

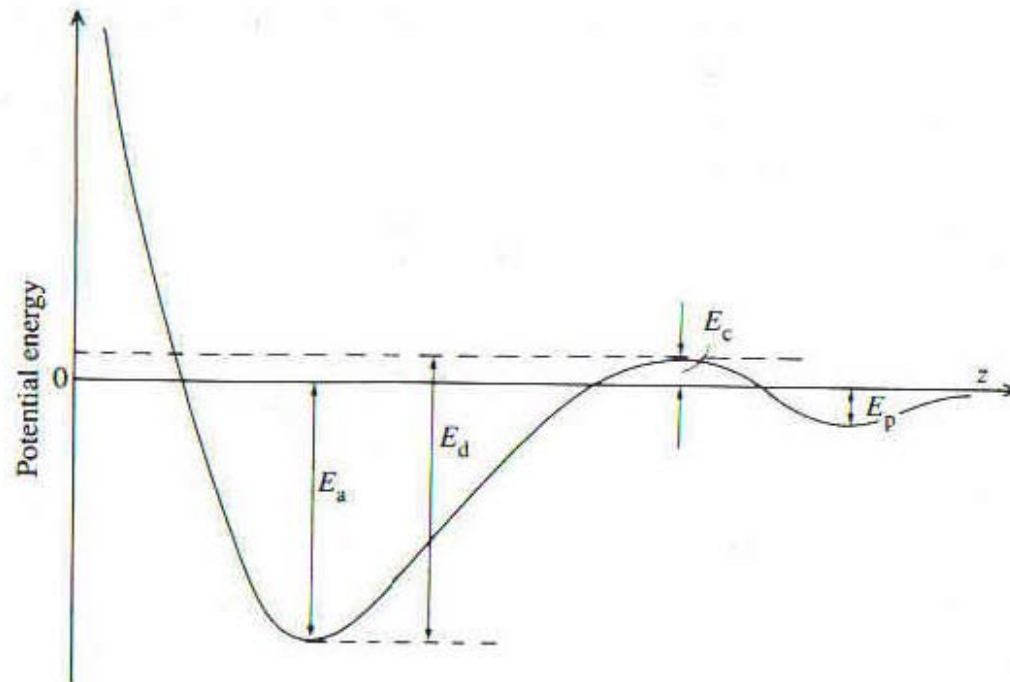
Wiederholung

- Rekonstruktionen
- Kristall = Gitter „+“ Basis (3D und 2D)
- Gitter: Mathematik im 3D / 2D Punktraum
- Basis: Anordnung der Atome / Moleküle im Gitter
- Oberfläche: Symmetriebruch → Komplexität, Chiralität (!)
- Reziprokes Gitter (3D und 2D)
- Wood Notation: Abbildung von tats. Oberflächenstruktur auf 3D (bulk) Gitter

Wiederholung II

- Ionenstreuung → Rekonstruktionen und Relaxationen
- Dampfdruck / Verdampfung (Quelle und Vakuumproblem)
- Adsorption / Desorption
 - a) Physisorption – VdW / Lennart Jones
 - b) Chemisorption

Chemisorption



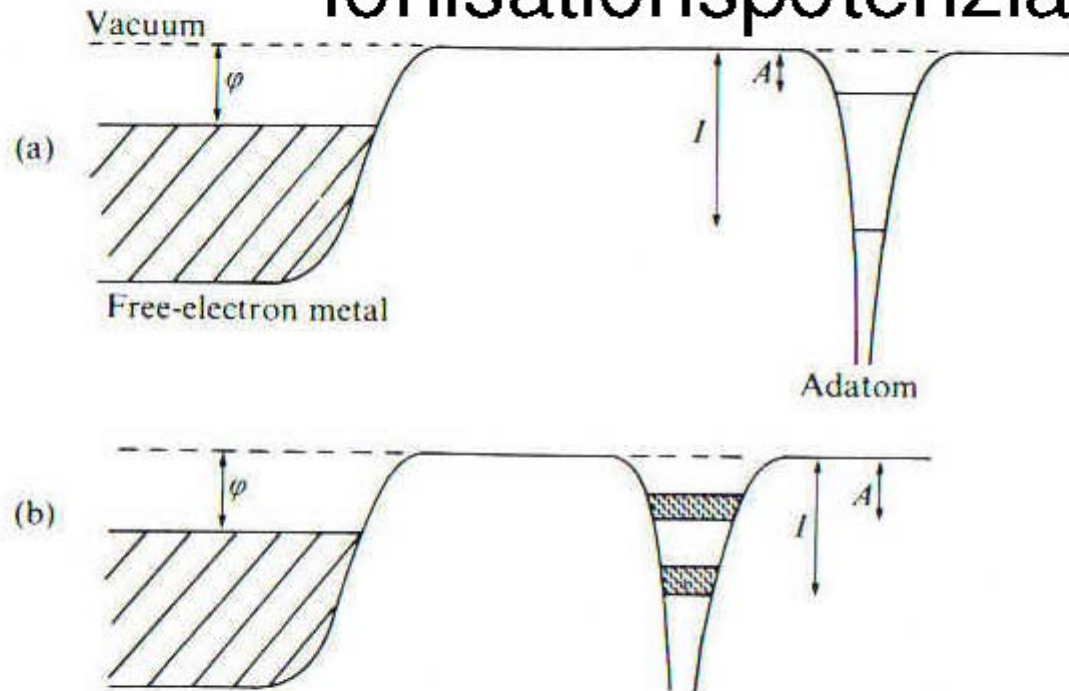
Precursor-Zustand:
Zuerst schwach adsorbiert
Adatom kann über der Oberfläche
herumdifundieren bis es
in den chemisorbierten Zustand
Wechselt.

