Submonolayer Growth, Second Layer Nucleation and Cluster Formation on Surfaces

I Submonolayer growth of binary alloys

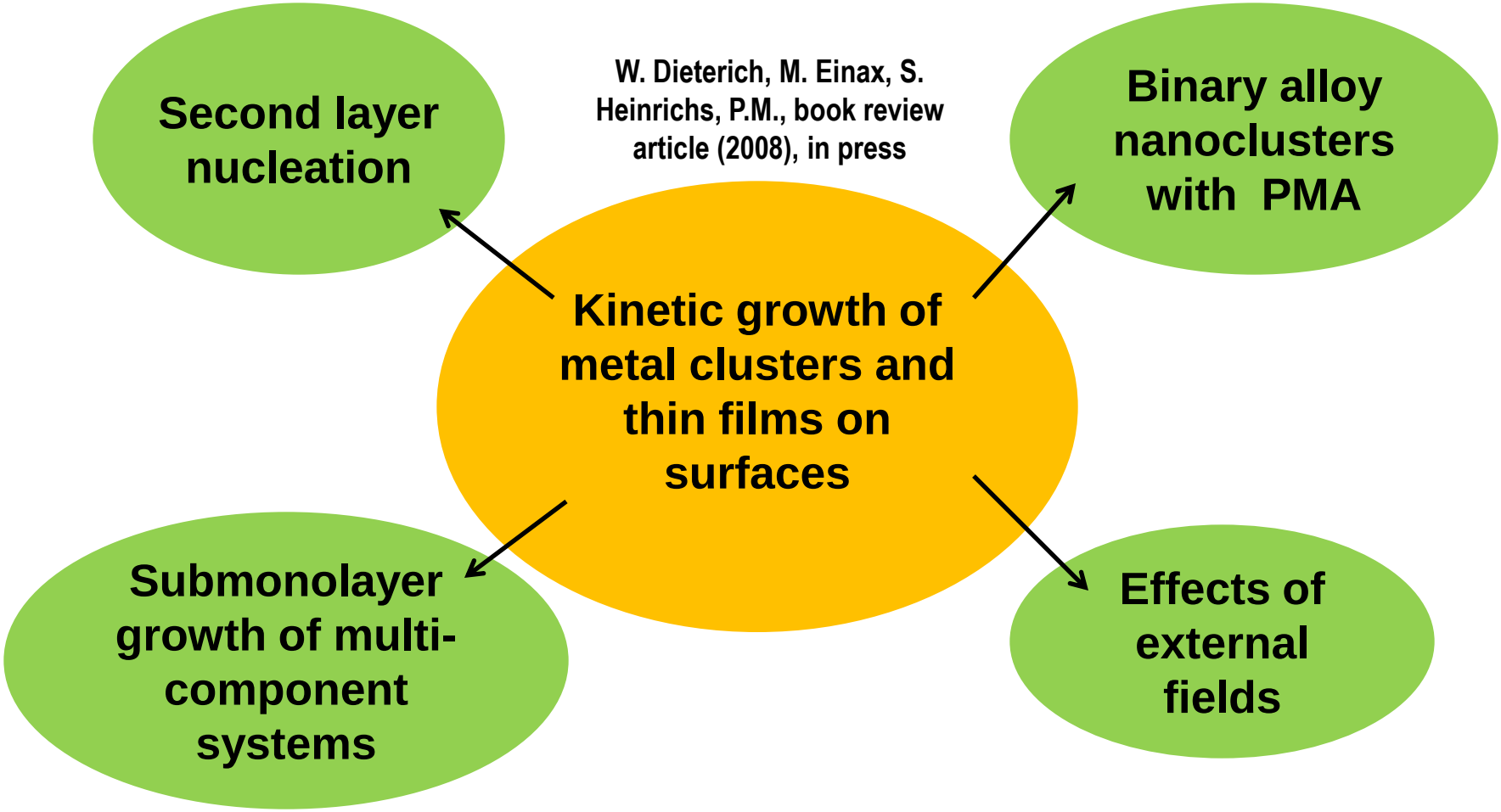
II Cluster growth of binary alloys and the occurrence of perpendicular magnetic anisotropy

III Second layer nucleation on top of islands

Philipp Maass, Technische Universität Ilmenau, Germany

J. Rottler, P.M , PRL 83, 3490 (1999); S. Heinrichs, J. Rottler, P.M., PRB 62, 8338 (2000); S. Heinrichs, P.M., PRL 87, 149605 (2001); S. Heinrichs, P.M., PRB 66, 73402 (2002)

S. Heinrichs, W. Dieterich, P. M., EPL 75, 167 (2006); *ibid.*, PRB 75, 085437 (2007)

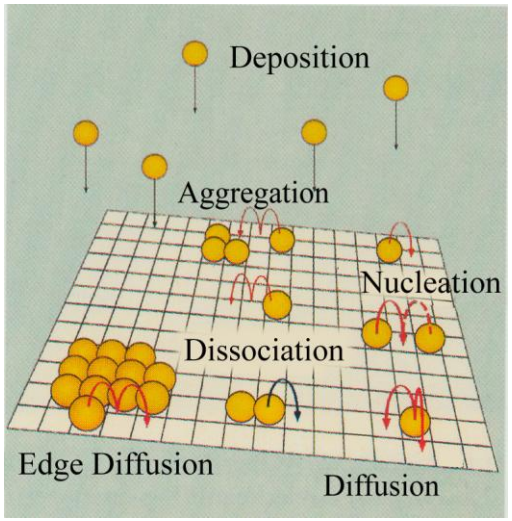


W. Dieterich, M. Einax, S. Heinrichs, P.M., book review article (2008), in press

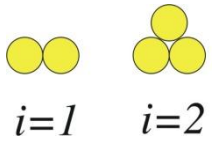
M. Einax, S. Ziehm, W. Dieterich, P.M., PRL 99, 016106 (2007); W. Dieterich, M. Einax, P. M., EPJ Special Topics (2008), in press

M. Einax, S. Heinrichs, P.M., A. Majhofer, W. Dieterich, JPCM 19, 086227 (2007); *ibid.*, Mat. Sci. Eng 27, 1325 (2007)

Elementary Processes During Epitaxial Growth



- Deposition rate:
  Fa^2 (a: lattice constant)
- Adatom jump rate:
  $D/a^2 = \nu_t \exp(-E_D/k_BT)$
- Dissociation rates:
  $W_j^{dis} \propto D\exp(-\Delta E_j^{dis}/k_BT)$
- Size of critical radius i:
  $"\Delta E_{i+1}^{dis} = \infty"$

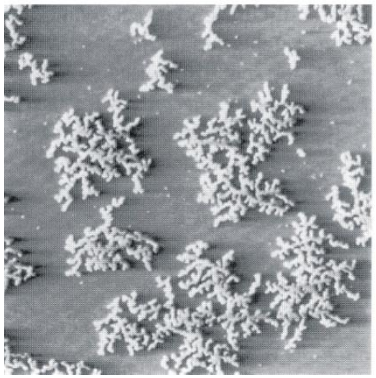


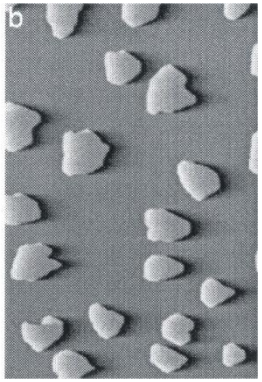
etc.

Morphologies:

H.Brune, Surf. Sci. Rep. 31, 121 (1998)

Ag/Pt(111), 110K





Pt/Pt(111), 400K

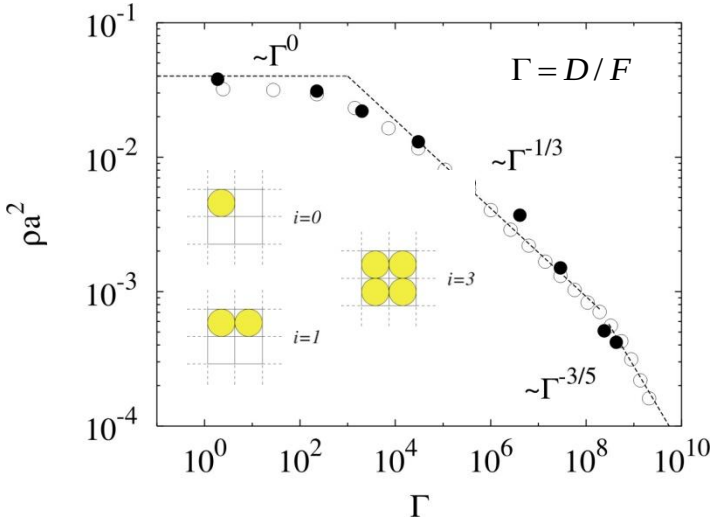
Island density:

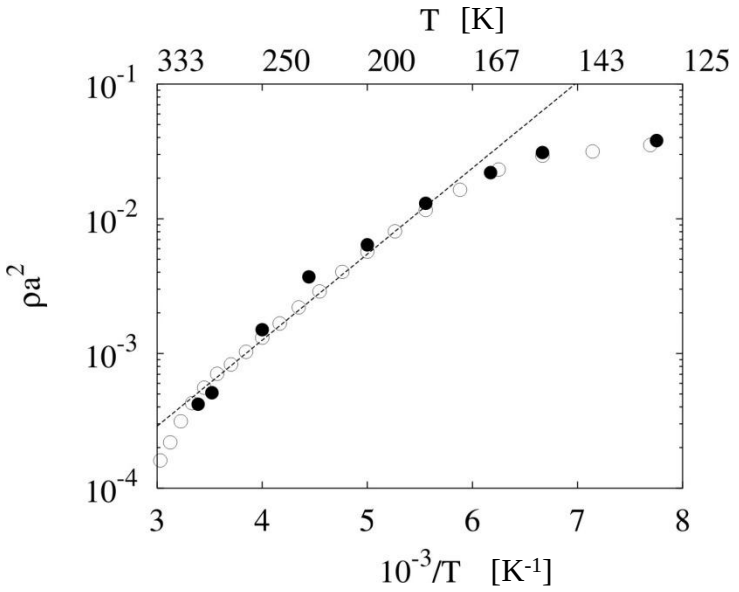
$$\rho \propto \left(\frac{D}{F}\right)^{-\frac{i}{i+2}}$$

Example: Growth of Ag/Ag(100) and Monte Carlo Simulations

Island density at coverage Fa^2t=10% (Fa^2=0.006ML/s)
Comparison between experiment (•) and simulations (◦)
(analysis 0.5h after evaporation)

$$\rho \propto (D/F)^{-i/(i+2)}, \quad D = \nu \exp(-E_D / k_B T)$$





parameters in simulation: $E_D = 0.38\text{eV}$, $E_{NN} = -0.3\text{eV}$, $\nu = 2\times10^{12}\text{s}^{-1}$

S. Frank, H. Wedler, R. J. Behm, J. Rottler, P. M., K. J. Caspersen, C. R. Stoldt, P. A. Thiel, J. W. Evans, Phys. Rev. B 66, 155435 (2002)

Submonolayer Growth of Binary Alloys

Assumptions: no evaporation of adatoms (low T), cluster are immobile

Mean-field rate equations:

$\boldsymbol{n_\alpha}$: adatom concentrations ($\alpha = A, B$), $\boldsymbol{F_\alpha = x_\alpha F}$: deposition fluxes ($\alpha = A, B$)

$\boldsymbol{n_{j,k}}$: concentration of (j,k)-clusters with j A atoms and k B atoms;

$\boldsymbol{K^\alpha_{j,k}}$: rate of dissociation of (j,k)-cluster by detachment of α atom; for stable clusters: $\boldsymbol{K^\alpha_{j,k} = 0}$

$$\frac{dn_A}{dt} = \underbrace{F_A}_{\text{flux}} \underbrace{-2D_A\sigma_1 n_A^2 - (D_A + D_B)\sigma_1 n_A n_B}_{\text{dimer formation}} \underbrace{+2K_{2,0}n_{2,0} + K_{1,1}n_{1,1}}_{\text{dimer dissociation}} \underbrace{-D_A n_A \sum_{2\geq(j+k)} \sigma_{j+k} n_{j,k}}_{\text{attachments to clusters}} \underbrace{+ \sum_{3\geq(j+k)} K^A_{j,k} n_{j,k}}_{\text{detachment from clusters}}$$

$$\frac{dn_{j,k}}{dt} = \underbrace{D_A n_A \sigma_{j+k-1} n_{j-1,k} + \ldots - (D_A n_A + D_B n_B)\sigma_{j+k} n_{j,k}}_{\text{gain and loss terms due to attachments}} \underbrace{+K^A_{j+1,k} n_{j+1,k} + \ldots - (K^A_{j,k} + K^B_{j,k}) n_{j,k}}_{\text{gain and loss terms due to detachments}}$$

Quasi-equilibrium for subcritical clusters (generalized Walton relations):

$$K^A_{j,k} n_{j,k} = D_A n_A \sigma_{j+k-1} n_{j-1,k}, \ldots \rightarrow n_{j,k} = C_{j,k} n_A^j n_B^k \quad \left(C_{j,k} = \frac{\prod_{s=1}^{j+k-1} \sigma_s}{j!k!\gamma_{j,k}}, \ \gamma_{j,k} : \text{product of dissociation rates} \right)$$

Quasi-stationarity, since $D_\alpha / F >> 1$ (10^5-10^{12} in experiments): $\boldsymbol{F_\alpha \sim D_\alpha n_\alpha \bar{\sigma} N}$

$$N = \sum_{\{K_{j,k}=0\}} n_{j,k} : \text{ concentration of stable islands} \qquad \bar{\sigma} = \frac{1}{N} \sum_{\{K_{j,k}=0\}} n_{j,k}\sigma_{j,k} : \text{ mean capture number of stable islands}$$

1. Situation: Cluster stability solely determined by cluster size

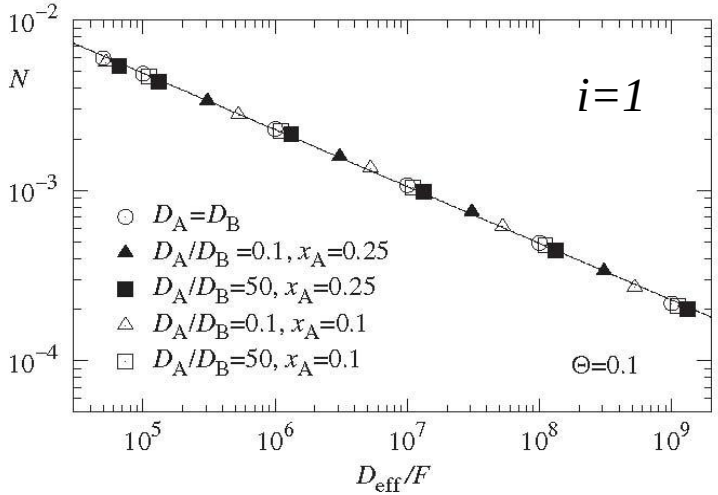
All clusters of size $(j+k)>i$ are stable irrespective of their composition:

$$N \sim \left[\eta_i \theta \sum_{j=0}^{i} \binom{i}{j} \frac{1}{\gamma_{i-j,j}} \left(\frac{F_A}{D_A}\right)^{i-j} \left(\frac{F_B}{D_B}\right)^{j} \right]^{\frac{1}{i+2}}$$

$$\eta_i = (i+2)\frac{\prod_{s=1}^{i}\sigma_s}{i!\bar{\sigma}^{i+1}}, \quad \theta = Ft: \text{ coverage}$$

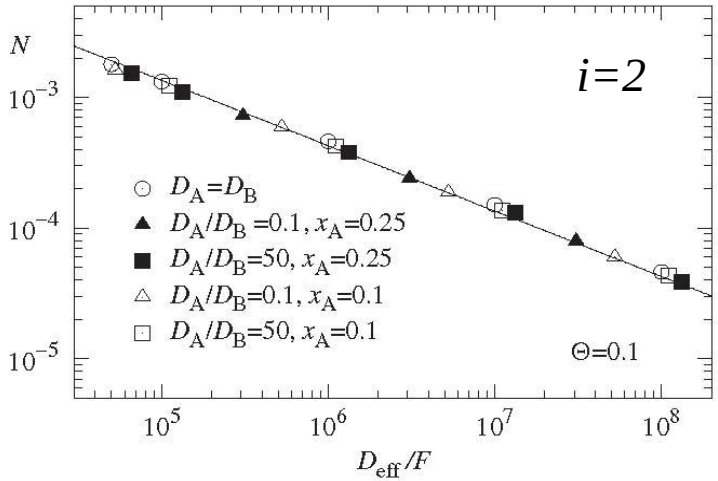
(a) if binding energies of unstable clusters are negligible:

$$N \sim \left(\frac{D_{eff}}{F}\right)^{-\frac{i}{i+2}}, \quad D_{eff}^{-1} = x_A D_A^{-1} + x_B D_B^{-1}$$



