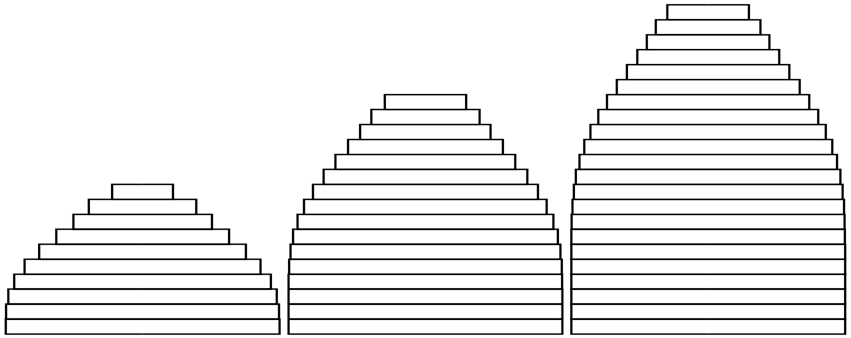
Growth morphology evolution in real time and real space

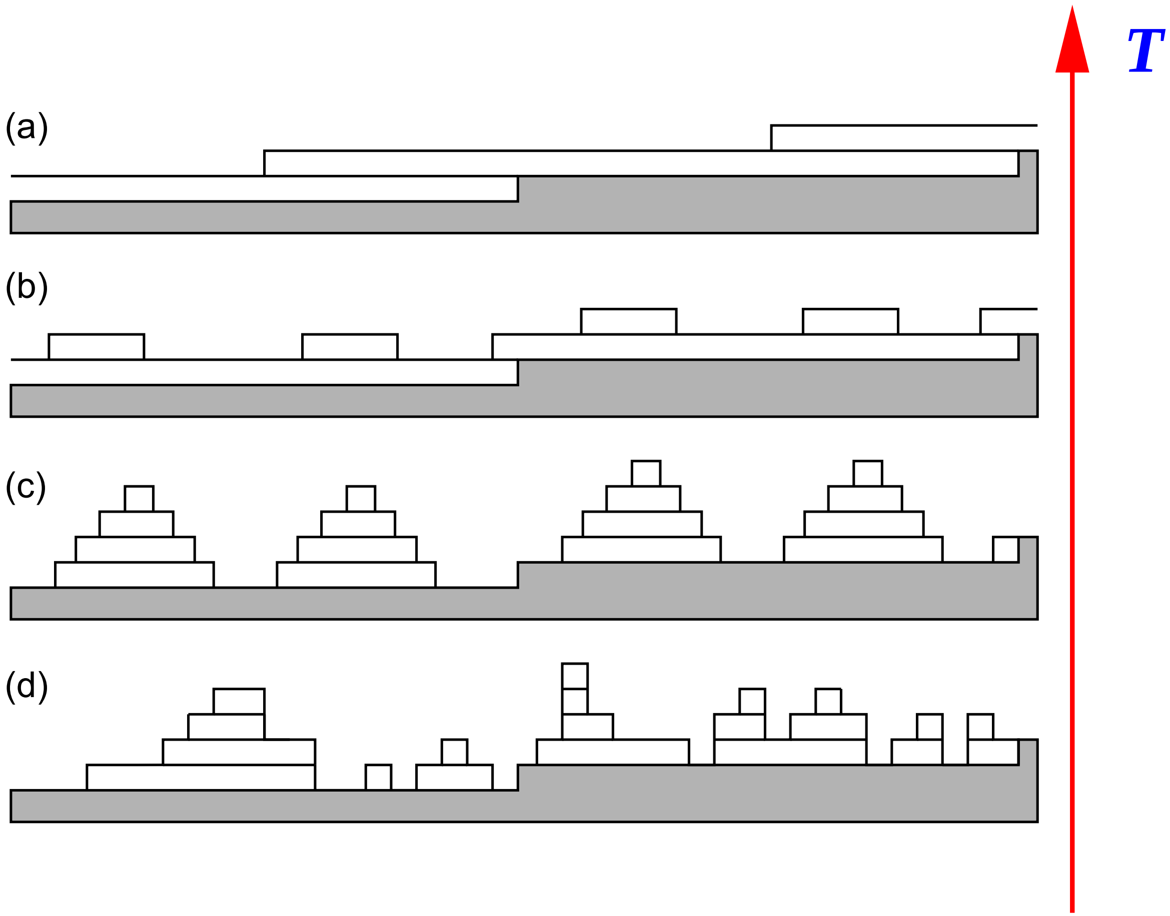
Joachim Krug
Institut für Theoretische Physik, Universität zu Köln



- Multilayer growth modes and interlayer transport
- The Ehrlich-Schwoebel effect
- Mounds and spirals
- Rapid roughening