Chemisorption: $E_A > 0.25\text{eV}$

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: Zustände \rightarrow Bänder

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 ($I=3.87\text{eV}$) und Wolfram ($\phi\approx 4.5\text{eV}$)

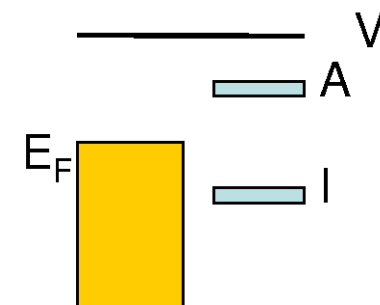
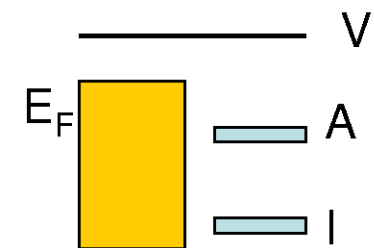
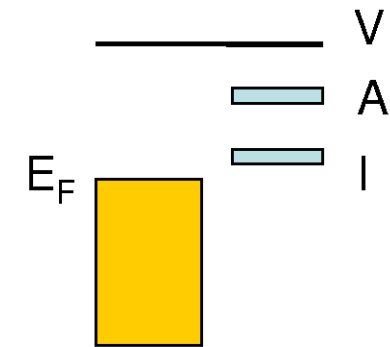
Fall 2:

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

Fall 3:

$I > \phi > A$

z.B. Wasserstoff: $I=13.6\text{eV}$ und $A=0.7\text{eV}$. D.h. Wasserstoff wird auf denmeisten Metallen ($\phi\approx 4-6\text{eV}$) neutral gebunden.



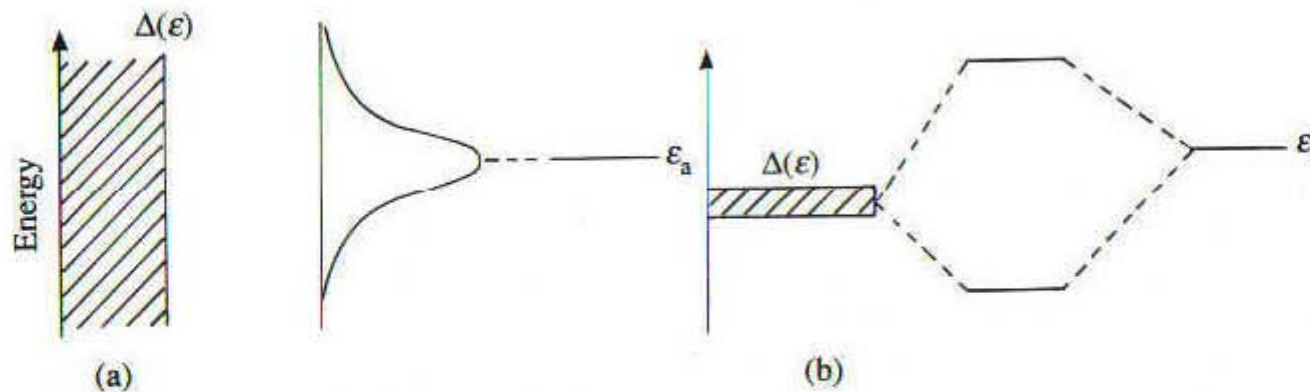
Theorie der Chemisorption

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.

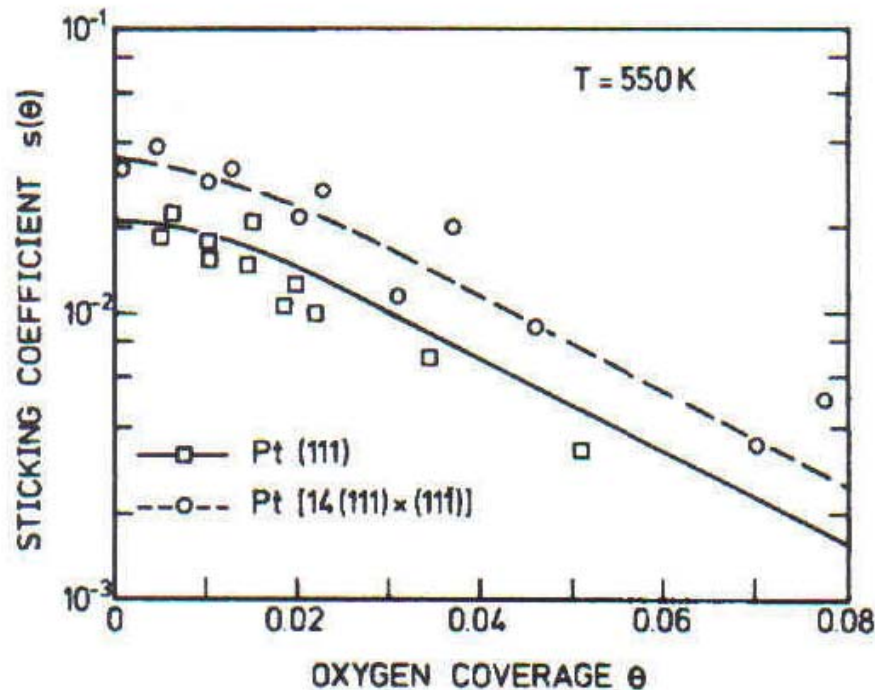
Bsp.: schwache Chemisorption: Sauerstoff auf Aluminium

Starke Chemisorption: CO auf Ni(111)



Adsorptionswahrscheinlichkeit

Die Adsorptionswahrscheinlichkeit („sticking coefficient“) hängt stark von der Orientierung der Oberfläche und von der Rauigkeit. 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

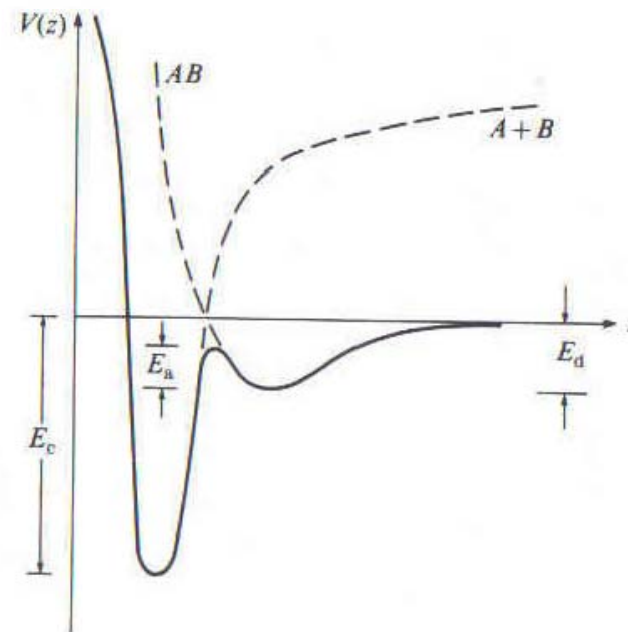
Adsorptionswahrscheinlichkeiten (sticking coefficients) sind erstaunlich klein.

