh surfaces at different T (Ayrault & Ehrlich, JCP 1974)



N: number of jumps in 3 min

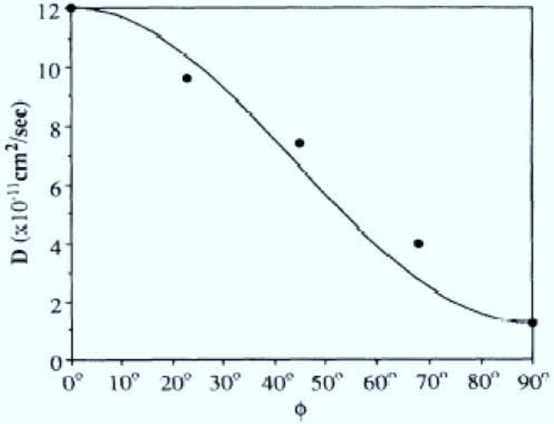
ℓ: jump distance

- At given T the differences in the diff. coeff. can be several orders of magnitude!

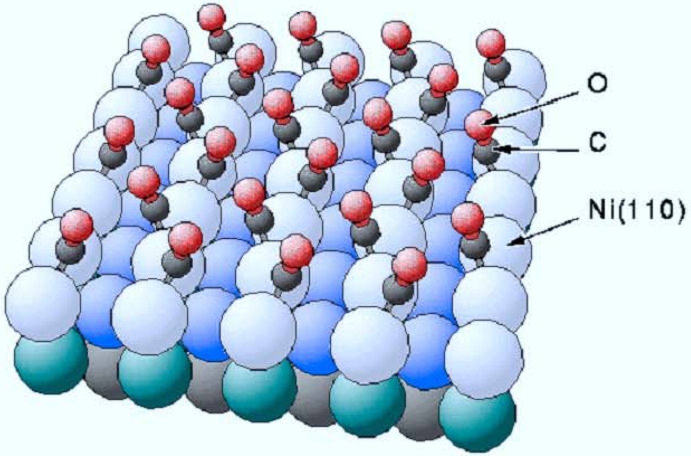
Anisotropy of Surface Diffusion

- **Directional Anisotropy:** the diffusion coefficient depends on the direction at the surface

- Rectangular lattice → directional anisotropy (Xiao et al., PRL 1991)

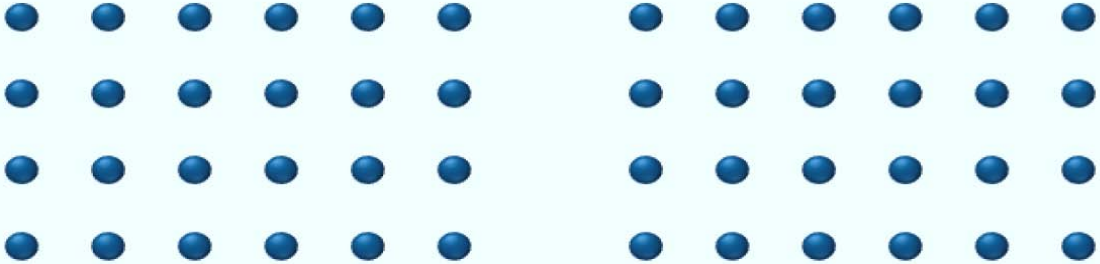


$$D(\varphi) = D_x \cos^2 \varphi + D_y \sin^2 \varphi$$

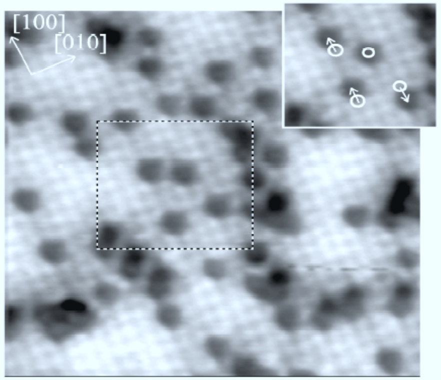


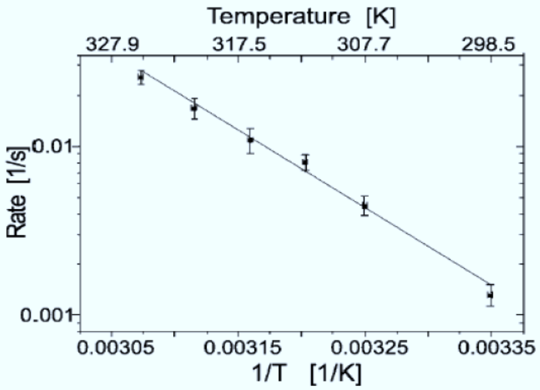
Atomistic Mechanisms

1) Hopping mechanism:



- Example: N adatoms on Fe(100) (Pedersen et al., PRL 2000)

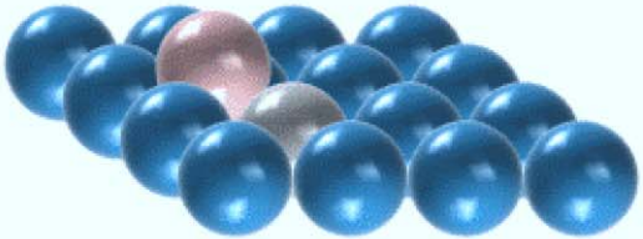


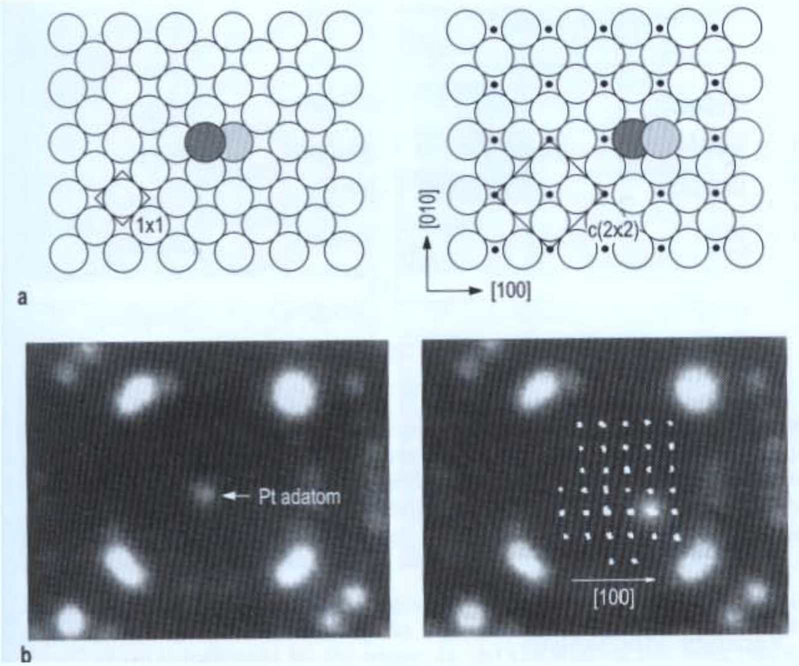


→ Arrhenius law with $\nu \sim 10^{12}\ \mathrm{s}^{-1}$, $E_{diff} = 0.92$ eV

Atomistic Mechanisms

2) Atomic exchange mechanism:





- Example: Pt adatom on Pt(100) (Kellogg, SSR 1994)

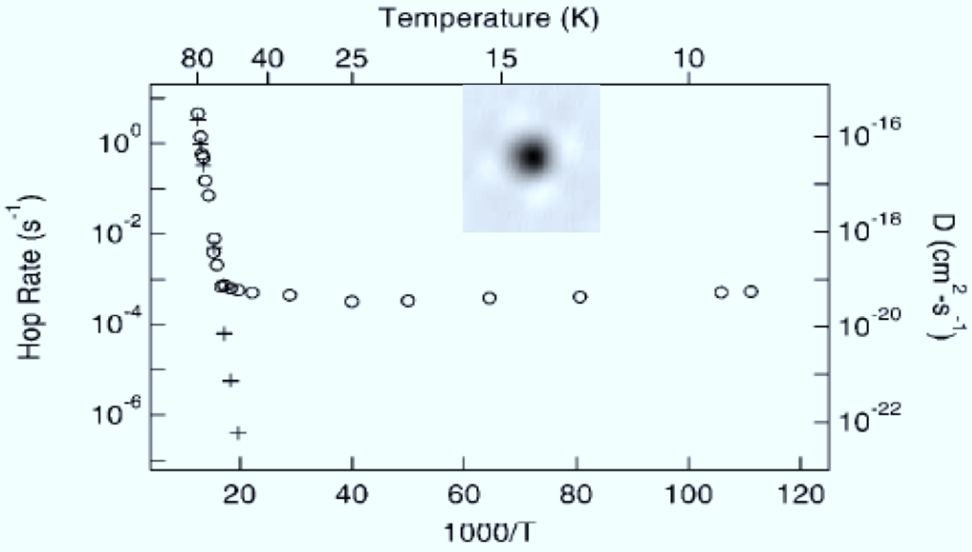
- Observed also on heterosystems [Pt on Ni(110), Ir on Pt(100), Re on Ir(100)]

