Diffusion nucleation growth and molecular nanostructures on surfaces

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Diffusion

Random walk

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

$\langle \Delta r^2 \rangle$ is the mean square displacement, ν the jump rate (generally around $1 \times 10^{13}\,\mathrm{s}^{-1}$), a the jump distance and t the time. This gives rise to the diffusion coefficient (diffusivity) or the time dependent ratio of the mean square displacement:

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

Where z is the number of possible jumps (2 is 1d, 4 is 2d square, 6 is 2d hexagonal). The frequency can be found as a function of temperature and barrier:

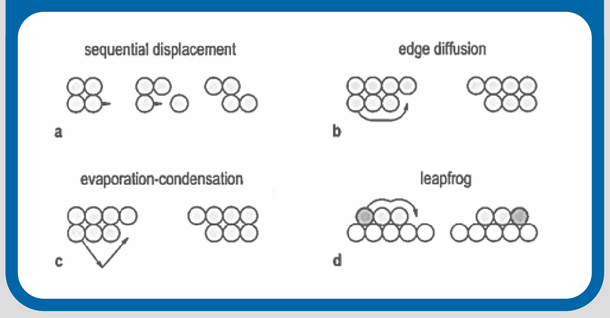
$$\nu = \nu_0 e^{-\frac{E_{\mathrm{diff}}}{k_b T}}$$

D might not be equal in every direction, a 1d system could have a small chance of jumping in another direction, if this is the case the diffusion is anisotropic, it could also be caused by the unit cell not being symmetric:

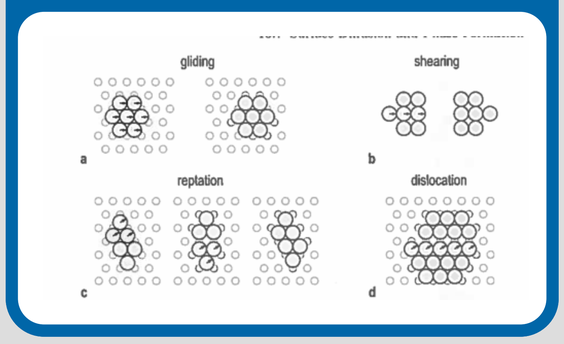
$$D(\phi) = D_x \cos^2\phi + D_y \sin^2\phi$$

Cluster diffusion

Single atom



Atom Group



ways to walk

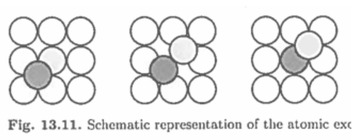
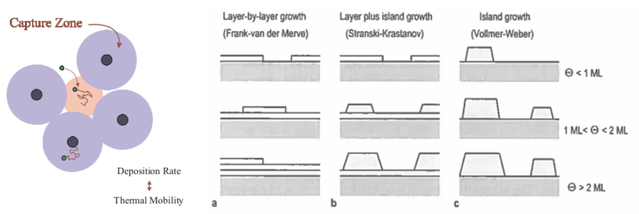


Fig. 13.11. Schematic representation of the atomic exc

Islands

Capture zone+modes



Ostewald ribening + coalescene

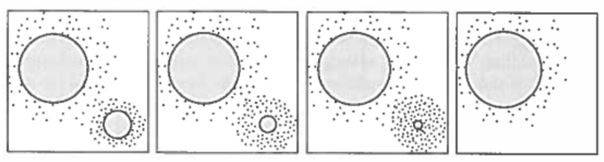


Fig. 14.16. Schematic diagram showing sequential stages of island ripening

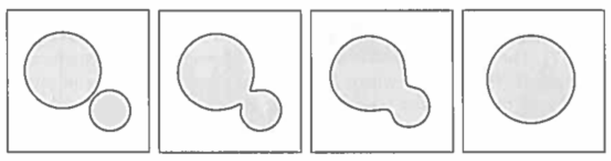
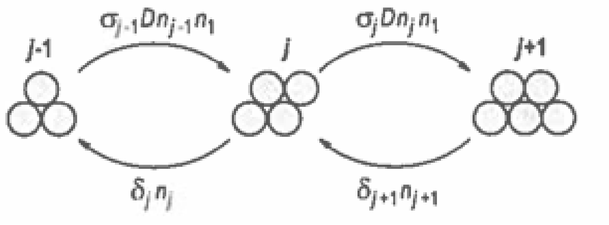