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.

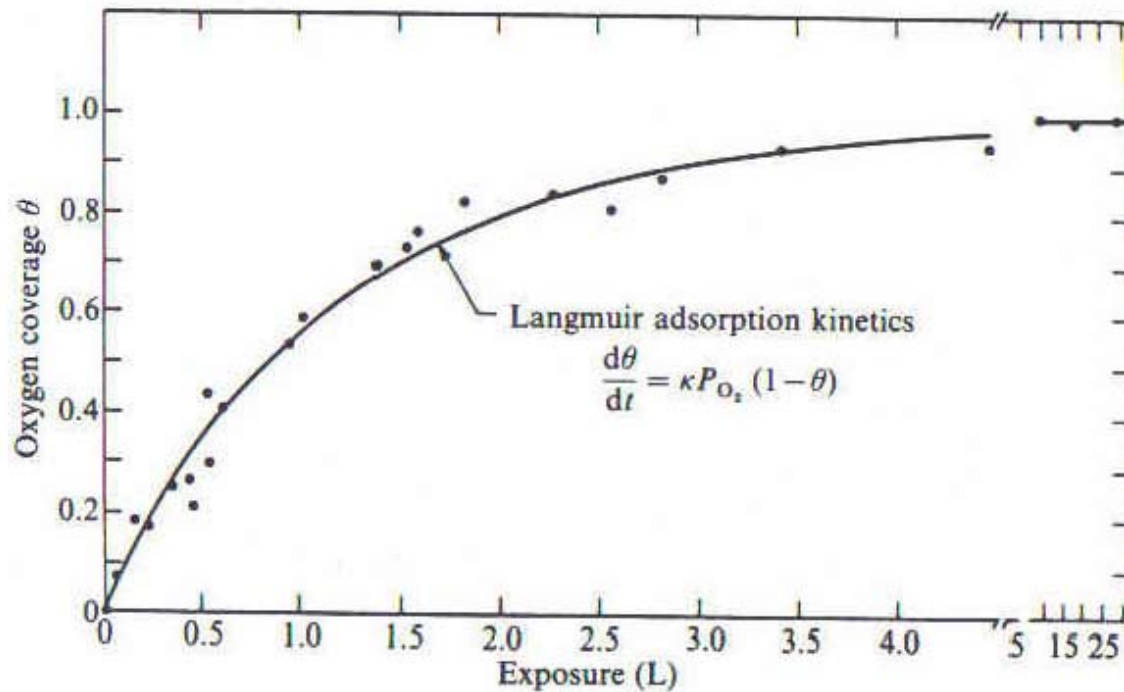
Es existiert somit eine Aktivierungsenergie. Da dieser Precursor-Zustand nur sehr schwach gebunden ist (schwache Physisorption) kann das Molekül leicht desorbiert werden, was zu den kleinen sticking coefficients führt.

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

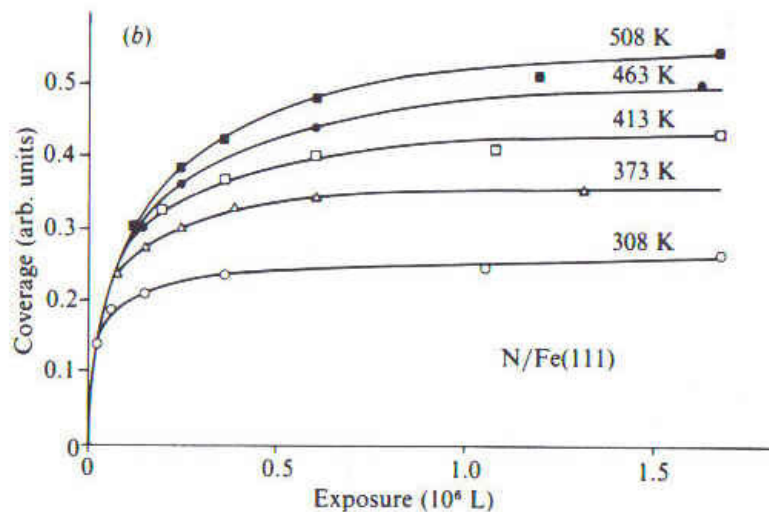
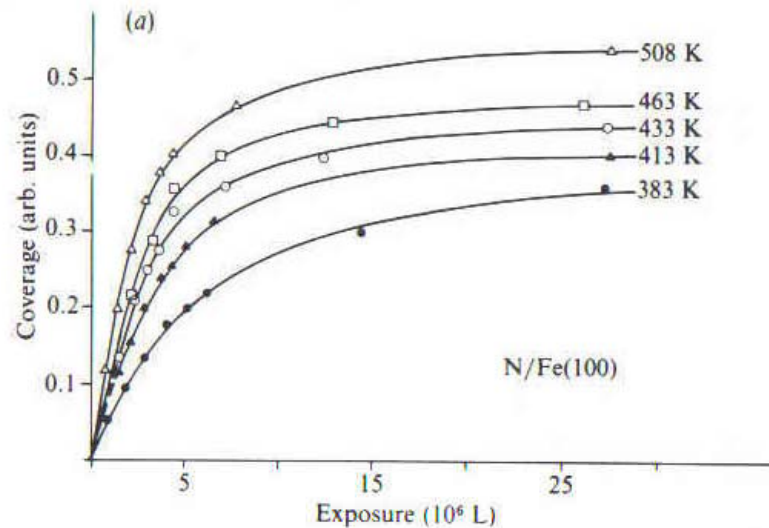
Fig. 14.2. $O_2/Rh(111)$ adsorption kinetics at 335 K. The unit of exposure is $1 L = 10^{-6}$ Torr s (Yates, Thiel & Weinberg, 1979).