Symposium on Real Time Growth Studies
DPG Spring Meeting, Regensburg 2007

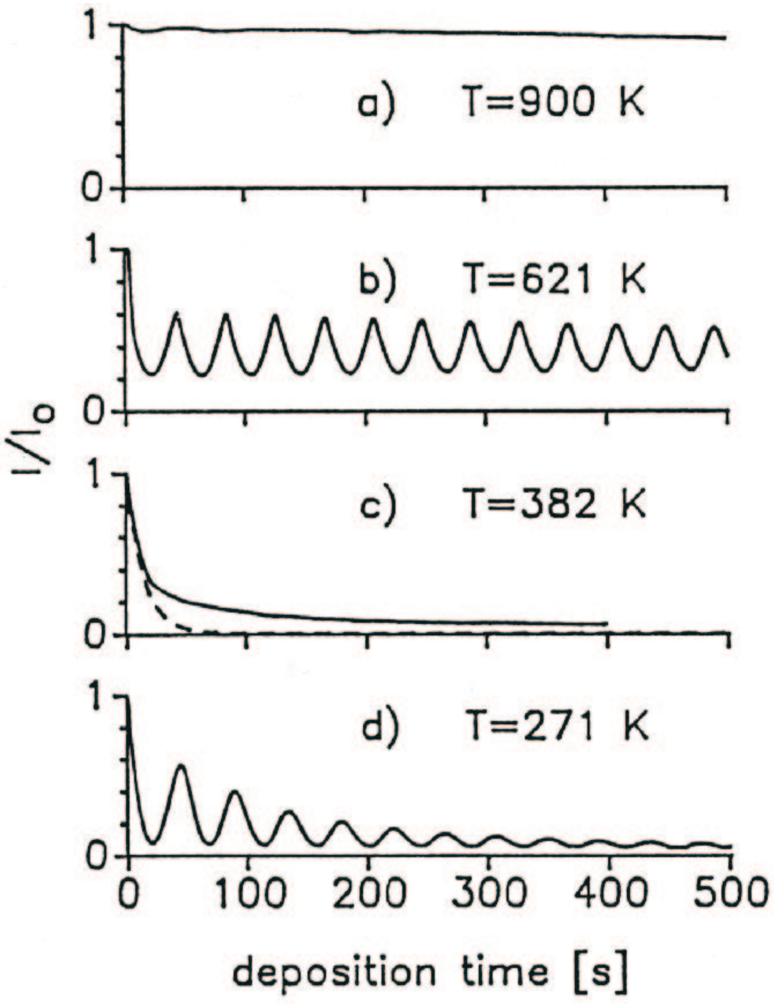
Kinetic growth modes



- step flow
- layer-by-layer
- mounds
- self-affine rough

Key factors: In-layer and inter-layer mobility

Reentrant layer-by-layer growth on Pt(111)



- Nonmonotonic temperature dependence of inter-layer mobility

R. Kunkel, B. Poelsema, L.K. Verheij, G. Comsa, Phys. Rev. Lett. **65**, 733 (1990)

Layer coverages and roughness measures

- Vertical film structure described by **layer coverages** θ_n with $n = 1, 2, 3, \ldots$, $0 \leq \theta_n \leq 1$

- Substrate $\theta_0 = 1$, total coverage $\Theta = \sum_{n \geq 1} \theta_n$

- Exposed coverage/height probability distribution $\varphi_n = \theta_n - \theta_{n+1} \geq 0$

- Surface roughness $W^2 = \sum_{n \geq 0} (n - \Theta)^2 \varphi_n = d^{-2} \langle (h - \langle h \rangle)^2 \rangle$

$h(\vec{r})$: surface profile $\quad$ d: monolayer thickness

- Anti-phase Bragg intensity $I_{\mathrm{anti}} = |\sum_{n \geq 0} (-1)^n \varphi_n|^2$

- Perfect layer-by-layer growth:

$$W^2_{\mathrm{LBL}} = (\Theta - [\Theta])(1 - \Theta + [\Theta]), \quad I_{\mathrm{anti,LBL}} = (1 - 2(\Theta - [\Theta]))^2$$

$[X]$: integer part of X

Statistical growth

- In the absence of interlayer transport layer n incorporates the entire flux incident on the exposed part of layer $n-1$:

$$\frac{d\theta_n}{dt} = \Omega F(\theta_{n-1} - \theta_n)$$

F: flux Ω: atomic area

- The solution is a **Poisson distribution** of heights:

$$\varphi_n = \frac{e^{-\Theta}\Theta^n}{n!}, \quad W = W_{\text{stat}} = \sqrt{\Theta}, \quad I_{\text{anti}} = e^{-4\Theta}$$

- For large Θ

$$\varphi_n \to \frac{1}{\sqrt{2\pi\Theta}} \exp[-(n-\Theta)^2/2\Theta], \quad \theta_n \to \frac{1}{2}\{1 - \text{erf}[(n-\Theta)/\sqrt{2\Theta}]\}$$

Distributed growth models

P.I. Cohen et al., Surf. Sci. **216**, 222 (1989)

- Fraction α_n of atoms deposited in layer n incorporate into layer $n-1$:

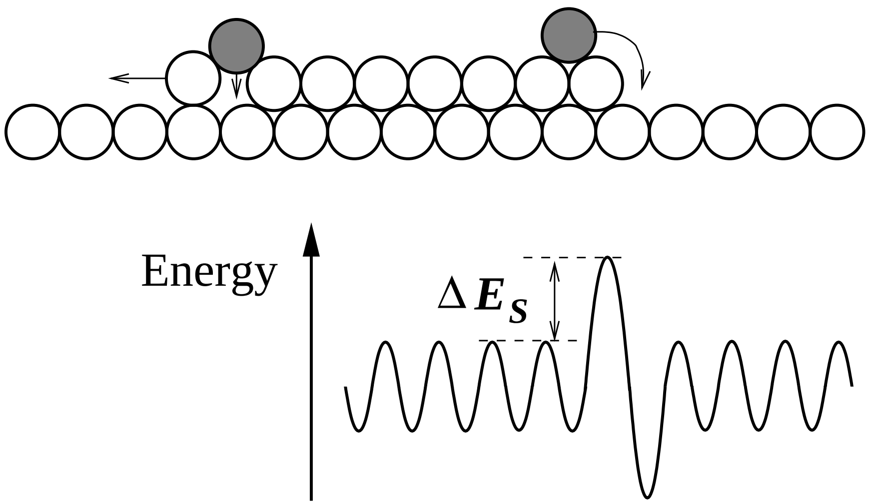
$$(\Omega F)^{-1}\frac{d\theta_n}{dt} = (1-\alpha_n)(\theta_{n-1}-\theta_n) + \alpha_{n+1}(\theta_n - \theta_{n+1})$$

  with the constraint that $\alpha_n = 0$ when $\theta_n = 1$.

- Simplest case: $\alpha_n \equiv \alpha$ — L. Brendel (2001)
- $\alpha < 1/2$: Gaussian height distribution of width $W \approx \sqrt{(1-2\alpha)\Theta}$
- $\alpha > 1/2$: Finite width $W(\Theta \to \infty) \to W_\infty \sim (2\alpha - 1)^{-1}$ for $\alpha \to 1/2$
- $\alpha = 1/2$: $W \sim \Theta^{1/3}$ with Airy function height probability distribution

