Surface Physics 2010

Surface Diffusion

UNI
BASEL

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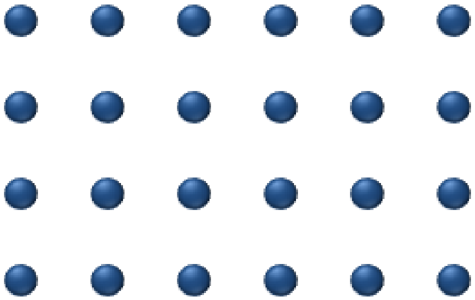
NCCR Nanoscale Science

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*:

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

a = jump distance; ν = hopping frequency

(Note that νt = number of hops!)

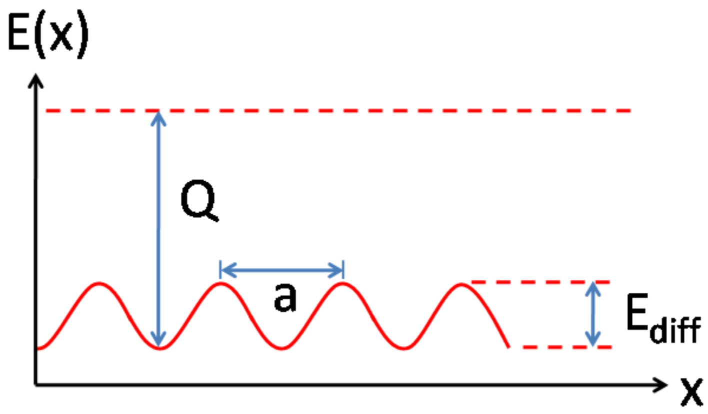
- **Diffusion coefficient**:

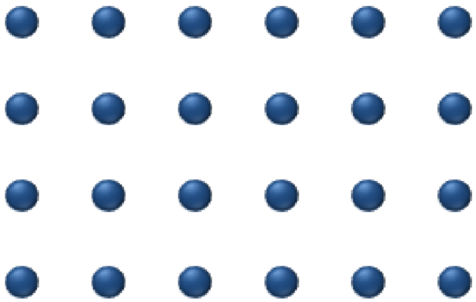
$$\boxed{D = \frac{\langle \Delta r^2 \rangle}{zt} = \frac{\nu a^2}{z}}$$

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

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):

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

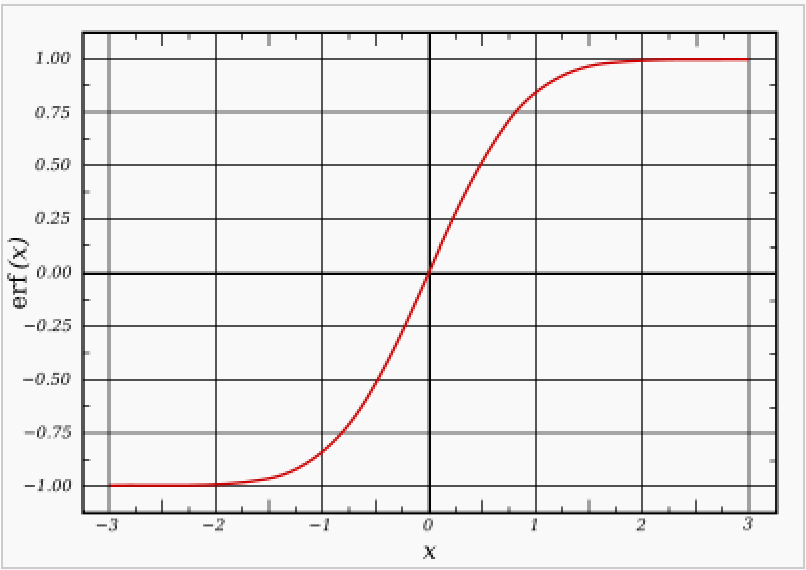
← from equation of continuity

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

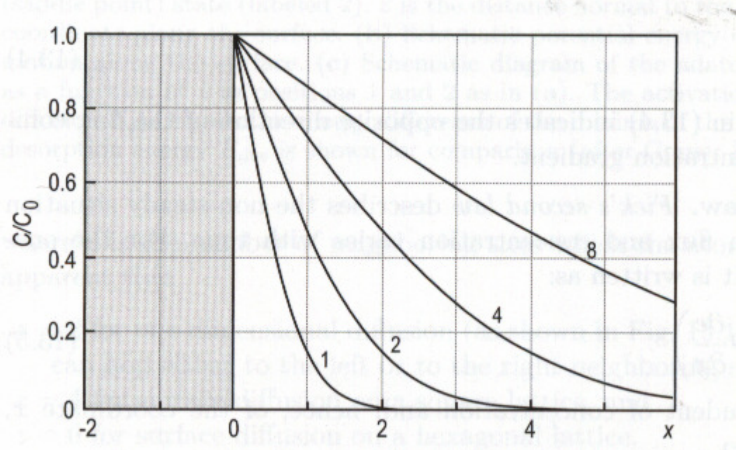
Analytical Solutions of Fick's Laws

- We introduce the **error function**

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



- Source of constant concentration:



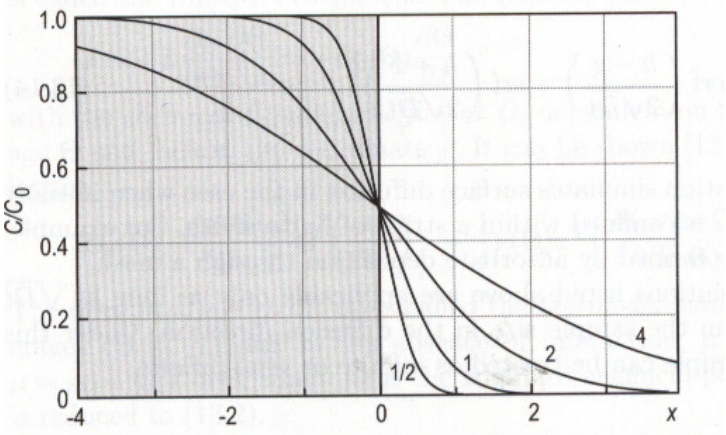
$$c(x,t) = c_0\left[1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right]$$