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 $K < 1$

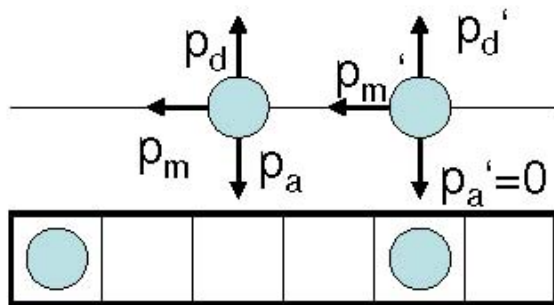
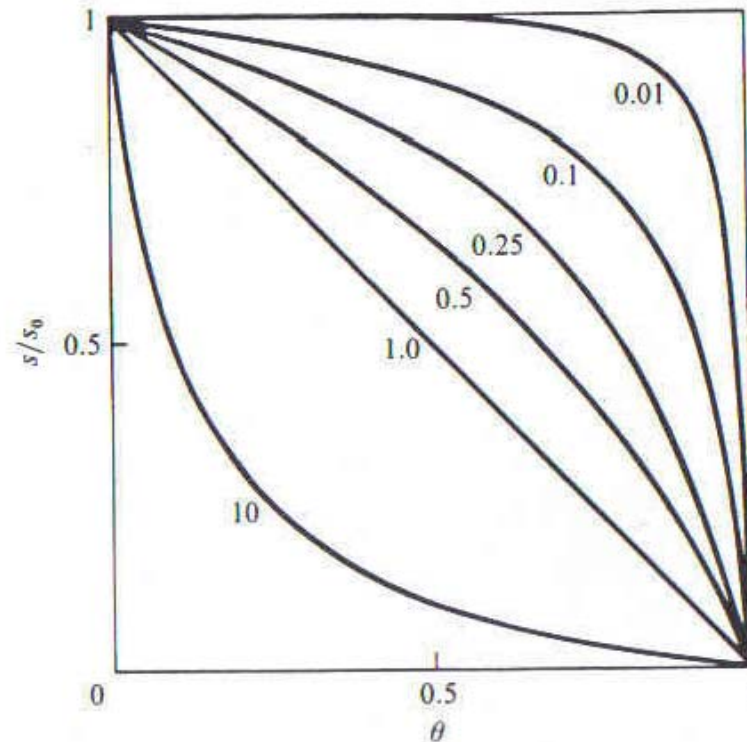


Fig. 14.6 Plot of s/s_0 as a function of the parameter K in the precursor model of adsorption (Kisliuk, 1957).



$P_a \sim 1 - \theta$: chemisorption

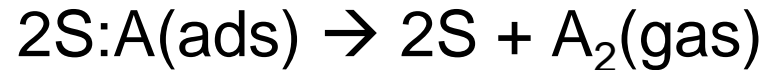
P_m : migration

P_d : desorption

Ann: physisorption unabh. von Bedeckung

adsorption / desorption kinetics / dynamics

- Adsorption can be treated like a chemical reaction:
 $A(\text{gas}) + S \rightarrow S:A(\text{ads})$ *atomic adsorption*



recombinative molecular desorption

→ gesamter thermodynamischer Apparat der Chemie
ist anwendbar (Oberflächenreaktionen / 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:

24346-01 Vorlesung mit Übungen: Oberflächenphysik 4 KP **Di, 10.00-12.00 wöchentlich verlegbar**

- Di, 26.02.2013 Fixing Dates, Intro to Vacuum Technology, Laboratory visit Basel (Toni Iväs, Sylwia Nowakowska, Roland Steiner)
- Di, 5.03.2013 Introduction, Concepts Samples and Structure (Thomas Jung)
- Di, 12.03.2013 Adsorption / Desorption (Thomas Jung)
- Di, 19.03.2013 Electronic Properties and Surface Electron Spectroscopies: XPS/UPS, Auger, ARPES (Andriy Romanyuk)
- Di, 26.03.2013 Diffusion and Growth (Thomas Jung)
- Di, 2.04.2013 Electron Diffraction Methods, in particular RHEED, LEED (Bert Müller)
- Di, 9.04.2013 X-ray Absorption Spectroscopy (Frithjof Nolting)
- Di, 16.04.2013 Surface Magnetism XMCD / PEEM (Armin Kleibert)
-
- Di, 23.04.2013 Local Probes and Experiments I, STM, Inelastic tunneling and STS (Thomas Jung)
- Di, 30.04.2013 Local Probes and Experiments II, AFM
- Di, 07.05.2013 AFM Surface Optics, Kelvin Probe (Thilo Glatzel)
- Di, 14.05.2013 Applications of Surface Science in Industry (M. de Wild)
- Di, 21.05.2013 Schlussprüfung (Jan Novakovski, Jan Girovsky, Harald Rossmann, Thomas Jung)
- Di, 28.05.2013 Excursion (all)



Verdampfung

H. Hertz (1882): Verdampfung von Hg
 $R_{ev} \approx p_e = p_{hydr}$

M. Knudsen (1915)

$$R_{ad} = \frac{N}{At} = \frac{p}{\sqrt{2\pi M k T}} \alpha$$

α : Verdampfungskoeffizient

Verdampfen ist ein Oberflächenprozess:

- ⇒ Phasendiagramm dp/dT (Clausius-Clapeyron)
- ⇒ Dampfdruck (vapour pressure)

Ausgangspunkt: beide Phasen sind an der Phasengrenze im Gleichgewicht
 $\Rightarrow \mu_S = \mu_V$ bzw. $\mu_L = \mu_V$

$$R_{ads} = A \exp(-E_a / RT) \times P^x = S \cdot F$$

E_a : activation energy for adsorption

A : pre-exponential (frequency) factor

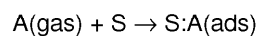
S : Sticking Coefficient

F : Flux

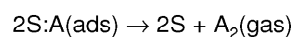
Adsorption/Desorption

Adsorption wird durch molekulare Auftrefferate R_{ad} und den „sticking Coefficient“ s bestimmt. Bei der Desorption unterscheidet man Desorption 1. Ordnung (nicht-dissoziativ) und 2. Ordnung (dissoziativ).