Atomistic Mechanisms

3) Tunneling mechanism:

- Diffusing particle with small mass
- Low potential barrier against diffusion

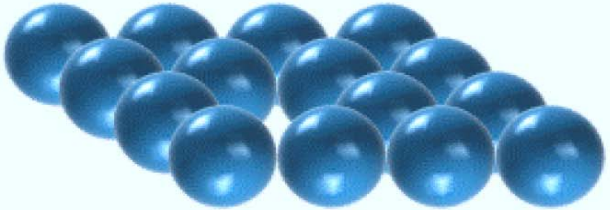
- Example: Hydrogen on Cu(100) (Lauhon & Ho, PRL 2000)



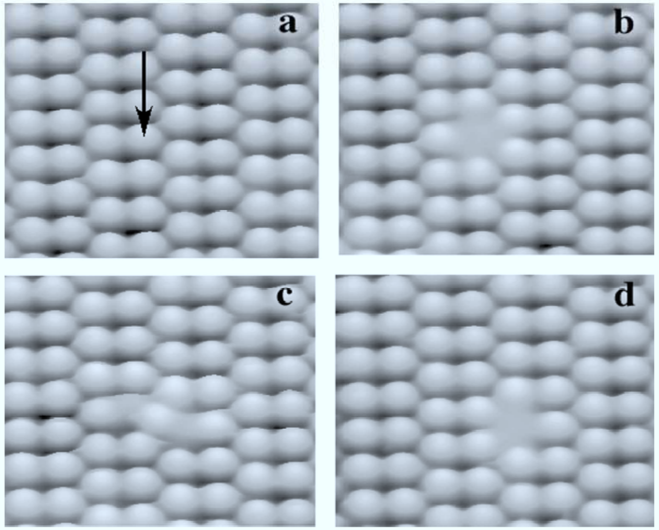
- Above 60 K: Arrhenius law with $\nu \sim 10^{13}\ s^{-1}$, $E_{diff} = 0.20$ eV
- Below 60 K: quantum tunnelling, T independent

Atomistic Mechanisms

4) Vacancy mechanism:



- Example: Ge(111)c(2x8) (Mayne et al., SS 2001)



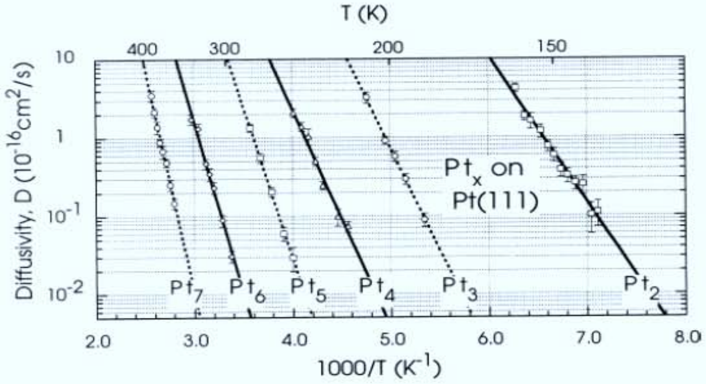
-Vacancy created with the STM tip

- T-activated hopping of neighboring atoms

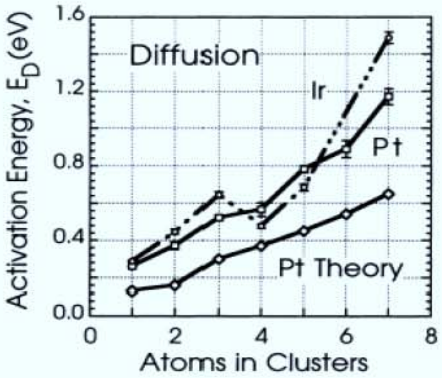
- Heterodiffusion by vacancy-exchange also reported