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

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

Analytical Solutions of Fick's Laws

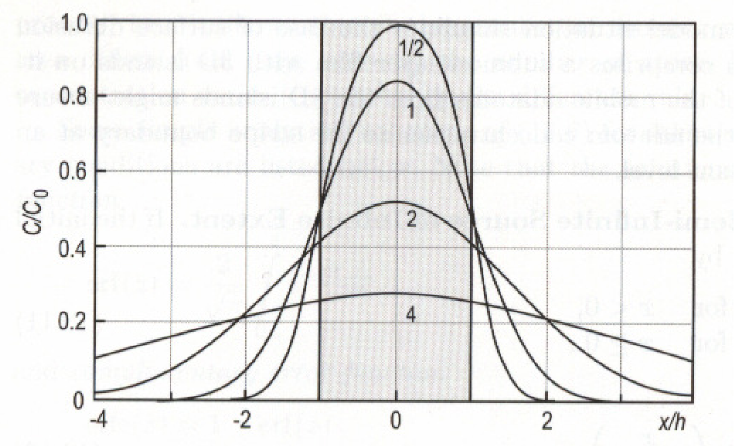
- Source of infinite extent:



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

- Example: Submonolayer film

- Source of limited extent:



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

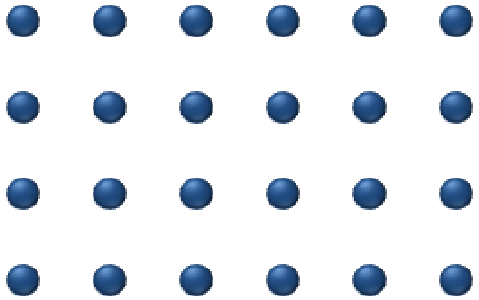
- Example: Submonolayer film confined in a stripe of finite width

Diffusion Mechanisms

- Depending on the 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:

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

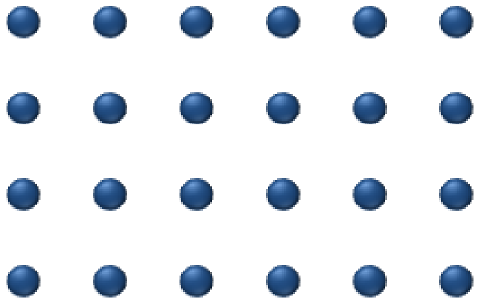
- For an ensemble of many particles:

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

(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)

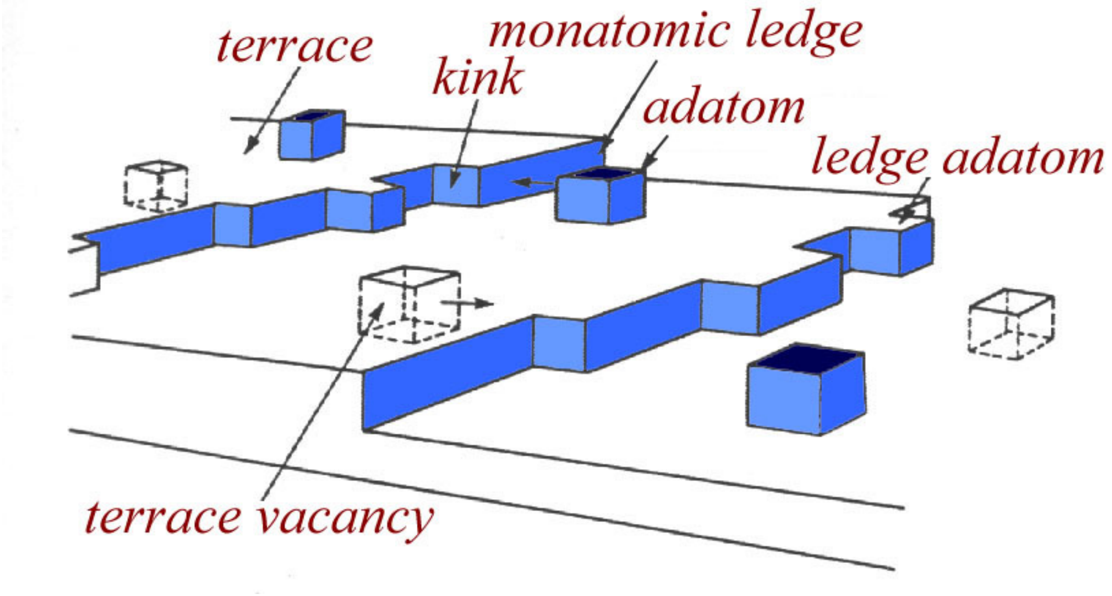
Diffusion Mechanisms

- 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 <u>defects</u> (steps, kinks, adatoms or vacancy clusters, etc.)