The Ehrlich-Schwoebel effect

G. Ehrlich, F. Hudda (1966); R.L. Schwoebel, E.J. Shipsey (1966)



D: In-layer diffusion

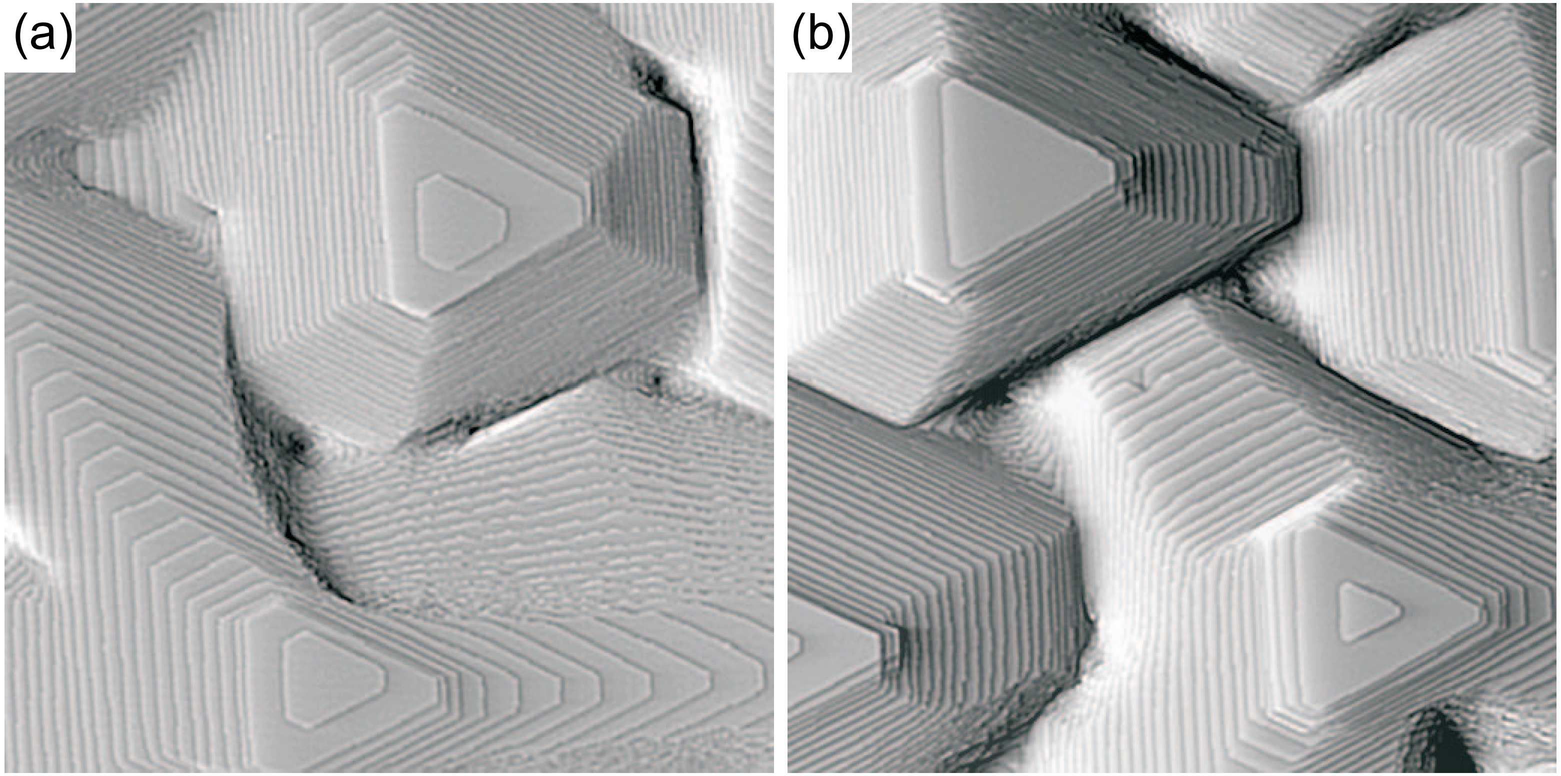
D': Interlayer transport

$$D'/D = \exp[-\Delta E_{\mathrm{S}}/k_{\mathrm{B}}T] < 1$$

- Growth instabilities of vicinal surfaces during growth and sublimation
  R.L. Schwoebel, 1969; G.S. Bales & A. Zangwill, 1990
- Diffusion bias $\Rightarrow$ “uphill” growth-induced mass current
  J. Villain, 1991; JK, M. Plischke, M. Siegert, 1993
- Enhanced two-dimensional nucleation on top of islands
  Kunkel et al., 1990; J. Tersoff, A.W. Denier van der Gon, R.M. Tromp, 1994

Mound formation on Pt(111) at 440 K

T. Michely, JK: Islands, Mounds and Atoms (2004)



⇒ mound shapes **visualize** the coverage distribution

Statistical growth with delayed nucleation

D. Cherns (1977); JK, P. Kuhn (2002)

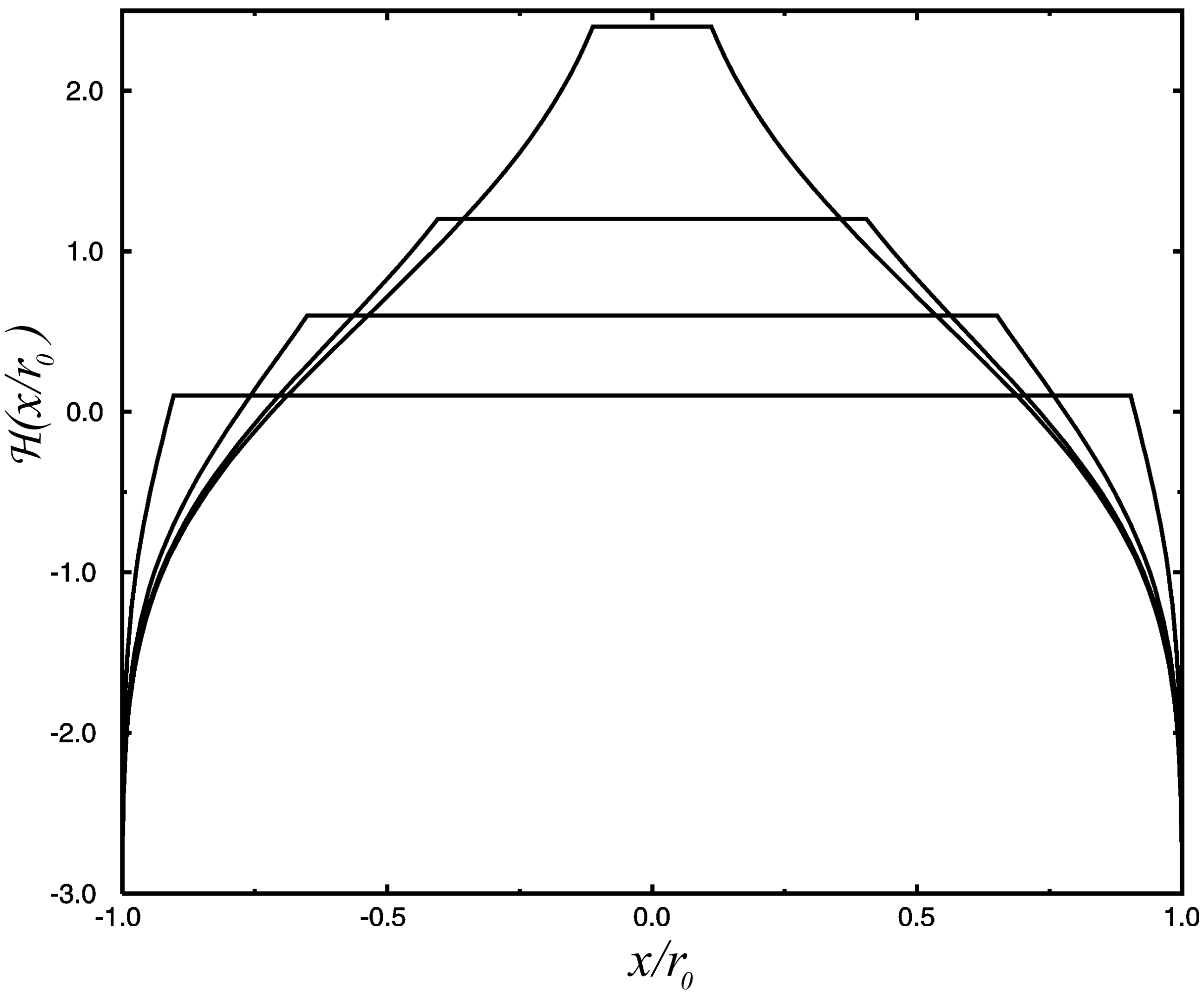
- Statistical growth dynamics for layers $0 \leq n \leq n_{\rm top} - 1$, and $\dot{\theta}_{n_{\rm top}} = F\Omega\theta_{n_{\rm top}-1}$
- New top layer nucleates $[n_{\rm top} \to n_{\rm top} + 1]$ when $\theta_{n_{\rm top}} = \theta_c$
- $\theta_c \to 0$: statistical growth $\theta_c \to 1$: layer-by-layer growth
- Layer distribution for large Θ is a cut-off error function with width