Cluster Diffusion

- The larger the cluster, the lower its mobility:

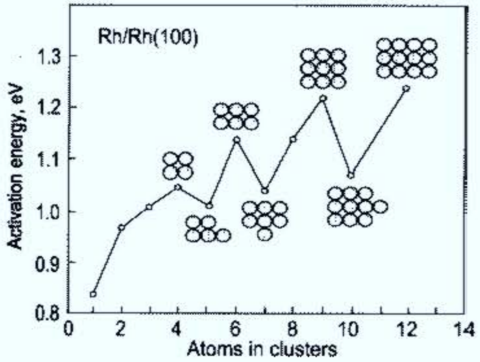


- Activation energy increases with cluster size:



(Kyuno & Ehrlich, SS 1999)

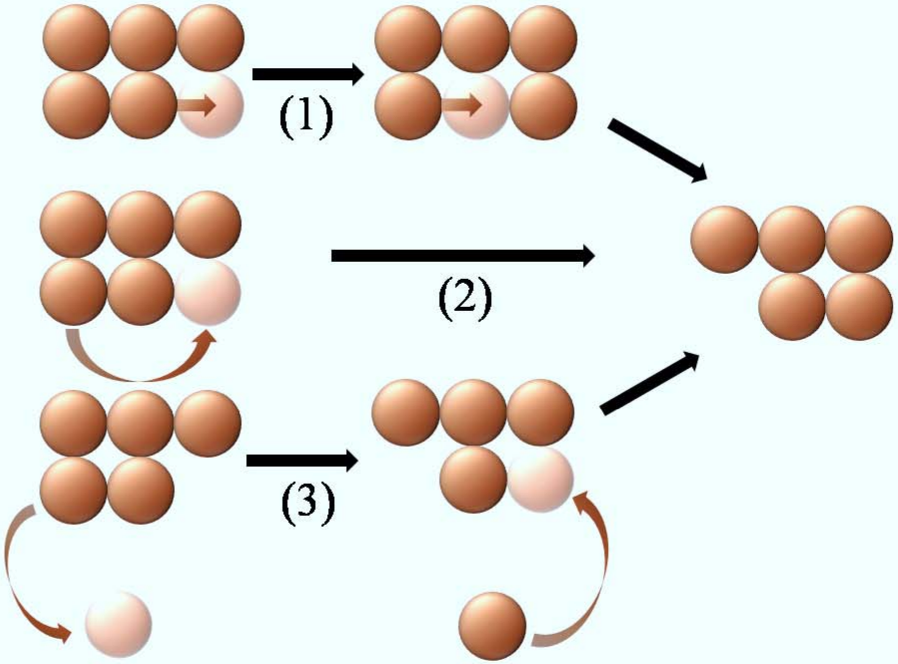
- Compact shapes are less mobile...



(Kellogg, PSS 1996)

Cluster Diffusion

Individual mechanisms:



(1) Sequential displacement

(2) Edge diffusion

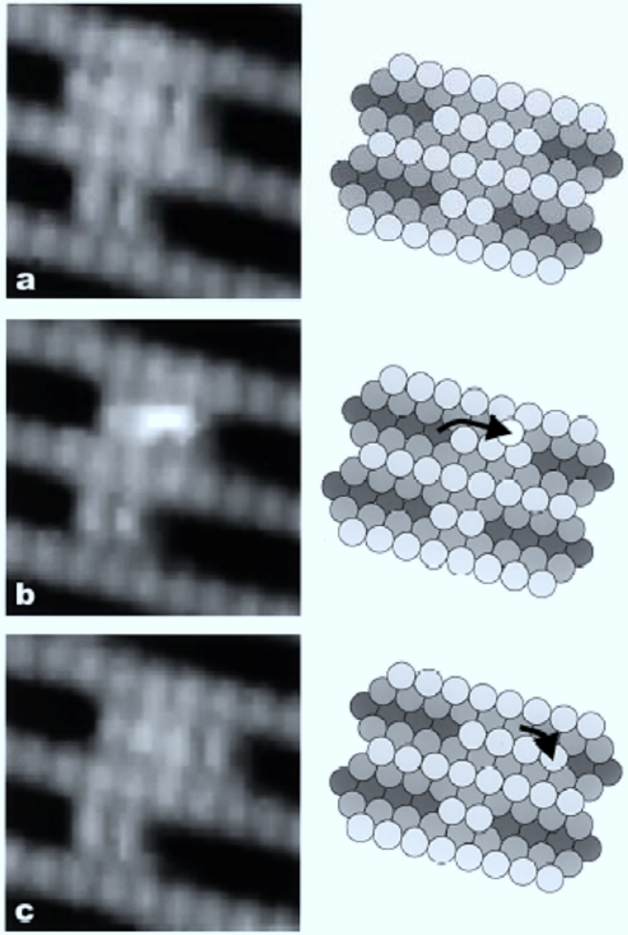
(3) Evaporation-condensation

Cluster Diffusion

Individual mechanisms:

(4) “Leapfrog” mechanism:

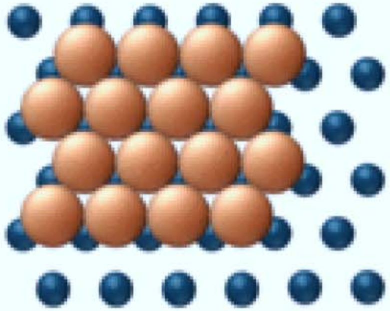
- Example: Pt(110)2x1
(Linderoth et al., PRL 1999)



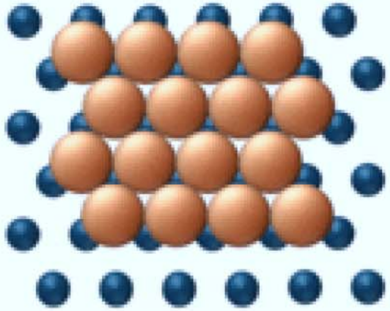
Cluster Diffusion

Concerted mechanisms:

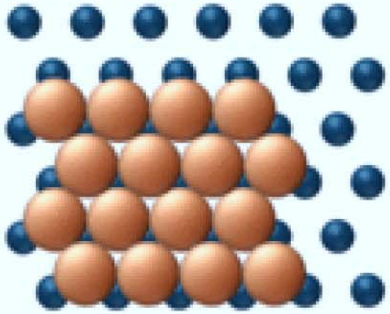
(1) Glide:



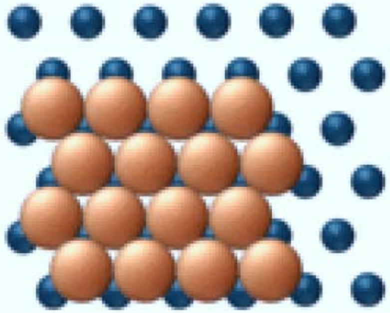
(2) Shear:



(3) Reptation:

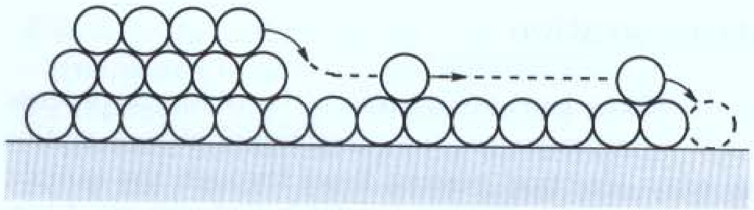


(4) Dislocation:



Phase Formation

- Coverage Θ ~ 0.1-1 ML→ formation of <u>surface phases</u>
- First layer atoms are usually immobile → “unrolling carpet” mechanism



Surface Electromigration

- Electric current through the sample → Directional atomic motion on the surface
- Self-electromigration → Changes in the step structure
- Hetero-electromigration → Mass transfer towards catode or anode