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

- If adatoms and substrate are the same chemical species:

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

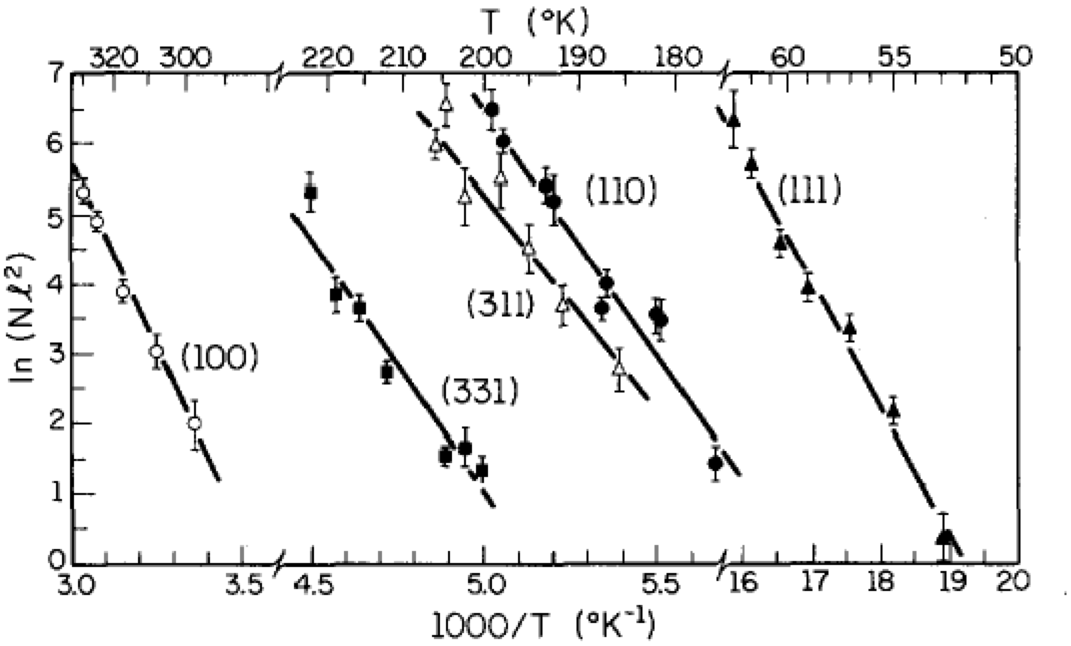
ΔG = energy of adatom formation

(→ 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

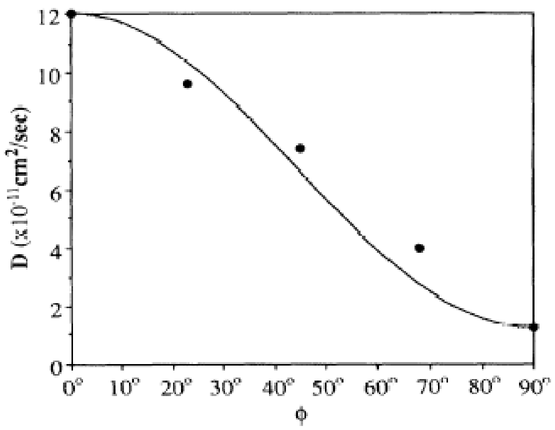
ℓ: jump distance

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

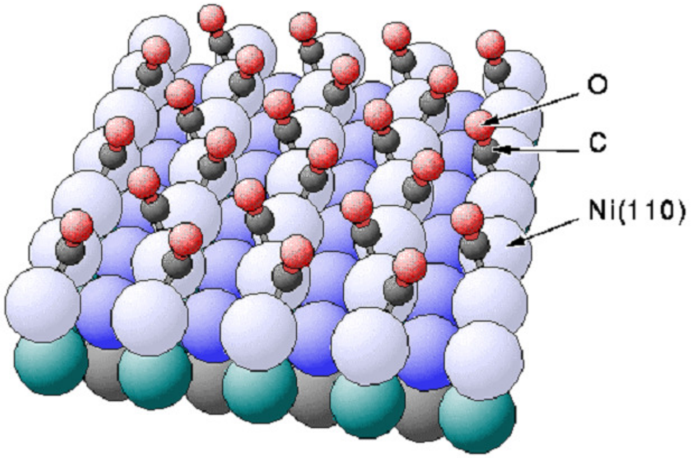
Anisotropy of Surface Diffusion

- **Directional Anisotropy:** the diffusion coefficient depends on the <u>direction at the surface</u>