(b) finite binding energies of unstable clusters, e.g. for $i=2$ $(K_{2,0} \propto \exp(-E_{AA}/k_B T), \ldots)$:

$$N^4 \sim e^{E_{AA}/k_B T}\left(\frac{F_A}{D_A}\right)^2 + 2e^{E_{AB}/k_B T}\left(\frac{F_A}{D_A}\right)\left(\frac{F_B}{D_B}\right) + e^{E_{BB}/k_B T}\left(\frac{F_B}{D_B}\right)^2$$



$\longrightarrow$ determination of $E_{\alpha\beta}$ by measurements of N for various F_A, F_B at different T (where $i=2$ is valid)

2. Situation: Cluster stability determined by size and composition

more complex situations, e.g. all clusters with $(j+k)>2$ stable,
both AB and BB dimers unstable but AA dimers stable:

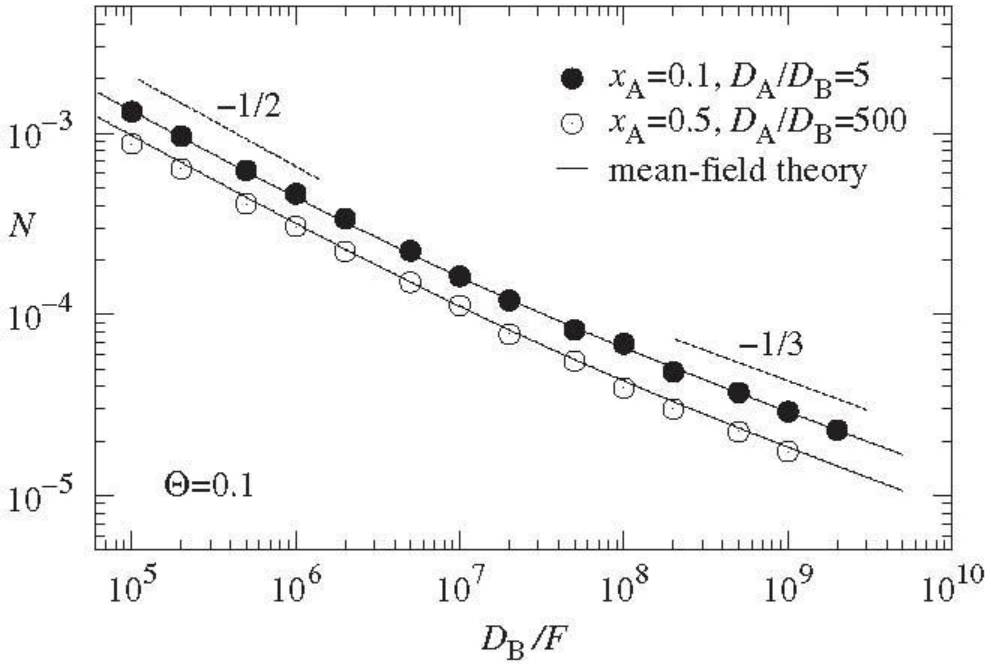
$$\frac{dN}{d\theta} = \frac{a}{N^2} + \frac{b}{N^3} \qquad \left(a = x_A \frac{\sigma_3}{\bar{\sigma}^2} \frac{F_A}{D_A}, \quad b = \frac{\sigma_1 \sigma_2}{\bar{\sigma}^3} \frac{F_B}{D_B} \left(\frac{F_A}{K_{1,1}} + \frac{F_B}{K_{0,2}} \right) \right)$$

$$\longrightarrow N \sim \begin{cases} (4b\theta)^{1/4}, & N \ll b/a \\ (3a\theta)^{1/3}, & N \gg b/a \end{cases}$$

for D_A/D_B fixed and D_B/F varied:

$$N \sim \begin{cases} (D_B/F)^{-1/2}, & D_B/F \ll (D_B/F)_* \\ (D_B/F)^{-1/3}, & D_B/F \gg (D_B/F)_* \end{cases}$$

$$(D_B/F)_* = f(x_A, \theta; \ldots)$$



i=2 type regime with slope -1/2: dominant route for nucleation via formation of AB and BB dimers; "trimer route"

i=1 type regime with slope -1/3: dominant route for nucleation by formation of stable AA dimers; "dimer route"

M. Einax, S. Ziehm, W. Dieterich, P.M., Phys. Rev. Lett. **99**, 016106 (2007)

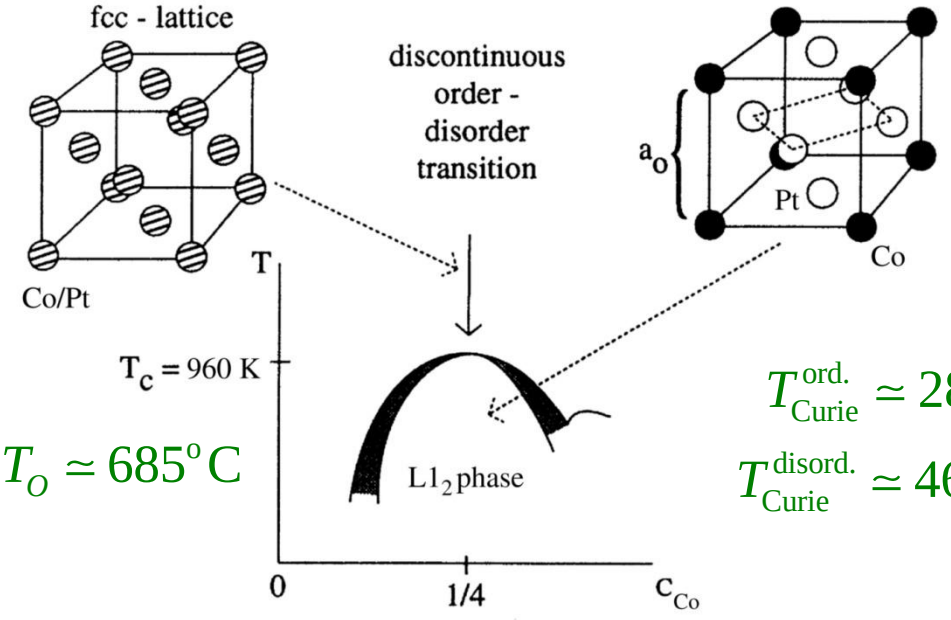
Cluster Growth of Binary Alloys

Motivation:
- understanding of phase separation and chemical ordering phenomena in the presence of kinetic growth limitations and surface induced effects (shape, modified interactions, etc.)
- connection of structural with magnetic properties

  → perpendicular magnetic anisotropy (PMA): easy axis of magnetization perpendicular to film plane

Example: $CoPt_3/WSe_2$ (0001)

bulk phase diagram



larger size of Pt yields nearly 100% Pt surface segregation in equilibrium

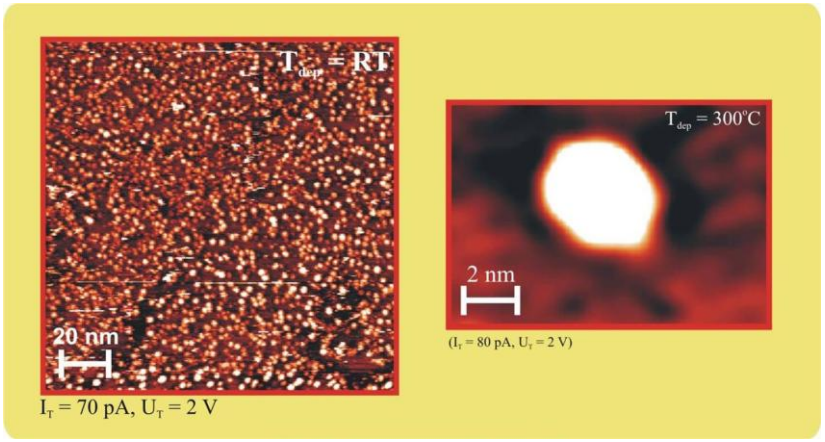
$T_O \simeq 685^{\circ}\mathrm{C}$

$T_{\mathrm{Curie}}^{\mathrm{ord.}} \simeq 288\mathrm{K}$ $\quad \mu^{\mathrm{Co}} \simeq 1.7\,\mu_B$

$T_{\mathrm{Curie}}^{\mathrm{disord.}} \simeq 468\mathrm{K}$ $\quad \mu^{\mathrm{Pt}} \simeq 0.3\,\mu_B$