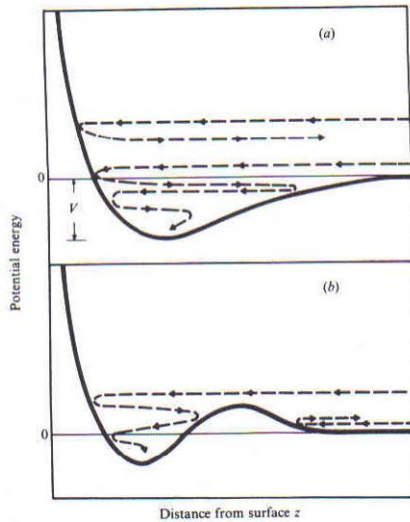
Wenn ein Gasatom oder Molekül $A(\text{gas})$ auf einem Substrat S gebunden wird:



Falls das Atom die Oberfläche wieder verlässt, bzw. mit einem anderen Adatom zu einem Molekül rekombiniert, dann in die Gasphase übergeht:



Adsorption/Desorption

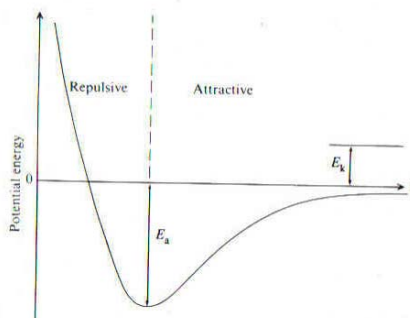


Was geschieht mit einem Atom/Molekül welches aus der Gasphase auf der Oberfläche landet?

(a) Je nach Energie:
Repulsion und Reflexion ins Vakuum
oder Umwandlung der kinetischen Energie
in Vibrations- und Rotationsfreiheitsgrade
und schliesslich Adsorption
(Physisorption oder Chemisorption)

(b) Auf gewissen Flächen können
auch niederenergetische Teilchen
reflektiert werden. Bzw. Verweilen
in einem Zwischenzustand.

Physisorption



Physisorption:
Relativ schwache Wechselwirkung
(Van der Waals Wechselwirkung)

Die kinetische Energie wird
in Phononen umgewandelt.

Um die Gleichgewichtslage wieder
zu verlassen muss die Aktivierungs-
Energie (Bindungsenergie) E_A
zugeführt werden.

Die Verweilzeit beträgt:
(residence time, stay time)

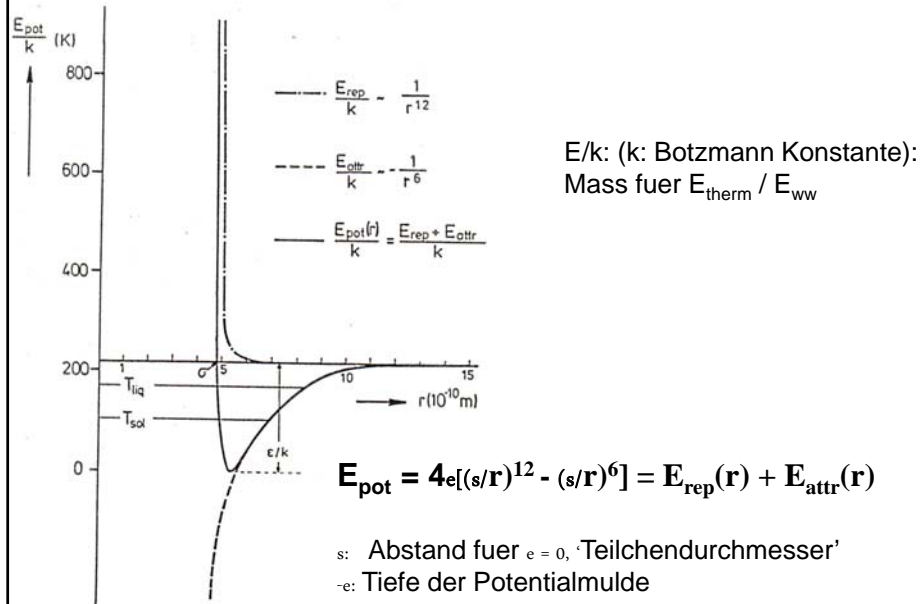
$$\tau = \tau_0 \cdot \exp\left(\frac{E_A}{k_B T}\right)$$

Physisorption:
Typ.: 50meV-0.25eV

Bsp.: He, Ne, CH₄ auf diversen Oberflächen

Lennard – Jones Potential

vereinfachtes 'workhorse' Potential, attraktiv (vdW) und repulsiv (Pauli Kontakt)



Wiederholung II

- Ionenstreuung → Rekonstruktionen und Relaxationen
- Dampfdruck / Verdampfung (Quelle und Vakuumpblem)
- Adsorption / Desorption
 - a) Physisorption – VdW / Lennart Jones
 - b) Chemisorption



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
Elektronenzuständen und Chemische Reaktionen /
Porphyrinen