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

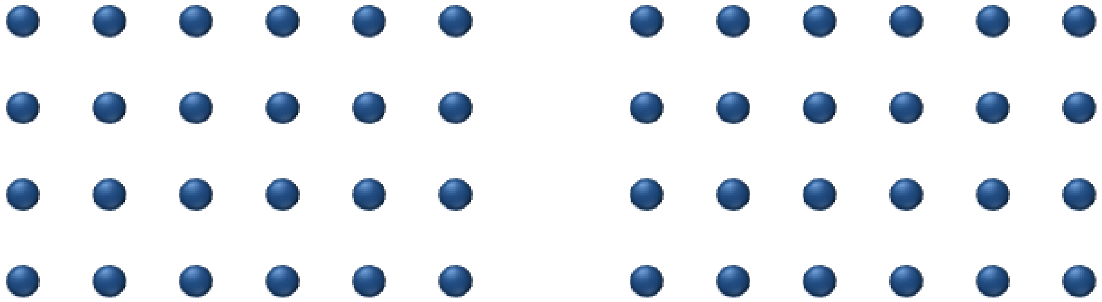


$$D(\varphi) = D_x \cos^2 \varphi + D_y \sin^2 \varphi$$

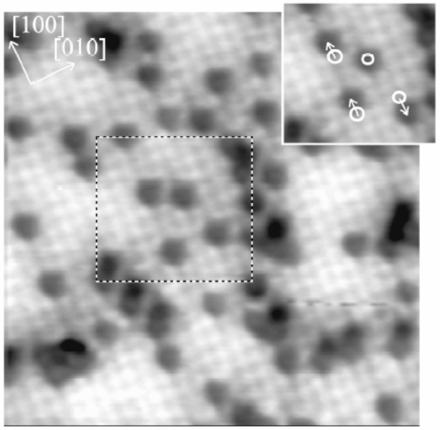


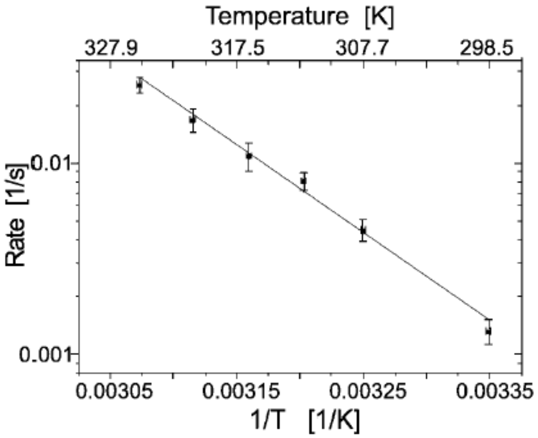
Atomistic Mechanisms

1) Hopping mechanism:



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

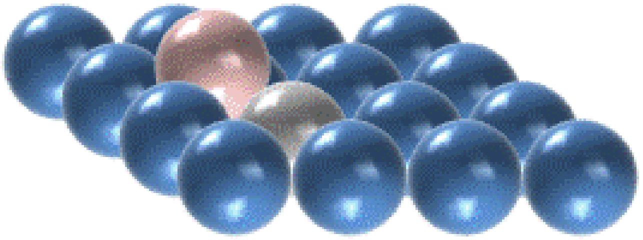




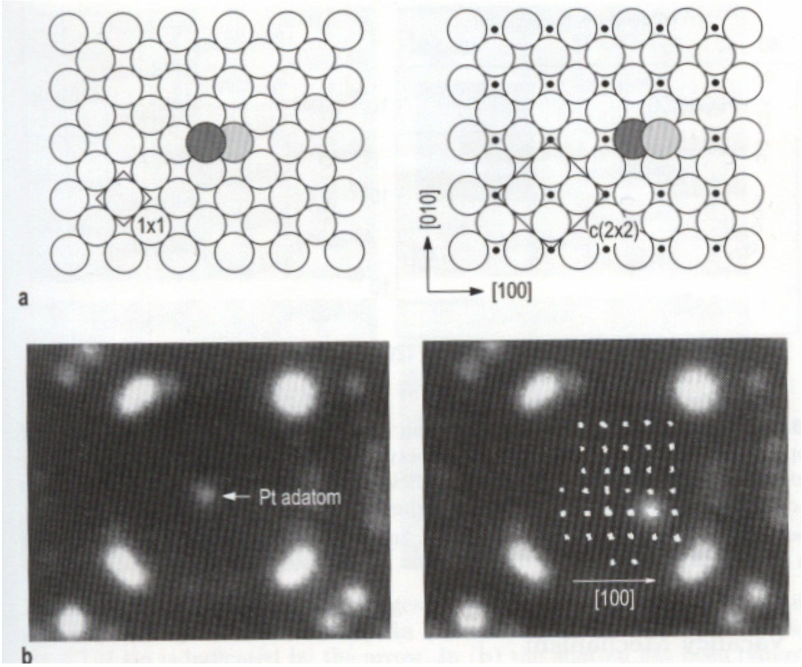
→ Arrhenius law with $\nu \sim 10^{12}\ \mathrm{s}^{-1}$, $E_{diff} = 0.92$ eV

Atomistic Mechanisms

2) Atomic exchange mechanism:



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



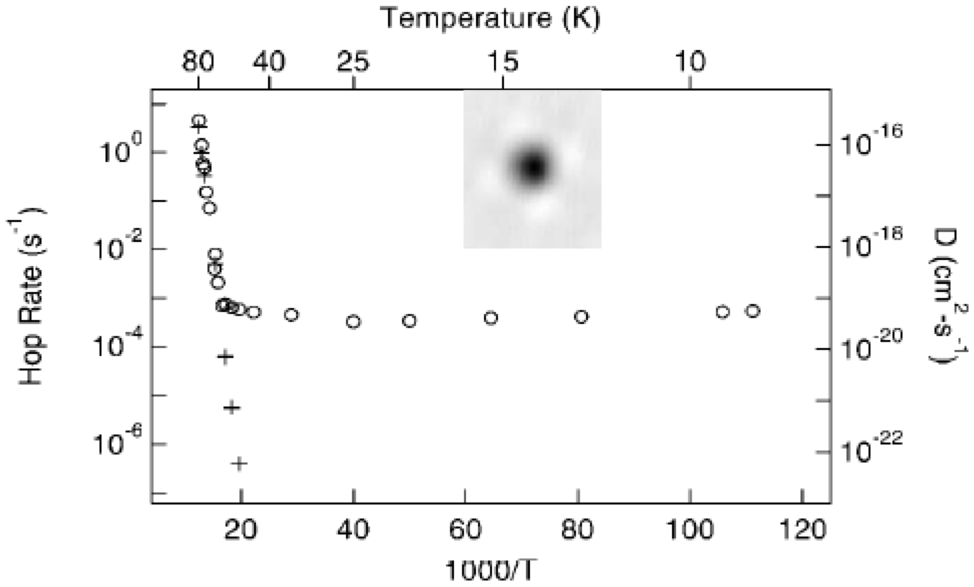
- Observed also on heterosystems [Pt on Ni(110), Ir on Pt(100), Re on Ir(100)]

Atomistic Mechanisms

3) Tunneling mechanism:

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

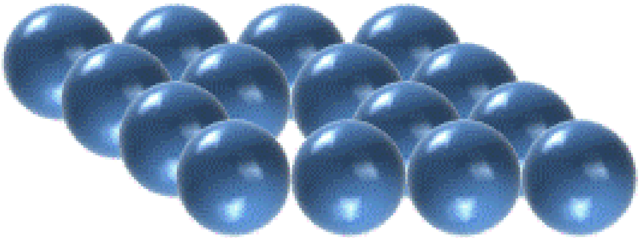
- Example: Hydrogen on Cu(100) (Lauhon & Ho, PRL 2000)



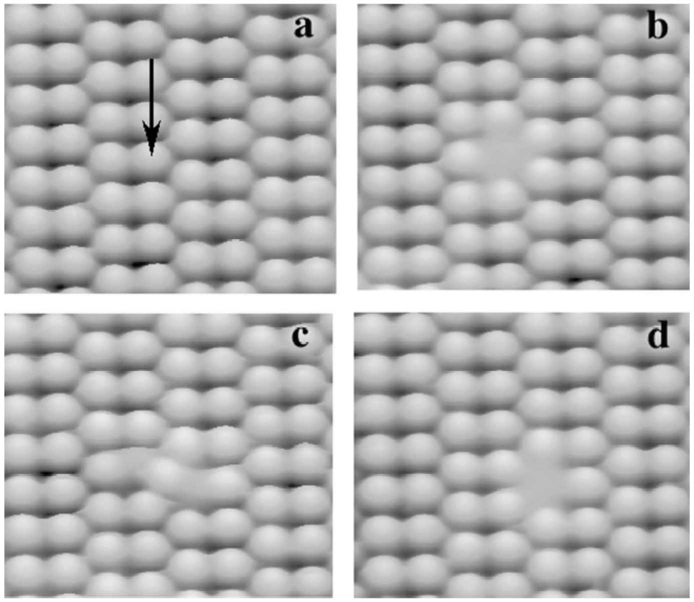
- Above 60 K: Arrhenius law with $\nu \sim 10^{13}\ s^{-1}$, $E_{diff} = 0.20$ eV
- Below 60 K: quantum tunnelling, T independent

Atomistic Mechanisms

4) Vacancy mechanism:



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



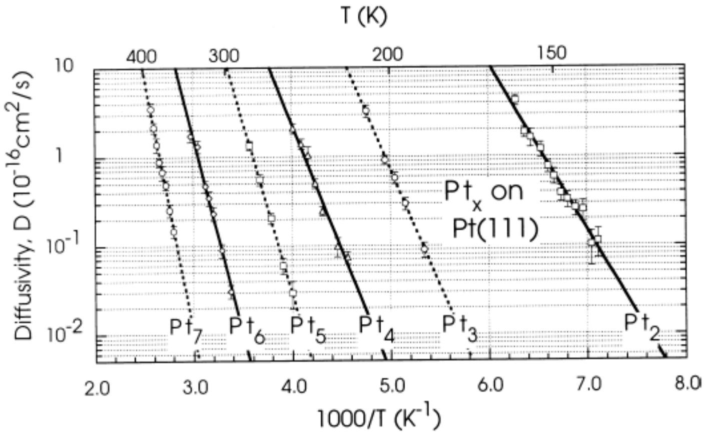
-Vacancy created with the STM tip

- T-activated hopping of neighboring atoms

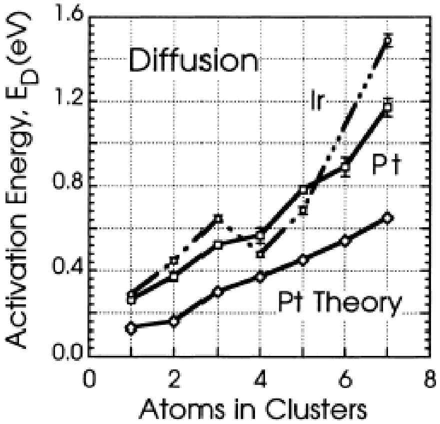
- Heterodiffusion by vacancy-exchange also reported

Cluster Diffusion

- The larger the cluster, the lower its mobility:

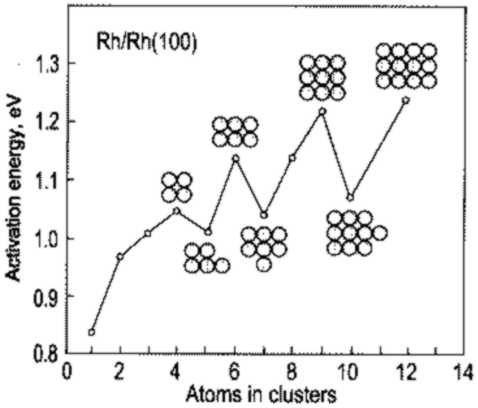


- <u>Activation energy increases</u> with cluster size:



(Kyuno & Ehrlich, SS 1999)