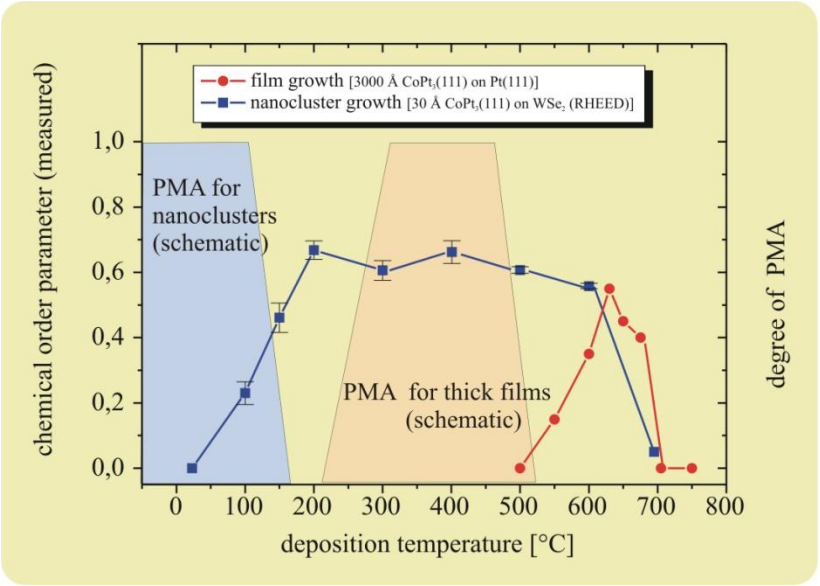
on $WSe_2(0001)$ surface → weak surface interaction + strong lattice mismatch

→ formation of nanoclusters with PMA at room temperature



STM pictures

M. Albrecht *et al.*, Europhys. Lett. 56, 884 (2001)



schematic kinetic phase diagrams for $CoPt_3$ films and nanoclusters

→ $L1_2$ ordering kinetically suppressed at low T

→ no PMA in the presence of $L1_2$ order

→ temperature window for PMA shifted to room temperature for nanoclusters

film data: A.L. Shapiro et al., Phys. Rev. B 60, 12826 (1999)

Questions:

What are the conditions on the growth parameters that clusters display a superstructure corresponding to their bulk long-range $L1_2$ order?

What is the mechanism causing PMA and how can one understand that in $CoPt_3$ clusters PMA occurs only in a certain temperature window near room temperature?

How large is the possible influence of magnetic anisotropy energies on the structural short range order, when clusters are grown in the presence of a strong magnetic field?

$\longrightarrow$ KMC simulations with bond picture for magnetic anisotropies

S. Heinrichs, W. Dieterich, P. M., Europhys. Lett. **75**, 167 (2006);
ibid., Phys. Rev. B **75**, 085437 (2007)
M. Einax *et al.*, J. Phys.: Condens. Matter **19**, 086227 (2007);
ibid., Material Science and Engineering **27**, 1325 (2007)

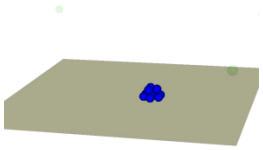
Kinetic Monte Carlo (KMC) Simulations

- fcc lattice with NN interactions between A=Co and B=Pt
- deposition of atoms with rate F and jumps between NN sites with Metropolis rates $\nu \exp(-\beta \Delta E_t) \min[1, \exp(-\beta(E_{fin}-E_{in})]$
- exchange processes between low-coordinated unlike atoms at surface (one atom with coordination 3-5, the other with 8-10): ΔE_x
- rejectionless continuous-time Monte Carlo algorithm

parameters: – NN interactions

bulk phase transition to $L1_2$ order at $T_0 = 958\text{K}$:

$$I = \frac{1}{4}(V_{AA} + V_{BB} - 2V_{AB}) \equiv 1 \quad (k_B T_0 = 1.83 I \Rightarrow k_B T_0 / 1.83 = 45\text{meV})$$



strong surface segregation of Pt: $h = V_{BB} - V_{AA} = 4$

average bond energy: $V_0 = (V_{AB} + V_{BB})/2 = -5$ (from estimation in $L1_2$ ordered phase)

$\longrightarrow V_{AA} = V_{AB} = -7,\ V_{BB} = -3$

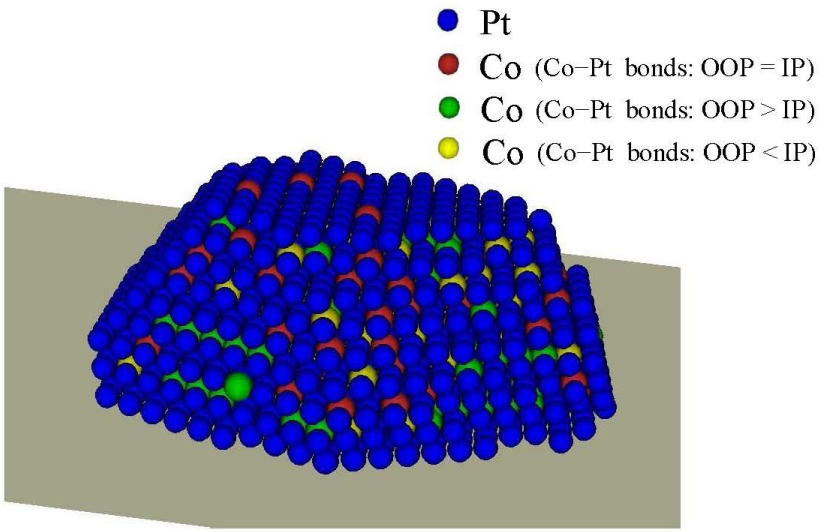
weak attractive surface potential: $V_s = -5$ (total energy for A and B atoms)

– kinetic quantities

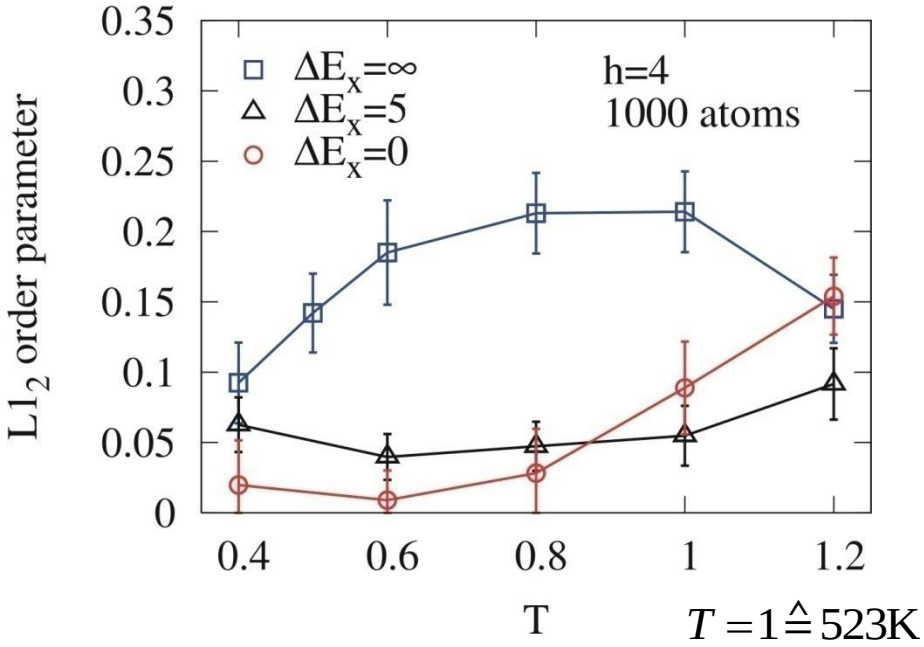
from diffusion of Pt on Pt(111): $\nu = 5 \times 10^{12}\text{s}^{-1},\ \Delta E_t = 5$

F=3.5-21 ML/s (larger than in experiments)

Growth Kinetics and $L1_2$ Ordering



facetting (100, 111) and
Pt surface segregation



kinetic freezing (at low T), Pt surface segregation (and exchange processes promoting segregation) impede $L1_2$ ordering

$$\psi = (I - I_{\mathrm{ran}})/(I_{\mathrm{id}} - I_{\mathrm{ran}})$$

(I : av. intensity of $L1_2$ superstr. peaks)

Magnetic Anisotropy – Relation to Cluster Structure

- dipolar interaction: favors $\vec{M} \parallel$ film plane (shape anisotropy) $\longrightarrow E_{\mathrm{dip}}$
- crystalline magnetic anisotropy within bond picture:

$$H_{\mathrm{a}} = -\sum_{\langle i,\vec{\delta}\rangle} \sum_{\alpha=\mathrm{Co,Pt,V}} A^{\mathrm{Co}\alpha} \left(\vec{\mu}_i^{\mathrm{Co}} \cdot \vec{\delta}\right)^2 / \left(\left|\vec{\mu}_i^{\mathrm{Co}}\right| \left|\vec{\delta}\right|\right)^2$$