$$W = \sqrt{(1 - \theta_c)\Theta}$$

- Inflection point of the coverage profile at $n = \Theta$
- Microscopic interpretation of θ_c: JK, P. Politi, T. Michely (2000)

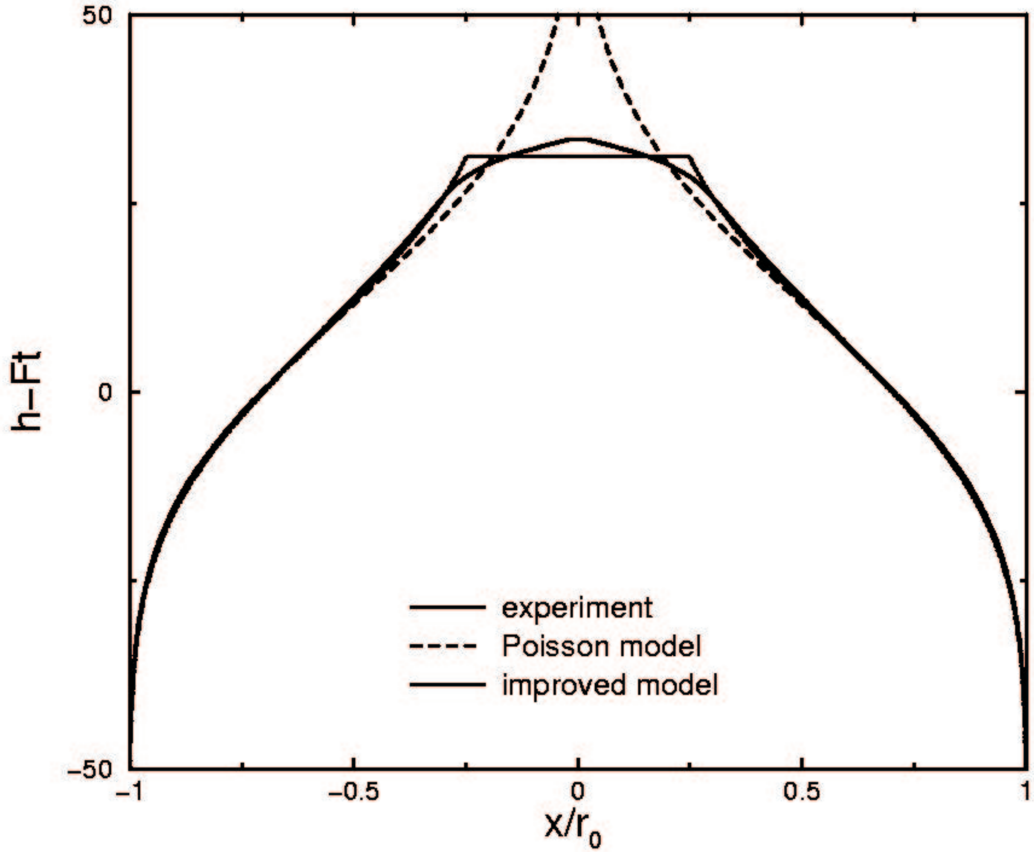
$$\theta_c \sim \left(\frac{R_{\rm top}}{R_{\rm base}} \right)^2 \sim \left(\frac{D'}{D} \right)^{2/5}$$