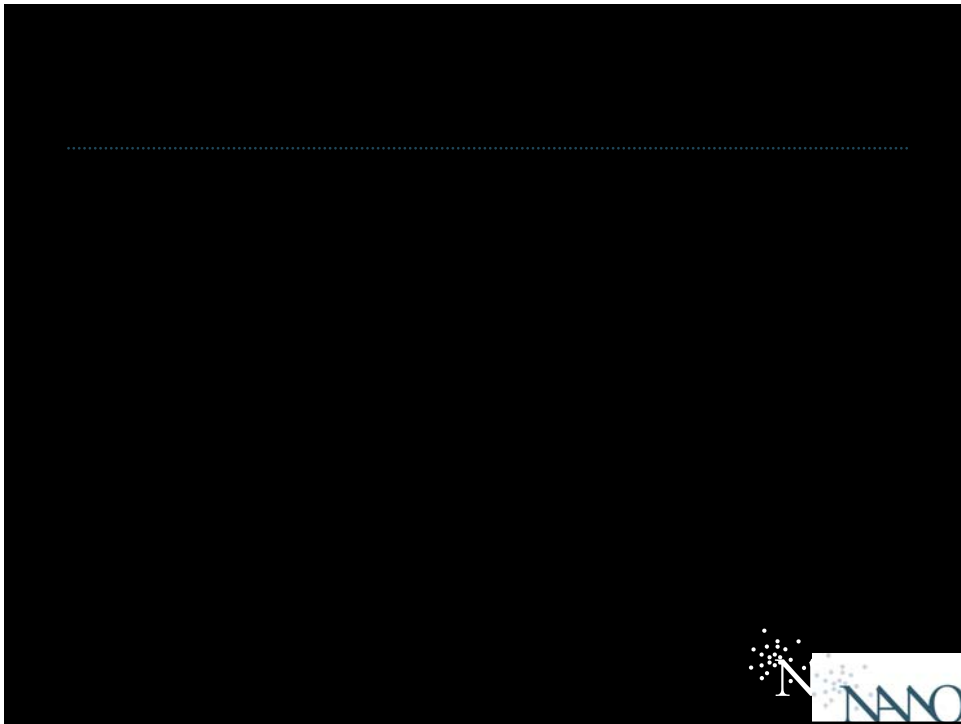
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Di, 21.02.2012 Fixing Dates, Intro to Vacuum Technology, Laboratory visit Basel (Toni Ivas, Sylwia Nowakowska, Roland Steiner)

Di, 28.02.2012 Fasnacht

- Di, 06.03.2012 Introduction, Concepts Samples and Structure (Thomas Jung)
- Di, 13.03.2012 Adsorption / Desorption (Thomas Jung)
- Di, 20.03.2012 Electronic Properties and Surface Electron Spectroscopies: XPS/UPS, Auger, ARPES (Andriy Romanyuk)
- Di, 27.03.2012 Diffusion and Growth (Thomas Jung)
- Di, 03.04.2012 Electron Diffraction Methods, in particular RHEED, LEED (Bert Müller)
- Di, 10.04.2012 Local Probes and Experiments I, STM, Inelastic tunneling and STS (Thomas Jung)
- Di, 17.04.2012 X-ray Absorption Spectroscopy (Frithjof Nolting)
- Di, 24.04.2012 Surface Magnetism XMCD / PEEM (Frithjof Nolting)
- Di, 01.05.2012 Surface Optics, Kelvin Probe (Thilo Glatzel)
- Di, 08.05.2012 Local Probes and Experiments II, AFM FIM (Thomas Jung)
- Di, 15.05.2012 Applications of Surface Science in Industry (M. de Wild)
- Di, 22.05.2012 Schlussprüfung (Jan Girovsky, Thomas Jung)
- Di, 29.05.2012 Excursion (Thomas Jung)





Surface Physics 2010

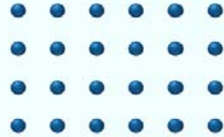
Surface Diffusion



Lecturer: Dr. Enrico Gneco
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 :

$$\langle \Delta r^2 \rangle = \nu a^2 t$$

a = jump distance; ν = hopping frequency

(Note that ν = number of hops!)

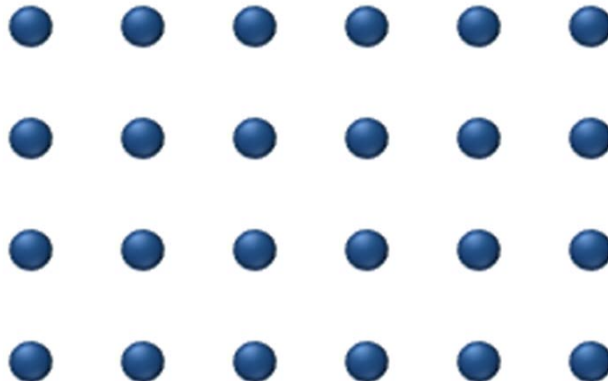
$$\langle \Delta^2 r(t) \rangle = \frac{1}{N} \sum_{i=1}^N \langle [R_i(t) - R_i(0)]^2 \rangle$$

- Diffusion coefficient:

$$D = \frac{\langle \Delta r^2 \rangle}{z t} = \frac{\nu a^2}{z}$$

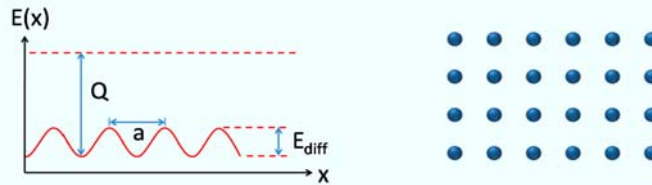
z = number of first neighbors = $\begin{cases} 2 \text{ in 1D diffusion} \\ 4 \text{ on a square lattice} \\ 6 \text{ on a hexagonal lattice} \end{cases}$

Diffusion



Random-Walk Motion

- Hopping → surmounting a potential barrier



- Arrhenius law:

$$v = v_0 \exp\left(-\frac{E_{diff}}{k_B T}\right)$$

v_0 = oscillation frequency of the atom in the well;
 E_{diff} = barrier height

Typically $E_{diff} \sim 5-20\%$ of Q (heat of desorption)

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

Fick's Laws

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

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

diffusion flux concentration gradient

(flux → region of lower concentration)