$A^{\mathrm{Co}\alpha}$: anisotropy energies associated with Co-α bonds

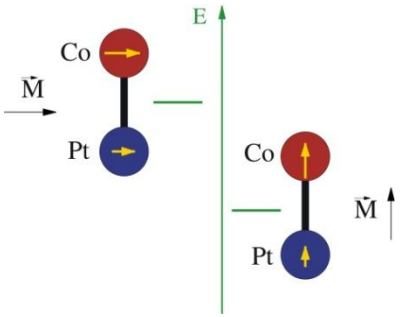
$\longrightarrow$ magnetic anisotropy energy caused by local chemical order:

$$E_s = H_a\left\{\vec{\mu}_i^{Co}\ in\ plane\right\} - H_a\left\{\vec{\mu}_i^{Co}\ out\ of\ plane\right\} = \frac{1}{2}\sum_{\alpha=Co,Pt}\left(A^{Co\alpha} - A^{CoV}\right)\left(n_{\perp}^{Co\alpha} - n_{\parallel}^{Co\alpha}\right)$$

from magnetic torque and MOKE measurements on Co-Pt multilayer structures: $A^{\mathrm{CoPt}} \simeq 250\mu\mathrm{eV}$

from measurements on Co-vacuum interfaces and electronic structure calculations of freely standing Co monolayer: $A^{\mathrm{CoV}} \simeq -67\mu\mathrm{eV}$

from nearest neighbor dipolar coupling of Co moments: $A^{\mathrm{CoCo}} \simeq 250\mu\mathrm{eV}$



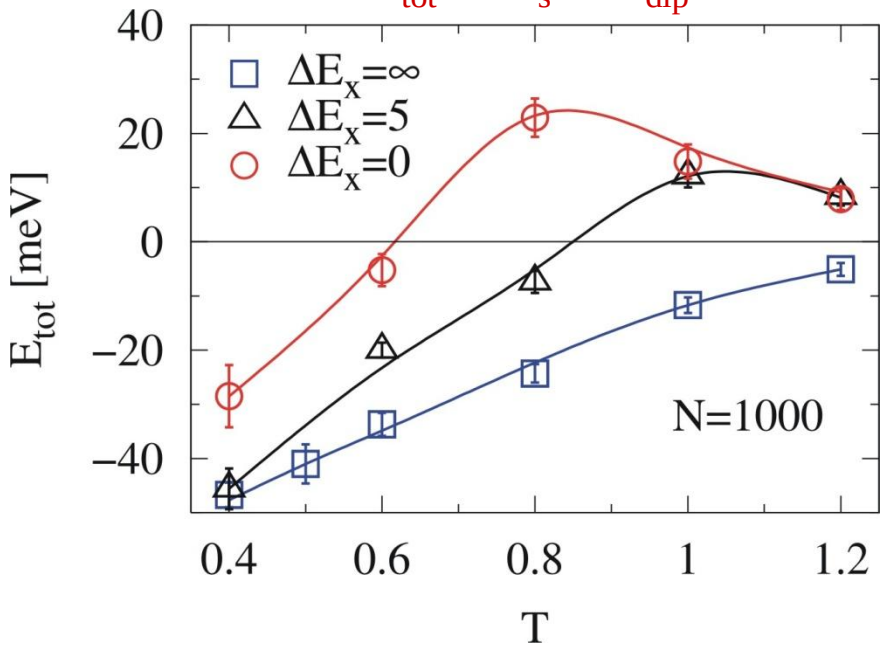
$\longrightarrow$ dominant term comes from Co-Pt bonds

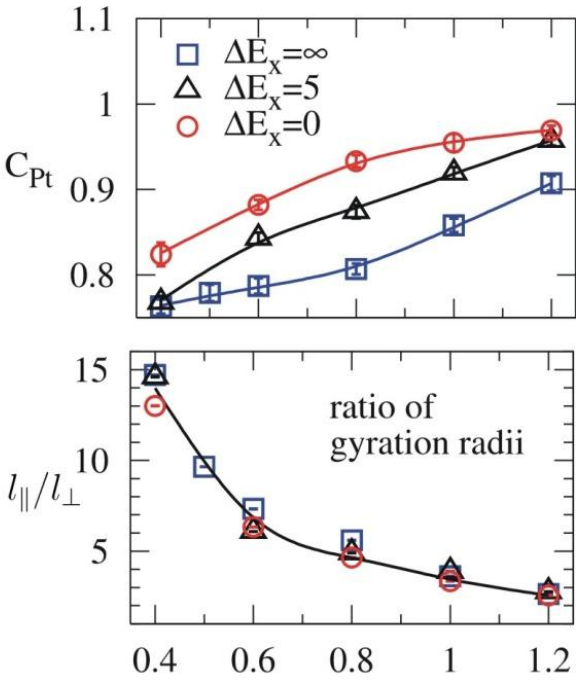
$$E_s \simeq \frac{1}{2}\Delta A^{CoPt}\left(n_{\perp}^{CoPt} - n_{\parallel}^{CoPt}\right)$$

model corroborated by measurements on multilayers and films with local anisotropic structures (XAFS, dependence of M on layer thickness)

PMA and Origin of Temperature Window

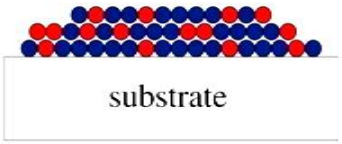
$$E_{tot} = E_s + E_{dip}$$

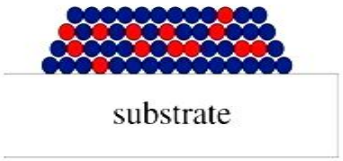


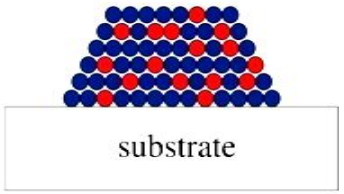


two competing effects:
low T: PMA limited by
insufficient
Pt segregeation
high T: PMA limited by
round cluster shapes

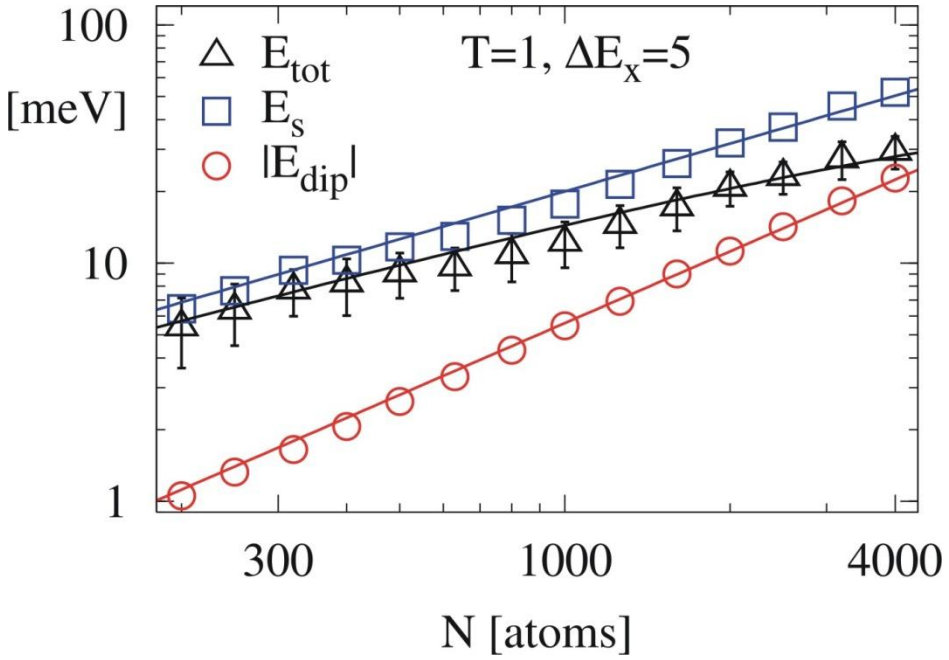
random order	sufficient segregation	strong segregation
flat	flat	round
$E_s<0$	$E_s>0$	$E_s<0$







Size Dependence of Magnetic Anisotropy



main contribution from Co-Pt bonds: $E_s \simeq \Delta A^{\mathrm{CoPt}} (n_{\perp}^{\mathrm{CoPt}} - n_{\parallel}^{\mathrm{CoPt}}) \sim N^{2/3}$

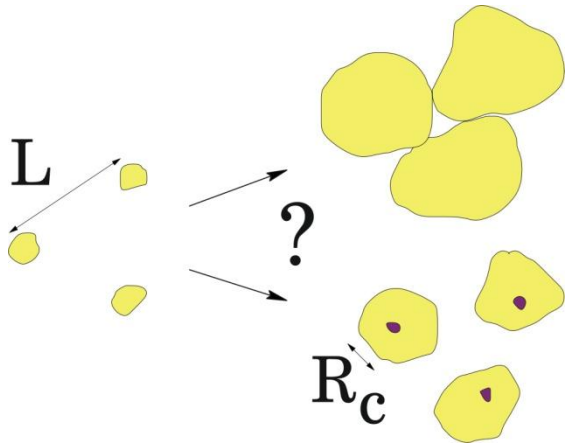
dipolar form anistropy: $E_{\mathrm{dip}} \sim N$

$$\rightarrow E_{\mathrm{tot}} = E_s + E_{\mathrm{dip}} \simeq K_s N^{2/3} - K_{\mathrm{dip}} N$$