Theoretical mound shapes



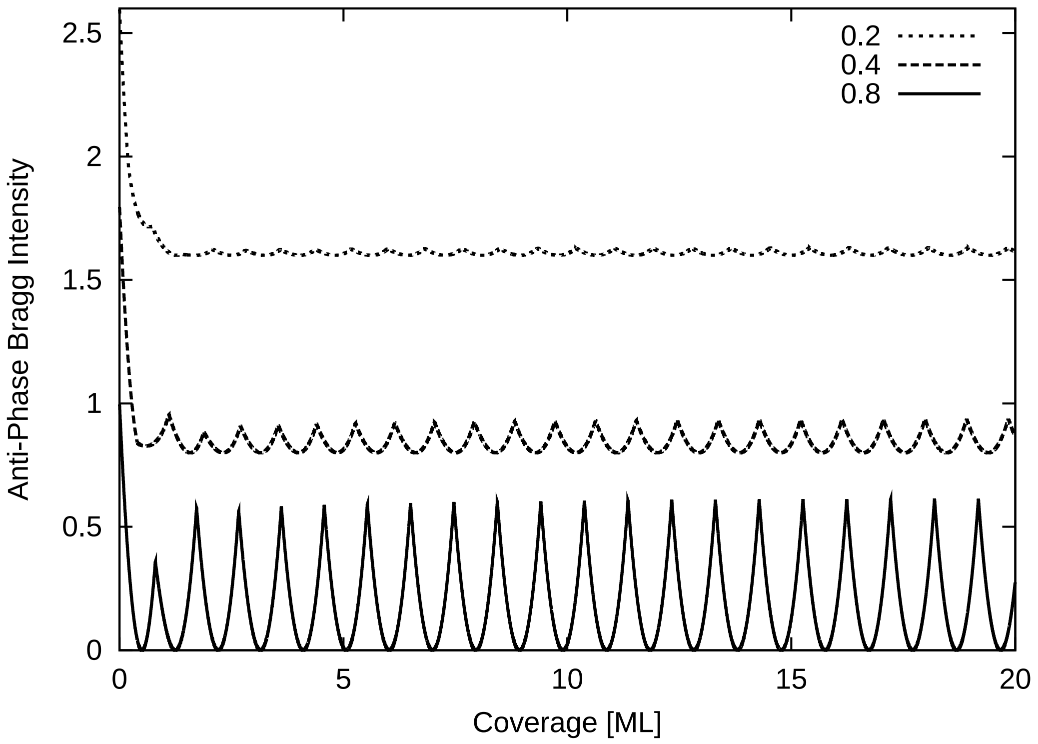
$\theta_c = 0.01, 0.15, 0.4, 0.8$

Fit to Pt(111) mound growth



$$\theta_c \approx 0.22 \quad \Rightarrow \quad \Delta E_S \approx 0.14\text{eV}$$

Anti-phase Bragg intensity



- Persistent oscillations of amplitude $\sim \theta_c^2$ despite unbounded increase of the surface width ($W \sim \sqrt{\Theta}$)

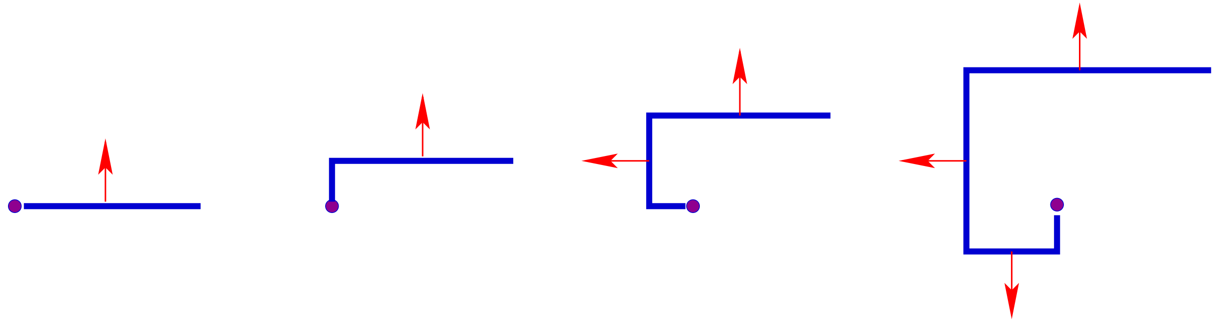
- On longer time scales oscillations are damped due to dephasing amoung different mounds

Spiral growth

Paul Klee: Heroische Rosen

Theories of spiral growth

- Kinematics of facetted spiral growth — I. Markov: Crystal Growth for Beginners



$\Rightarrow$ step spacing set by length of core segment

- Burton, Cabrera & Frank (1951): Normal step velocity

$$v_n = v_0(1 - \kappa R_c)$$

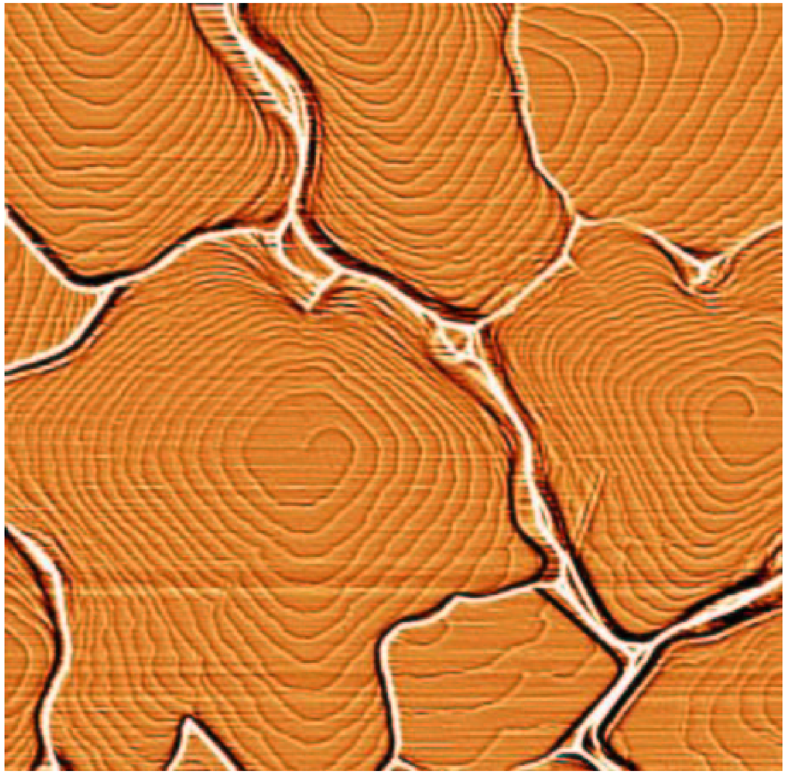
κ : curvature $\quad R_c$: radius of critical nucleus