Fig. 14.15. Schematic diagram showing sequential stages of coalescence

Math figure



Mathematics

n_1 is the density of adatoms, D the diffusion coefficient, σ the capture number (capability of cluster to capture atom) and $\partial_{j+1} = De^{-\frac{\Delta E_j^{j+1}}{k_B T}}$ is the decay rate of an island, ΔE_j^{j+1} is the energy difference between the two island sizes. n_x is now the number density of stable islands ($j > i$)

$$\frac{dn_1}{dt} = \underbrace{R}_{\text{desposition}} - \underbrace{\frac{n_1}{\tau_{\text{ads}}}}_{\text{dissociation}} + \left(\underbrace{2\partial_2 n_2}_{\text{nucleation}} + \underbrace{\sum_{j=3}^{i} \partial_j n_j}_{\text{growth}} - \underbrace{2\sigma_1 D n_1^2}_{\text{denucleation}} - \underbrace{n_1 \sum_{j=2}^{i} \sigma_j D n_j}_{\text{degrowth}} \right) - \underbrace{n_1 \sigma_x D n_x}_{\text{growth stable}}$$

$$\frac{dn_j}{dt} = \underbrace{n_1 \sigma_{j-1} D n_{j-1}}_{\text{growth}} - \underbrace{\partial_j n_j}_{\text{degrowth}} + \underbrace{\partial_{j+1} n_{j+1}}_{\text{degrowth}} - \underbrace{n_1 \sigma_j D n_j}_{\text{growth}}$$

$$\frac{dn_x}{dt} = \underbrace{n_1 \sigma_1 D n_1}_{\text{growth}}$$

This splits the system into 4 stages: "low coverage" (adatom density higher than island density), "intermediate coverage" (more islands than adatoms), "aggregation regime" (collecting the last adatoms) and the "coalescence and percolation regime" (Islands melting together). The number of island grown (normalized to sites) are:

$$\frac{n_x}{n_0} = \eta(\Theta, i) \left(\frac{4R}{\nu_0 n_0} \right)^{\chi} e^{\frac{\chi\left(E_{diff} + \frac{E_i}{i}\right)}{k_B T}}$$

$$\chi_{2d} = \frac{i}{i+2}$$

$$\chi_{1d} = \frac{i}{2(i+1)}$$

Here E_i is the binding energy of the critical cluster, η an exponential factor (10^{-2} to 10^{1}). The second formulae takes temperature dependence of diffusion coefficient into account.

size

$$N = \sum_{s>i} N_s \qquad \text{noncritical islands} \qquad \Theta = \sum_{s \geq 1} s N_s$$

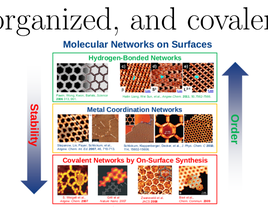
$$\langle s \rangle = \frac{\sum_{s>i} s N_s}{\sum_{s>i} N_s} = \frac{\Theta - \sum_{s \leq i} S N_s}{N} \underset{i=1}{=} \frac{\Theta - N_1}{N} \approx \frac{\Theta}{N}$$

$$f_i\left(\frac{s}{\langle s \rangle}\right) = \frac{N_s (s_{av})^2}{\Theta}$$

Self assembly

Hydrogen vs metal vs covalent

Hydrogen bonds are lower en energy, so it's easier for them to restructure into something organized, metal bonds are semi organized, and covalent bonds are completely random.



principle

"Molecular self-assembly is the spontanous association of molecules under equilibrium conditions into stable, structurally well defined aggregates joined by non-covalent bonds."

$$E_b > E_{\text{intermidiate}} \geq E_{\text{kin}} > E_{\text{dessorption}}$$