$\longrightarrow$ optimal cluster size $N_{\mathrm{opt}}=(2K_s/3K_{\mathrm{dip}})^3$

$\longrightarrow$ maximal cluster size $N_{\mathrm{max}}=(K_s/K_{\mathrm{dip}})^3=(3/2)^3\, N_{\mathrm{opt}}$

Second Layer Nucleation (one component)



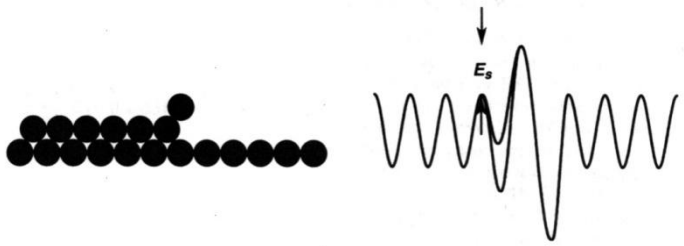
$$L \propto \rho^{-1/2} \propto (D/F)^{-i/2(i+2)}, \quad \Gamma \equiv D/F$$

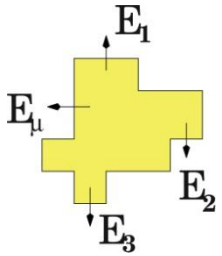
R_c: typical radius at onset of nucleation on top of islands

$R_c \gg L$: smooth layer-by-layer growth

$R_c \ll L$: rough multilayer growth

important parameter: Schwoebel barrier $\Delta E_S = E_S - E_D$





$$\Delta E_S / k_B T = -\ln\left\langle \exp(-\Delta E_\mu / k_B T) \right\rangle$$

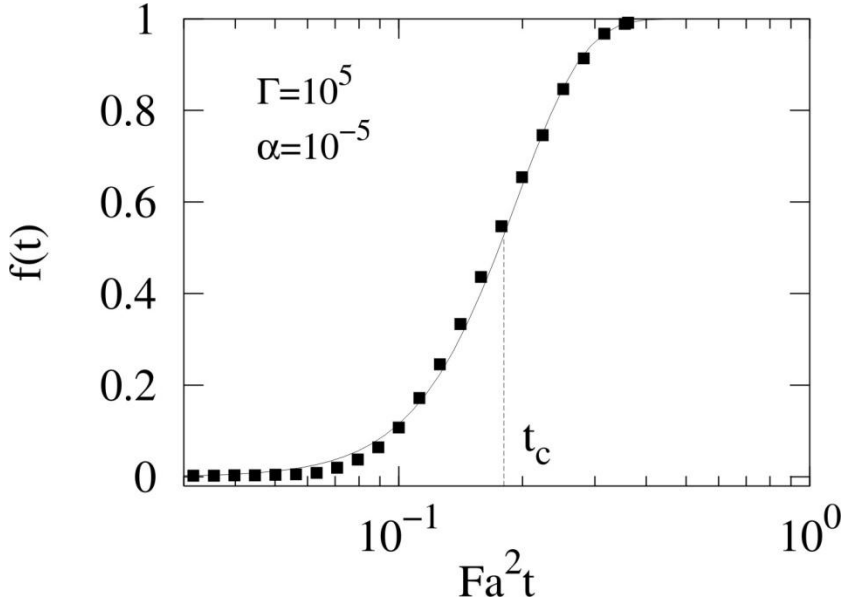
ΔE_S large $\Rightarrow$ R_c small

ΔE_S small $\Rightarrow$ R_c large

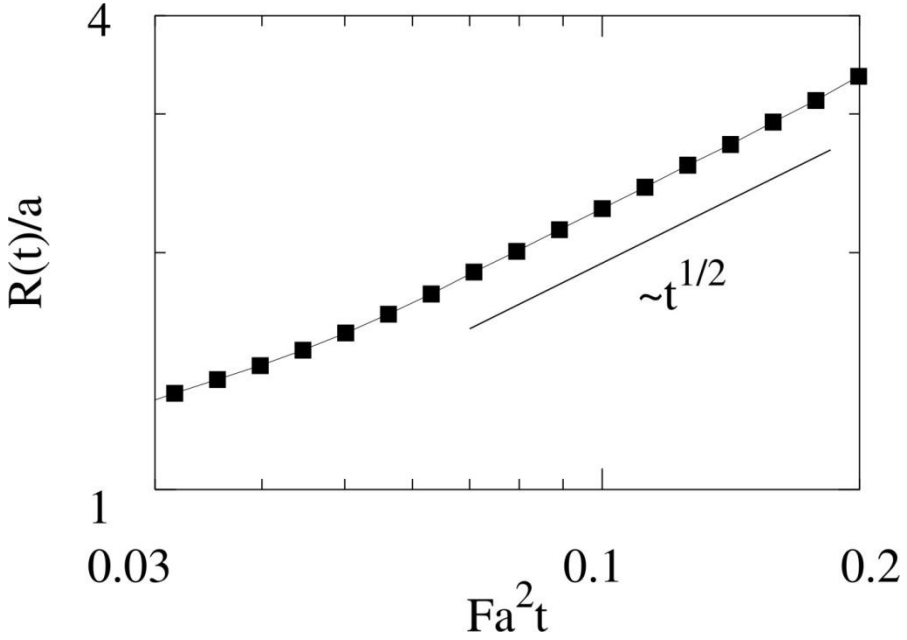
$$\alpha \equiv \frac{\nu_S}{\nu_t} \exp\left(-\frac{\Delta E_S}{k_B T}\right)$$

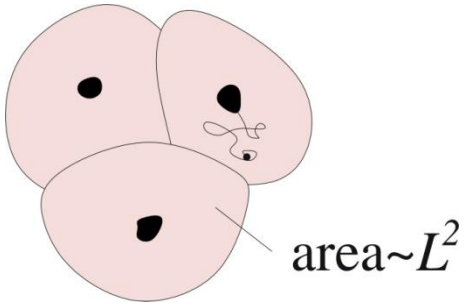
Fraction of Covered Islands and Mean Island Radius

$$f(t_c) = \frac{1}{2}$$



$$R_c = R(t_c)$$





$$\rightarrow \frac{R^2(t)}{a^2} \propto FL^2t$$

TDT Mean Field Theory

J. Tersoff, A.W. Denier van der Gon, R.M. Tromp, Phys. Rev. Lett. 72, 266 (1994)

$\rho_1(r)$: adatom density, i: critical size

- local nucleation rate: $\omega(r) = \kappa(D/a^2)\rho_1^{i+1}(r)$
- stationary diffusion equation with partially reflecting boundary: $D\Delta\rho_1^{st} + F = 0, \quad -D\partial_r\rho_1^{st}|_{r=R} = (\alpha D/a)\rho_1^{st}|_{r=R}$

$$\rightarrow \rho_1^{st}(r) = (4\Gamma a^4)[(1+(2a/\alpha R)R^2 - r^2]$$

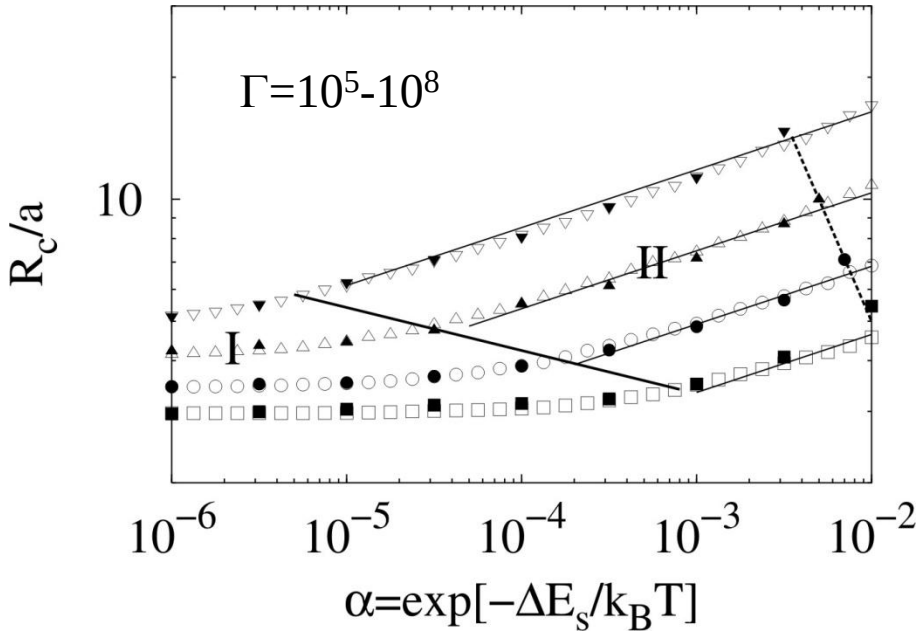
- total nucleation rate on island with radius R: $\Omega(R) = 2\pi\int_0^R dr\, r\, \omega(r)$
- fraction of covered islands: $f(t) = 1 - \exp\left[-\int_0^t dt'\,\Omega(R(t'))\right]$

$$\rightarrow \frac{R_c}{a} = \begin{cases} \Gamma^{\frac{i(i+3)}{(i+2)(i+5)}}\alpha^{\frac{i+1}{i+5}}, & \alpha \ll \Gamma^{-\frac{i}{2(i+2)}} \\ \Gamma^{\frac{i}{2(i+2)}}, & \alpha \gg \Gamma^{-\frac{i}{2(i+2)}} \end{cases}$$