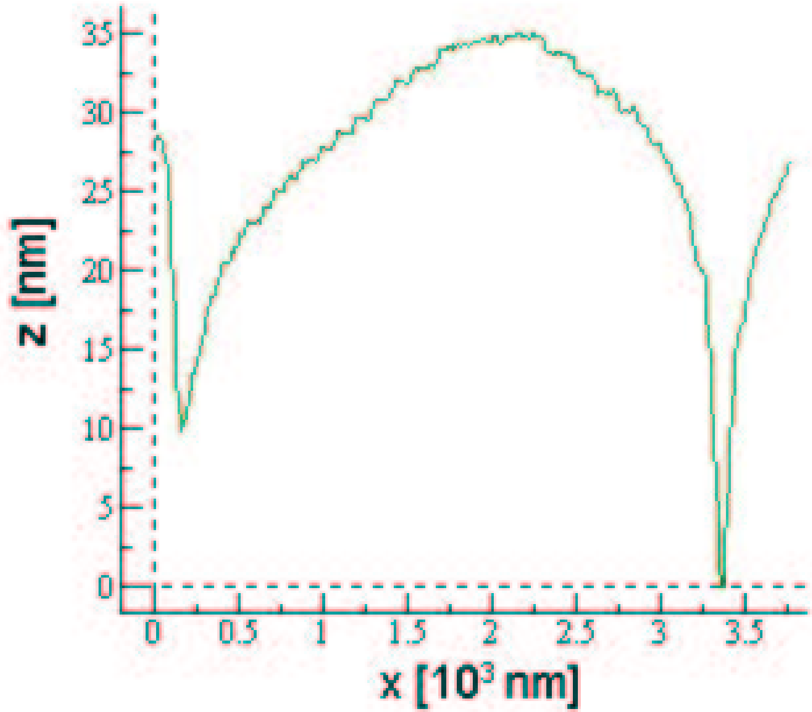
$\Rightarrow$ $\kappa = 1/R_c$ at the spiral core, asymptotic step spacing $\ell \approx 19.81 \times R_c$

- Karma & Plapp (1998): Nonlocal step dynamics without desorption

$\Rightarrow$ initial steepening, constant asymptotic step spacing depending on D/F