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

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

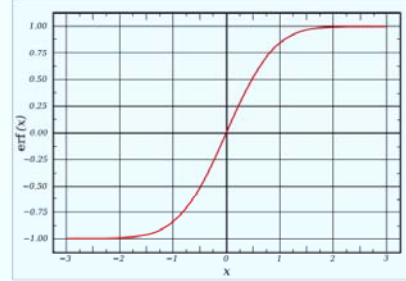
← from equation of continuity

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

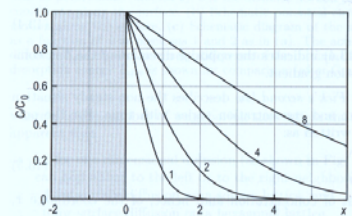
Analytical Solutions of Fick's Laws

- We introduce the **error function**

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



- Source of constant concentration:



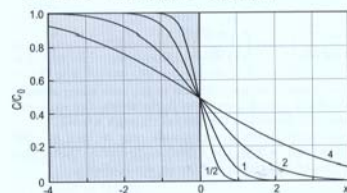
$$c(x,t) = c_0 \left[1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \right]$$

$2\sqrt{Dt}$: diffusion length

Example: Submonolayer film with 2D islands supplying mobile adatoms

Analytical Solutions of Fick's Laws

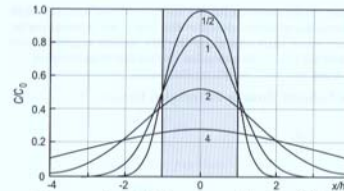
- Source of infinite extent:



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

- Example: Submonolayer film

- Source of limited extent:



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

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

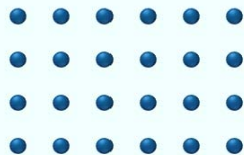
Diffusion Mechanisms

- Depending on the coverage 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:

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

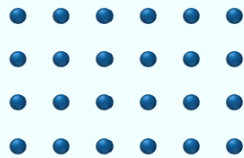
- For an ensemble of many particles:

$$D = \frac{1}{z N t} \sum_i \langle \Delta r_i^2 \rangle$$

(no relation to radioactive tracers!)

Chemical Diffusion

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



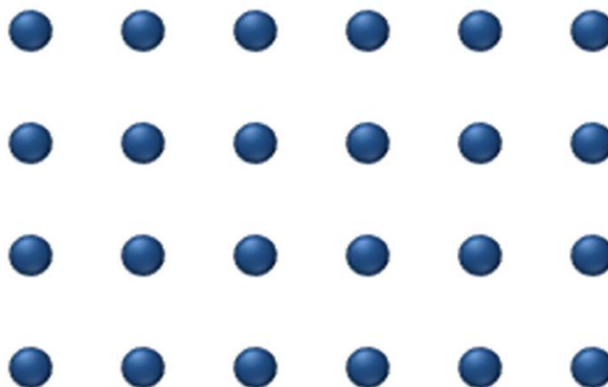
- Fick's first law can be generalized:

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

chem. diff. coefficient coverage

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

'Chemical Diffusion'



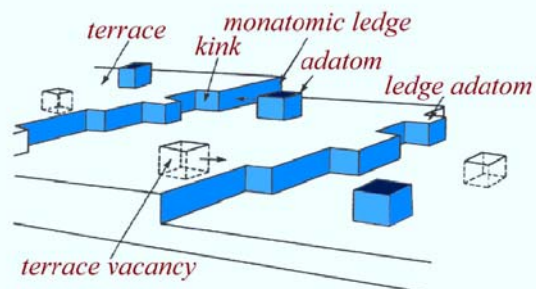
Diffusion Mechanisms

- 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

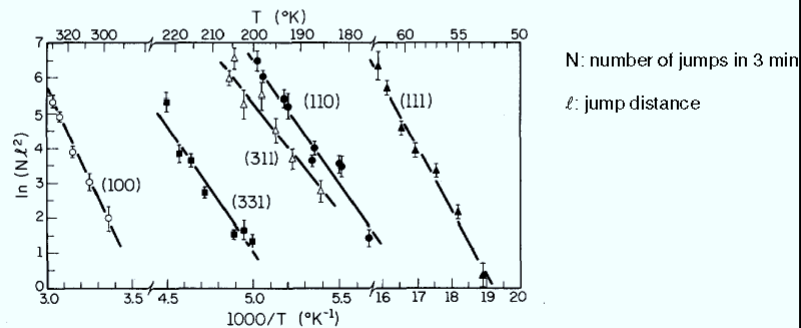
- Real surfaces contain defects (steps, kinks, adatoms or vacancy clusters, etc.)
- If average separation between defects < diffusion length → number of mobile particles (and diffusion) become strongly temperature dependent
- If adatoms and substrate are the same chemical species:

$$D = \frac{v_0 a^2}{z} \exp\left(-\frac{\Delta G + E_{diff}}{k_B T}\right) \quad \Delta G = \text{energy of adatom formation}$$

(→ two types of energy barriers!)

Anisotropy of Surface Diffusion

- **Orientation Anisotropy:** the diffusion coefficient depends on the orientation of the surface
- Example: Rh surfaces at different T (Ayrault & Ehrlich, JCP 1974)

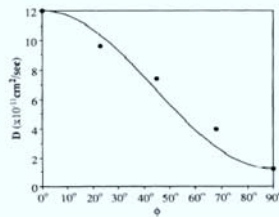


- At given T the differences in the diff. coeff. can be several orders of magnitude!

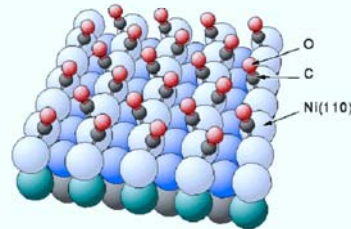
Anisotropy of Surface Diffusion

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

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

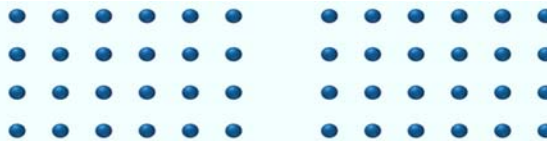


$$D(\phi) = D_x \cos^2 \phi + D_y \sin^2 \phi$$

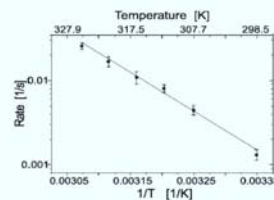
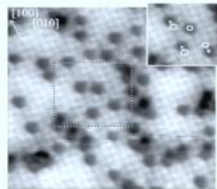