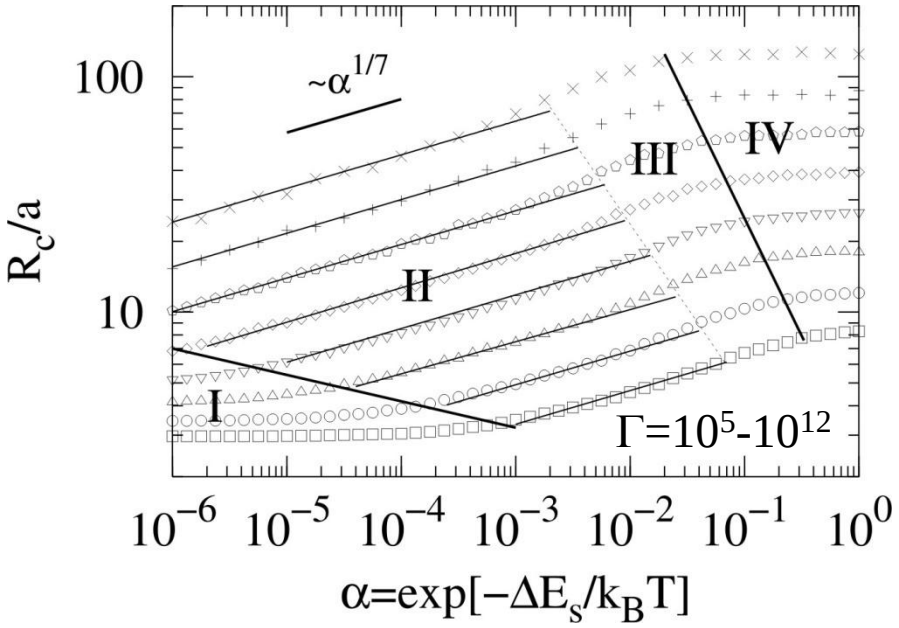
$$i=1: \quad \frac{R_c}{a} = \begin{cases} \Gamma^{2/9}\alpha^{1/3}, & \alpha \ll \Gamma^{-1/6} \\ \Gamma^{1/6}, & \alpha \gg \Gamma^{-1/6} \end{cases}$$

Critical Radius from Monte Carlo Simulations

Comparison: full simulation (•)
– single island model (∘)



Results for single island model



Disagreement with TDT theory!

Stochastic Theory

J. Rottler, P.M , Phys. Rev. Lett. 83, 3490 (1999); S. Heinrichs, J. Rottler, P.M., Phys. Rev. B 62, 8338 (2000)

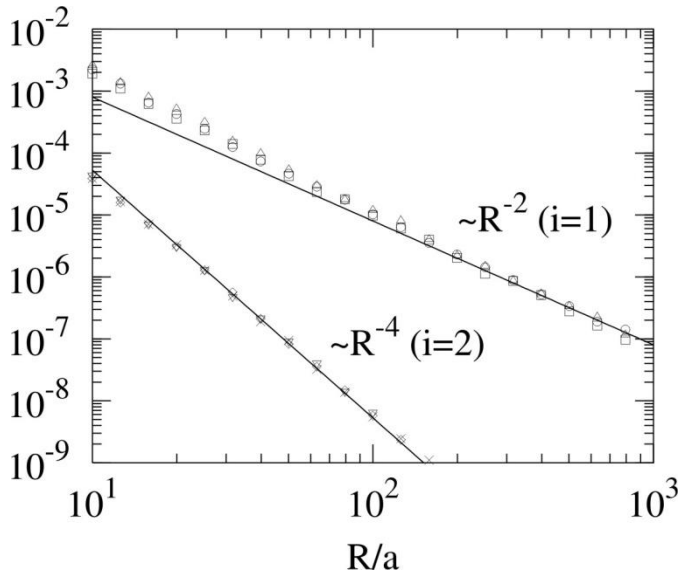
encounter rate of $i+1$ atoms in the presence of $n \geq i+1$ atoms (α=0):

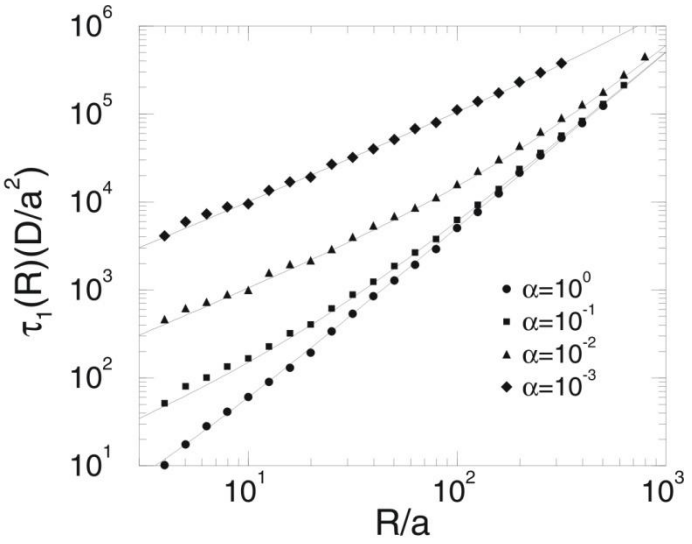
$$\omega_n(R) = \kappa_e \left[\prod_{k=0}^{i} (n-k) \right] \frac{D}{a^2} \left(\frac{a^2}{\pi R^2} \right)^{i+1} \frac{\pi R^2}{a^2}$$

lifetime of a state with n atoms ($\alpha \neq 0$):

$$\tau_n(R) = \frac{1}{n} \left(\kappa_1 \frac{R^2}{D} + \kappa_2 \frac{1}{\alpha} \frac{Ra}{D} \right)$$

$$\frac{\omega_n(a^2/D)}{\prod_{k=0}^{i}(n-k)}$$





$$\rightarrow \quad \bar{n}(R), \quad p_n(R) = \frac{\bar{n}(R)^n}{n!} \exp[-\bar{n}(R)]$$

- fluctuation dominated nucleation rate $(\bar{n}(R) \ll i+1)$:

  number of nucleations in a time interval $\Delta t \geq \tau_{i+1}(R)$:

$$\underbrace{\pi F R^2 \Delta t}_{\text{number of depos.}} \times p_i(R) \times \underbrace{\left(1-\exp[-\omega_{i+1}(R)\tau_{i+1}(R)]\right)}_{\text{encounter probability}}$$

$$\rightarrow \quad \Omega_{\text{fl}}(R) = \pi F R^2 p_i(R)\left(1-\exp[-\omega_{i+1}(R)\tau_{i+1}(R)]\right)$$

- mean field nucleation rate $(\bar{n}(R) \geq i+1)$:

$$\Omega_{\text{mf}}(R) = \sum_{n=i+1}^{\infty} p_n(R)\omega_n(R) = \kappa_{\text{e}} \frac{D}{a^2}\left(\frac{\bar{n}(R)}{\pi R^2}a^2\right)^{i+1}\left(\frac{\pi R^2}{a^2}\right)$$

$\longrightarrow$ corresponds to result of TDT theory

- decisive rate follows from self-consistency condition:

$\bar{n}(R_{\text{c}}) \ll i+1 \rightarrow$ fluctuation dominated situation; $i \leq 2$

$\bar{n}(R_{\text{c}}) \geq i+1 \rightarrow$ mean field situation (TDT theory); $i \geq 3$

Scaling Regimes (*i*=1)