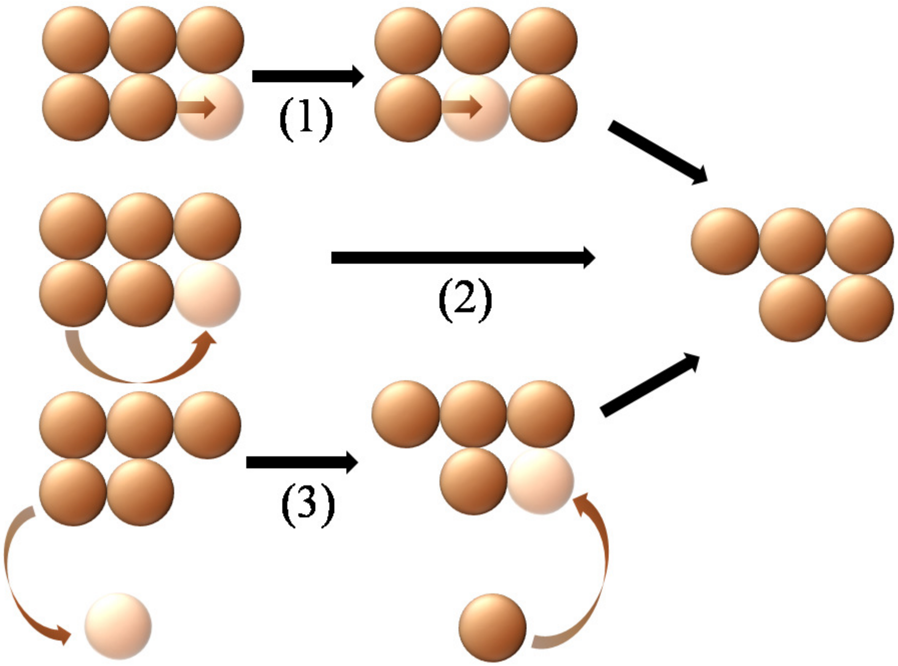
- Compact shapes are less mobile...



(Kellogg, PSS 1996)

Cluster Diffusion

Individual mechanisms:



(1) Sequential displacement

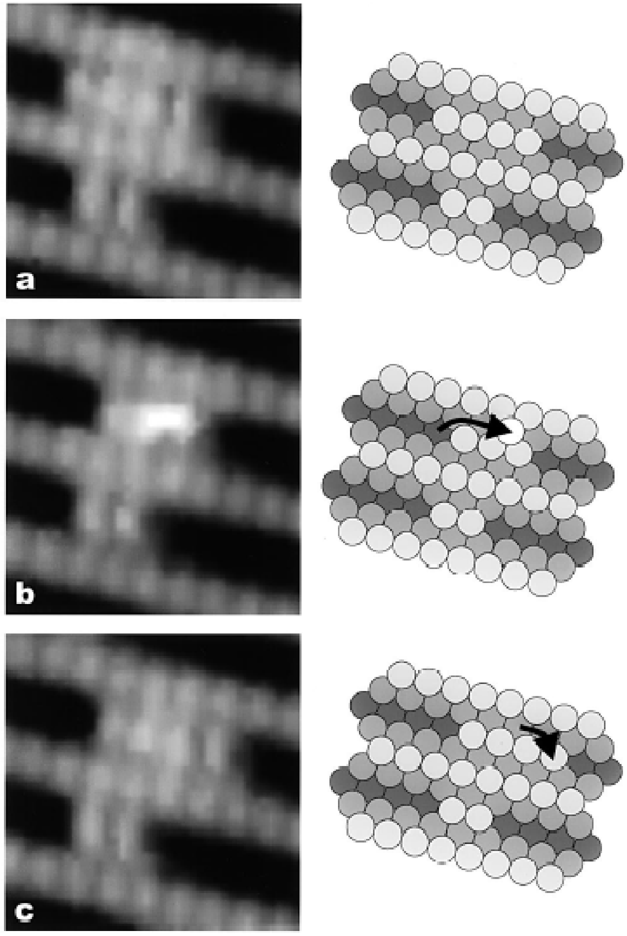
(2) Edge diffusion

(3) Evaporation-condensation

Cluster Diffusion

Individual mechanisms:

(4) “Leapfrog” mechanism:

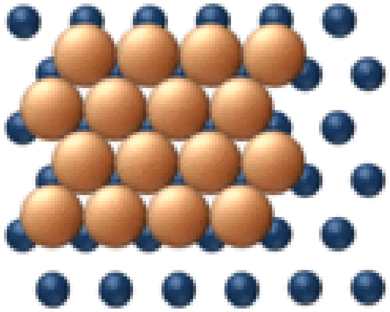


- Example: Pt(110)2x1 (Linderoth et al., PRL 1999)

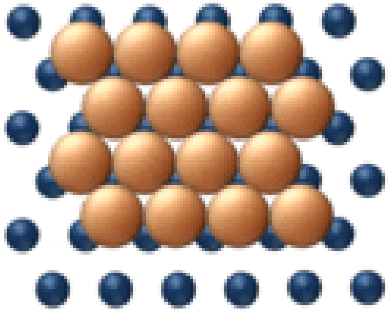
Cluster Diffusion

Concerted mechanisms:

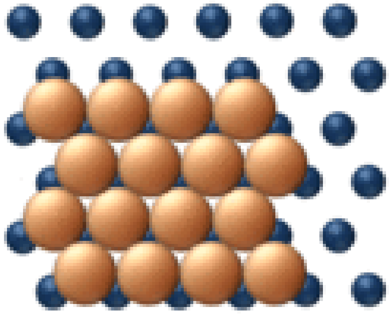
(1) Glide:



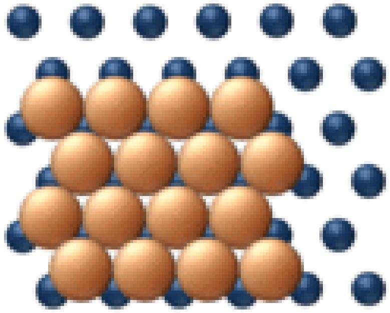
(2) Shear:



(3) Reptation:

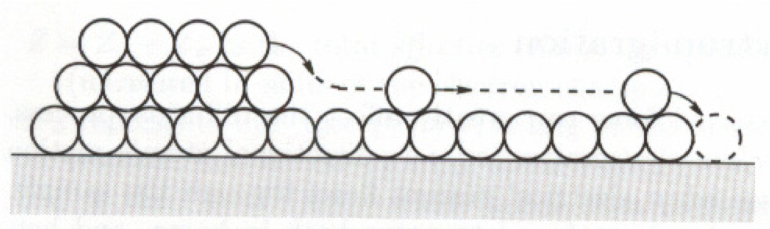


(4) Dislocation:



Phase Formation

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



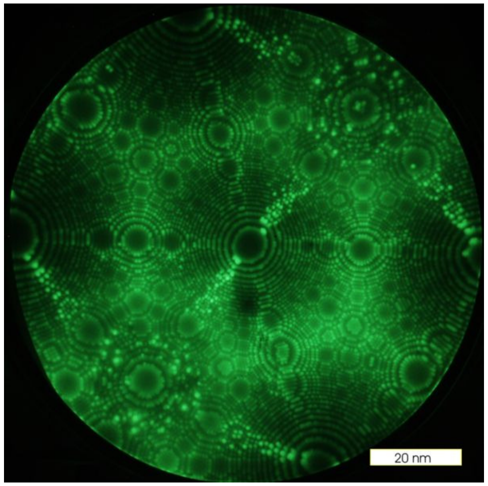
Surface Electromigration

- 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

Experimental Techniques

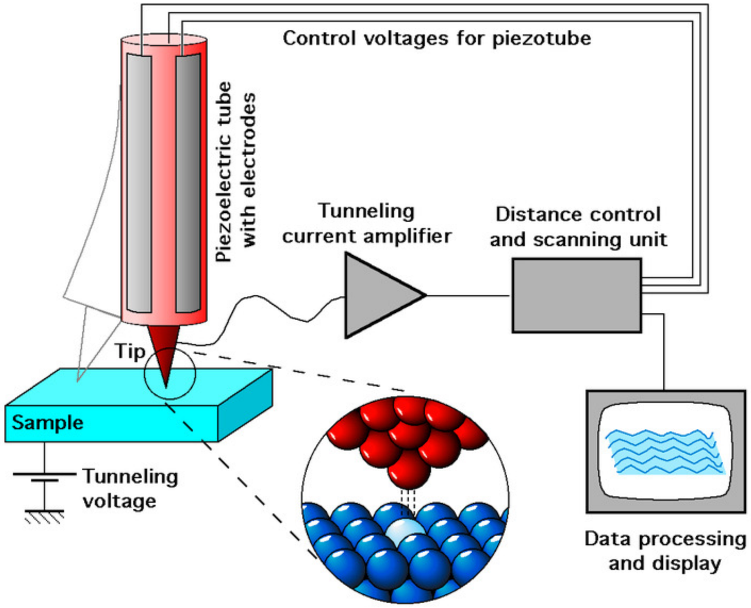
1) Direct observation:

- Field ion microscopy (FIM)
→ "image-anneal-image" technique



- Limited to refractory or noble metal surfaces

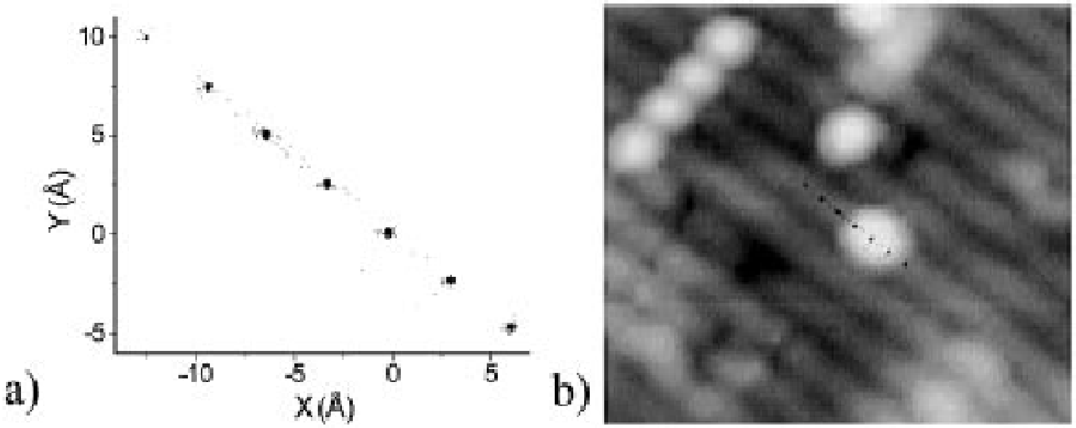
- Scanning tunneling microscopy (STM)
→ "image-while-hot" technique



- STM "movies" can be recorded
(at 0.01-1 frames per second)

Experimental Techniques

- Scanning tunneling microscopy (STM) → “atom-tracking” technique
  - STM tip locked onto an adparticle by 2D lateral feedback
  - Example: Si on Si(100) (Swartzentruber, PRL 1996)



  - Electric fields from the STM tip influence surface diffusion!