Atomistic Mechanisms

- 1) Hopping mechanism:



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



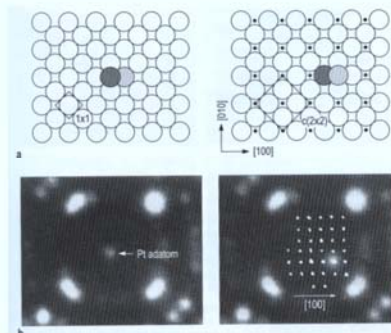
\rightarrow Arrhenius law with $\nu \sim 10^{12} \text{ s}^{-1}$, $E_{diff} = 0.92 \text{ eV}$

Atomistic Mechanisms

2) Atomic exchange mechanism:



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



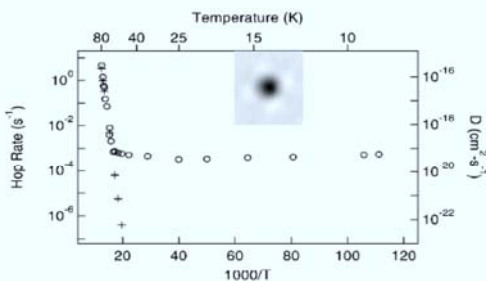
- Observed also on heterosystems [Pt on Ni(110), Ir on Pt(100), Re on Ir(100)]

Atomistic Mechanisms

3) Tunneling mechanism:

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

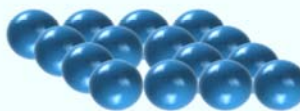
- Example: Hydrogen on Cu(100) (Lauhon & Ho, PRL 2000)



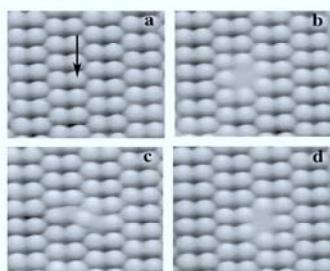
- Above 60 K: Arrhenius law with $\nu \sim 10^{13} \text{ s}^{-1}$, $E_{diff} = 0.20 \text{ eV}$
- Below 60 K: quantum tunnelling, T independent

Atomistic Mechanisms

4) Vacancy mechanism:



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

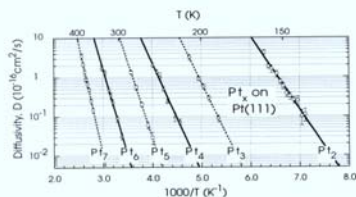


- Vacancy created with the STM tip
- T-activated hopping of neighboring atoms

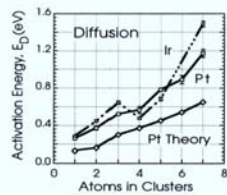
- Heterodiffusion by vacancy-exchange also reported

Cluster Diffusion

- The larger the cluster, the lower its mobility:

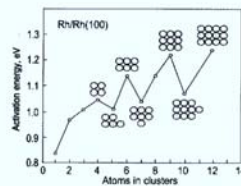


- Activation energy increases with cluster size:



(Kyuno & Ehrlich, SS 1999)

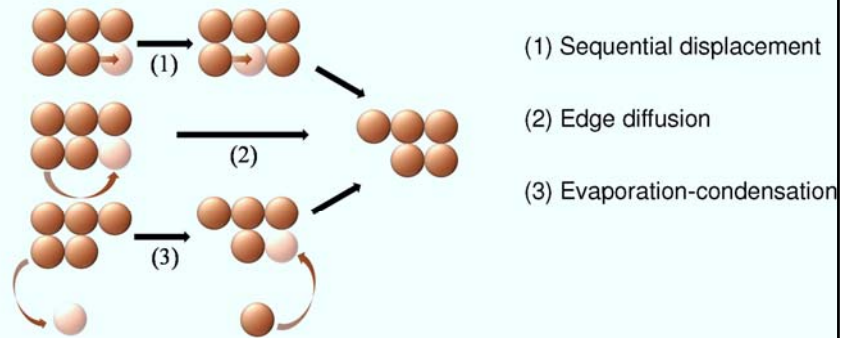
- Compact shapes are less mobile...



(Kellogg, PSS 1996)

Cluster Diffusion

Individual mechanisms:



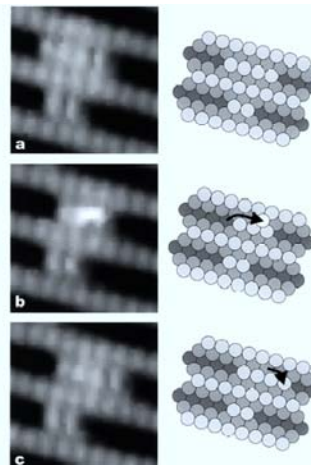
Cluster Diffusion

Individual mechanisms:

(4) "Leapfrog" mechanism:



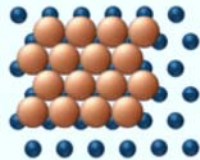
• Example: Pt(110)2x1
(Linderoth et al., PRL 1999)



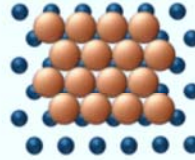
Cluster Diffusion

Concerted mechanisms:

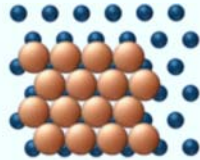
(1) Glide:



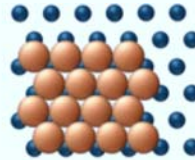
(2) Shear:



(3) Reptation:

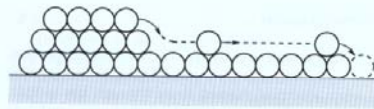


(4) Dislocation:



Phase Formation

- Coverage $\Theta \sim 0.1-1$ ML \rightarrow formation of surface phases
- First layer atoms are usually immobile \rightarrow “unrolling carpet” mechanism



Surface Electromigration

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