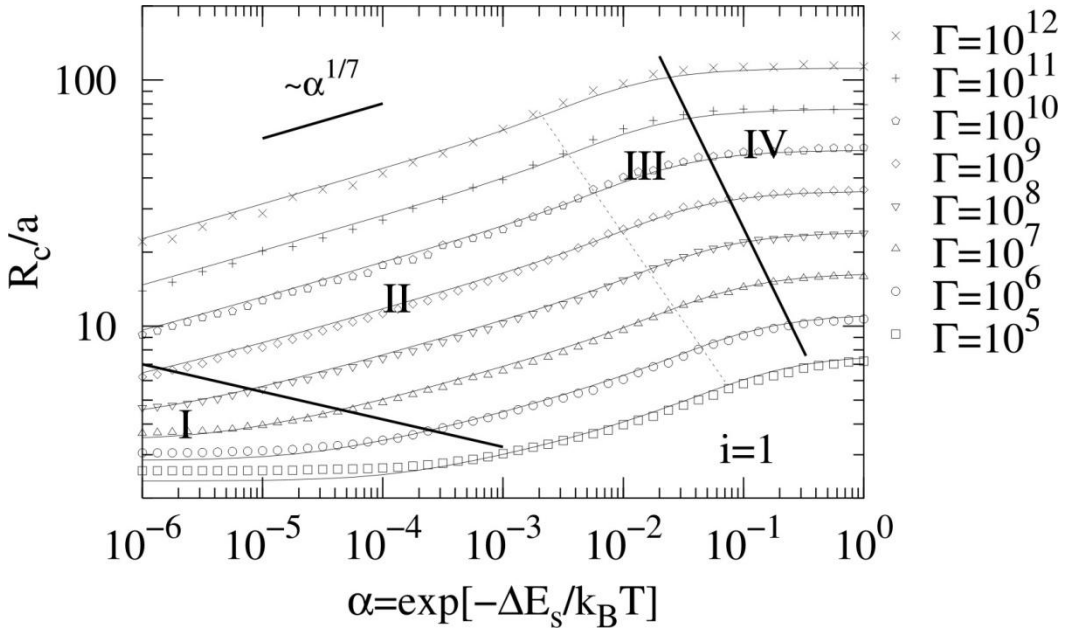
Regime I ($\alpha \ll \Gamma^{-3/4}$): $R_c \sim \Gamma^{1/12}$

Regime II ($\Gamma^{-3/4} \ll \alpha \ll \Gamma^{-1/6}$): $R_c \sim \Gamma^{4/21}\alpha^{1/7}$

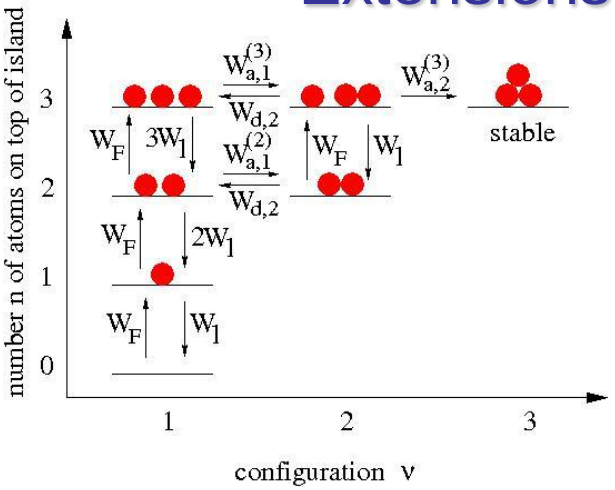
Regime III: transient regime

Regime IV ($\alpha \gg \Gamma^{-1/6}$): $R_c \sim \Gamma^{1/6}$

complete description:



Extensions to General Theory and Applications



$$\frac{dp_{n,\nu}}{dt} = \sum_{n',\nu'}\left[W(n',\nu' \to n,\nu)\,p_{n',\nu'} - W(n,\nu \to n',\nu')\,p_{n,\nu}\right], \quad p_{n,\nu}(0) = \delta_{n,0}$$

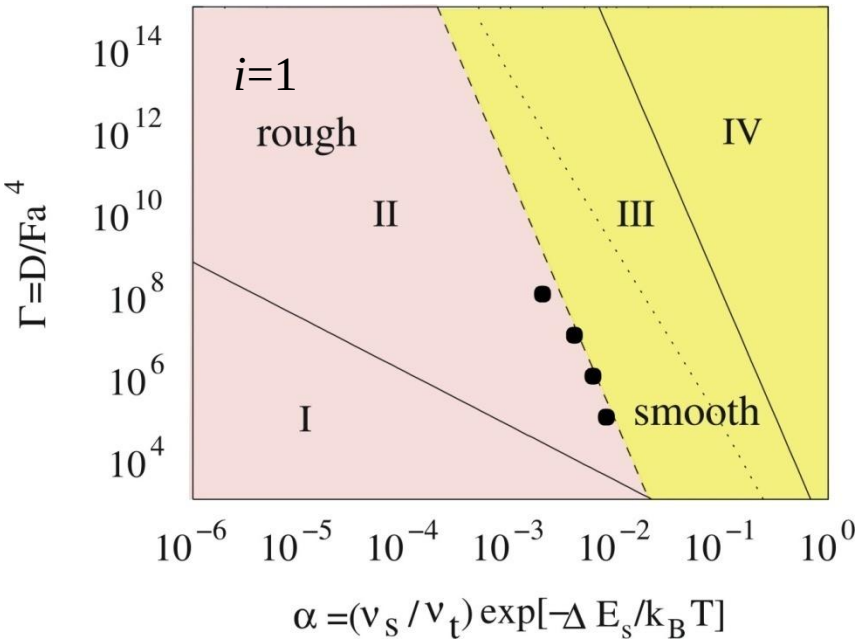
influence of metastable clusters

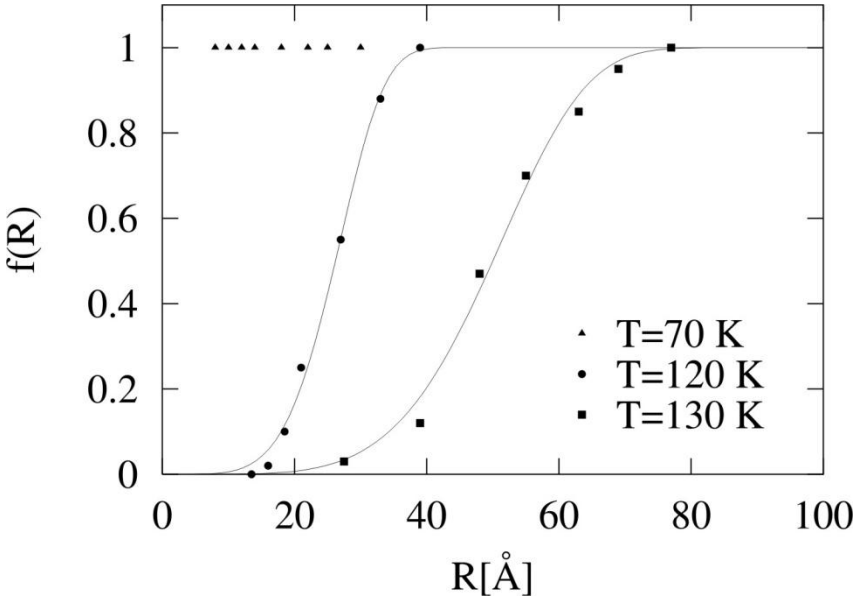
influence of interaction effects

S.Heinrichs, P.M.,
Phys. Rev. B 66, 73402 (2002)

determination of Schwoebel barriers

kinetic phase diagrams





S.Heinrichs, P.M.,
Phys. Rev. Lett. 87, 149605 (2001)

Summary and Conclusions

Submonolayer Growth of Alloys:

mean-field theory gives new scaling laws for island densities; complex crossovers when cluster stabilities dependent on composition; suggestion for determination of effective interactions

Magnetic Nanoalloys

growth model for $CoPt_3$ on weakly interacting vdW substrate allows one to understand the kinetic limitations for the development of $L1_2$ order; treatment of crystalline magnetic anisotropies within bond picture can explain occurrence of temperature window for PMA due to competition of Pt segregation and cluster shape effects

Second Layer Nucleation

mean-field theory fails for small critical nuclei due to fluctuations of atom numbers on islands; stochastic approach and extensions provide a general theory, including metastable subcritical clusters and adatom interactions; prediction of rough vs. smooth layer-by-layer growth; determination of Schwoebel barriers

Thanks to: Wolfgang Dieterich (Univ. Konstanz), Stefan Heinrichs (D-fine), Mario Einax (TU Ilmenau) , Jörg Rottler (UBC, Vancouver)