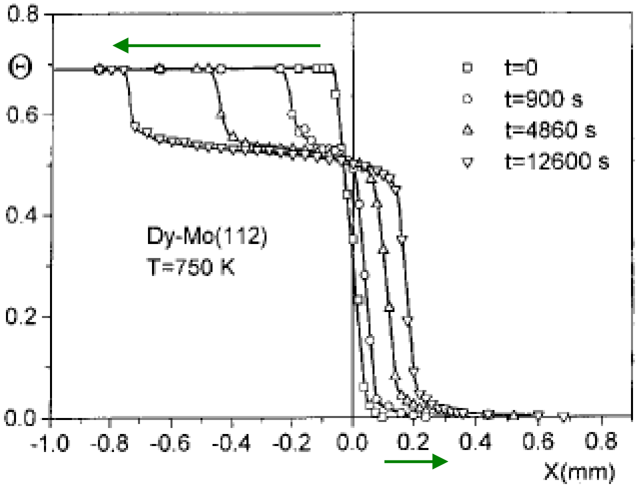
Experimental Techniques

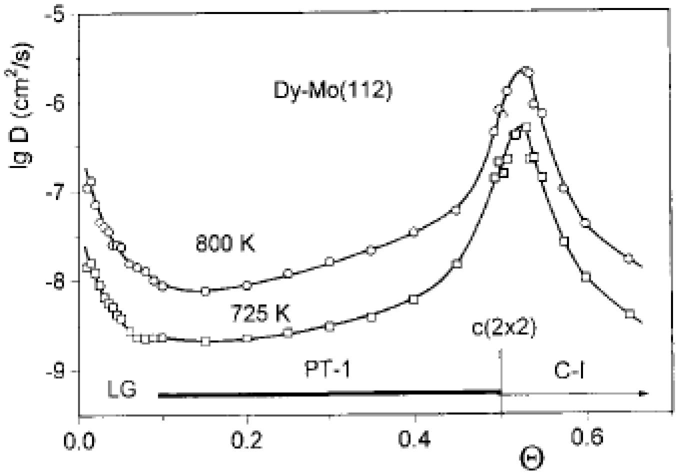
2) Profile evolution method:

- Smearing of a sharp initial concentration profile is monitored

  - Initial profile deposited using a mask
  - AES, SIMS, SEM or local work-function…
  - D(Θ) can be evaluated

- Example: Dy on Mo(112) (Loburets et al., SS 1998)





Experimental Techniques

3) "Capillarity" techniques:

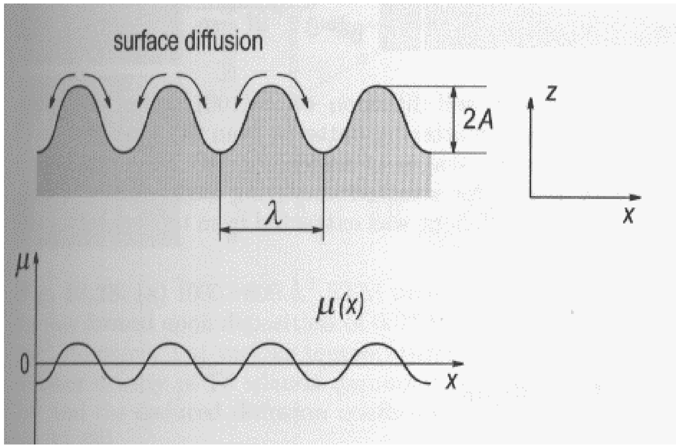
- A surface is perturbed from its lowest energy configuration...

... and allowed to relax via diffusion

- Relaxation rate → Coefficient of diffusion

- For a sinusoidal profile (Mullins, JAP 1999):

$$A(t) = A_0 \exp\left[-\frac{\gamma D n_0 V^2}{k_B T}\left(\frac{2\pi}{\lambda}\right)^4 t\right]$$

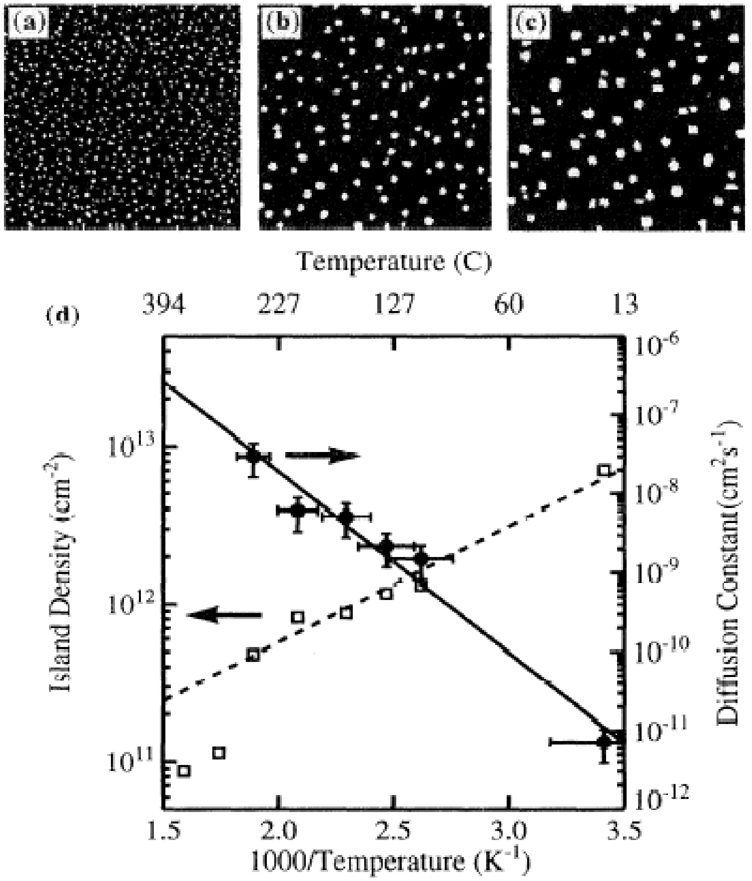


γ = surface tension; V = atomic volume; n_0 = surface density

Experimental Techniques

4) Island growth techniques:

- <u>Number density of islands</u> after submonolayer deposition <u>is monitored</u>
- Example: Fe on Fe(100) (Stroscio et al., PRL 1993)



deposition rate

$$N \propto \left(\frac{R\Theta}{\nu}\right)^{1/3}$$

hopping rate

Further Reading

- K. Oura et al., Surface Science, Springer 2003, chapter 13
- A.G. Naumovets & Yu.S. Vedula, Surf. Sci. Rep. 4 (1985) 365
- R. Gomer, Rep. Prog. Phys. 53 (1990) 917
- G.L. Kellogg, Surf. Sci. Rep. 21 (1994) 1