Spiral growth of perylene/Al_2O_3/glass

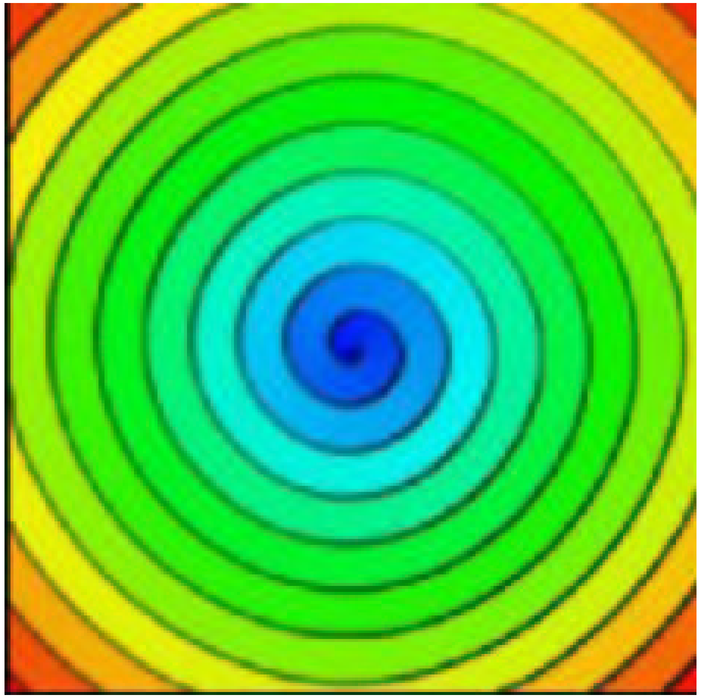




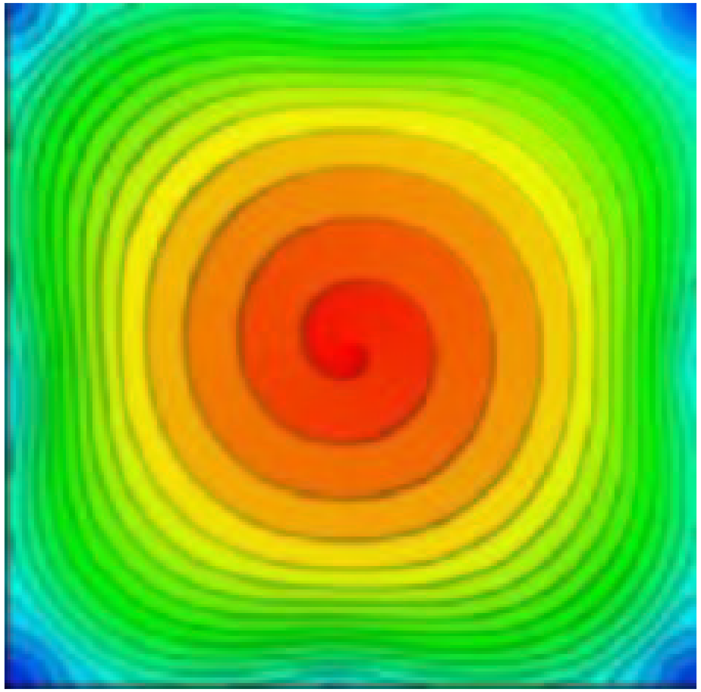
A. Farahzadi, M. Mohamadi, P. Niyamakom & M. Wuttig (RWTH Aachen)

- ”Nonclassical” spiral hillocks:
  Non-constant step spacing ⇔ mound-like height profile

Phase field modeling of spiral growth



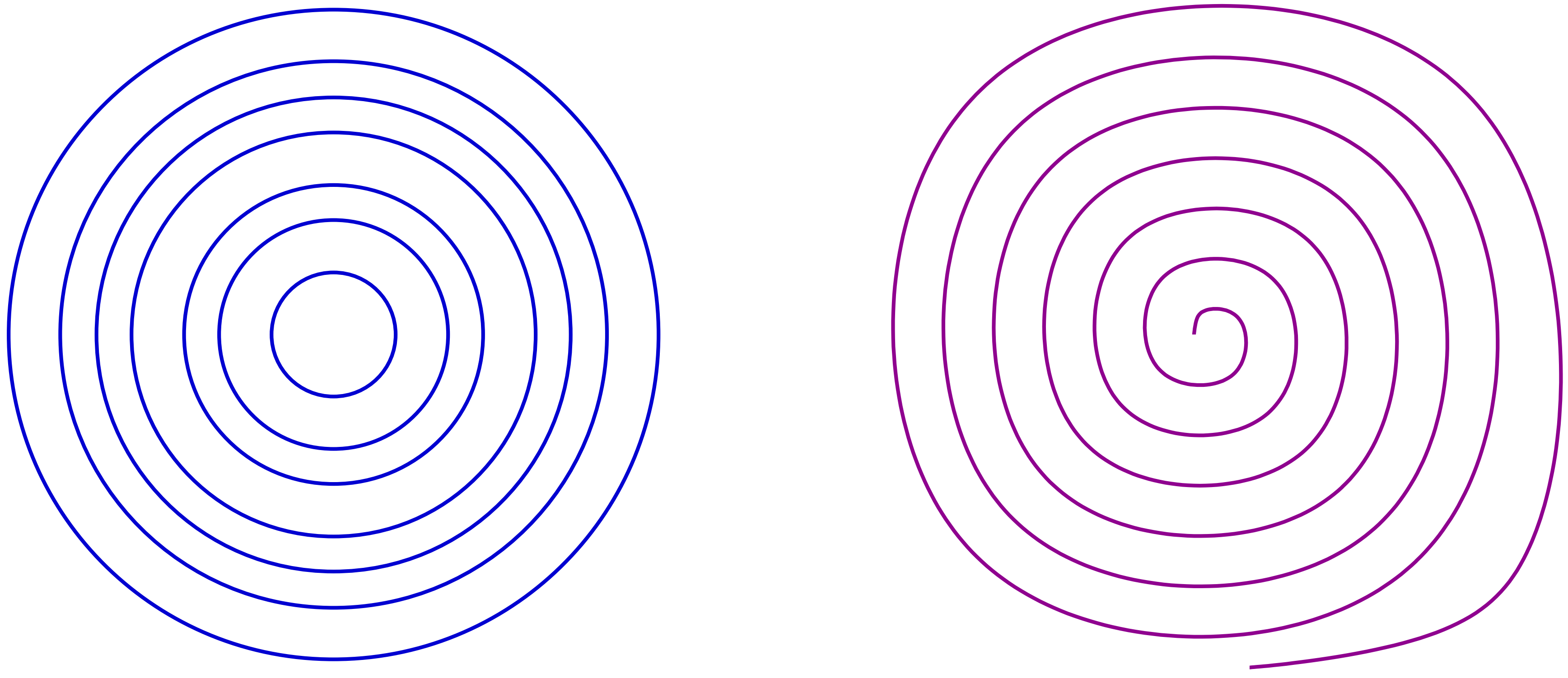
classical



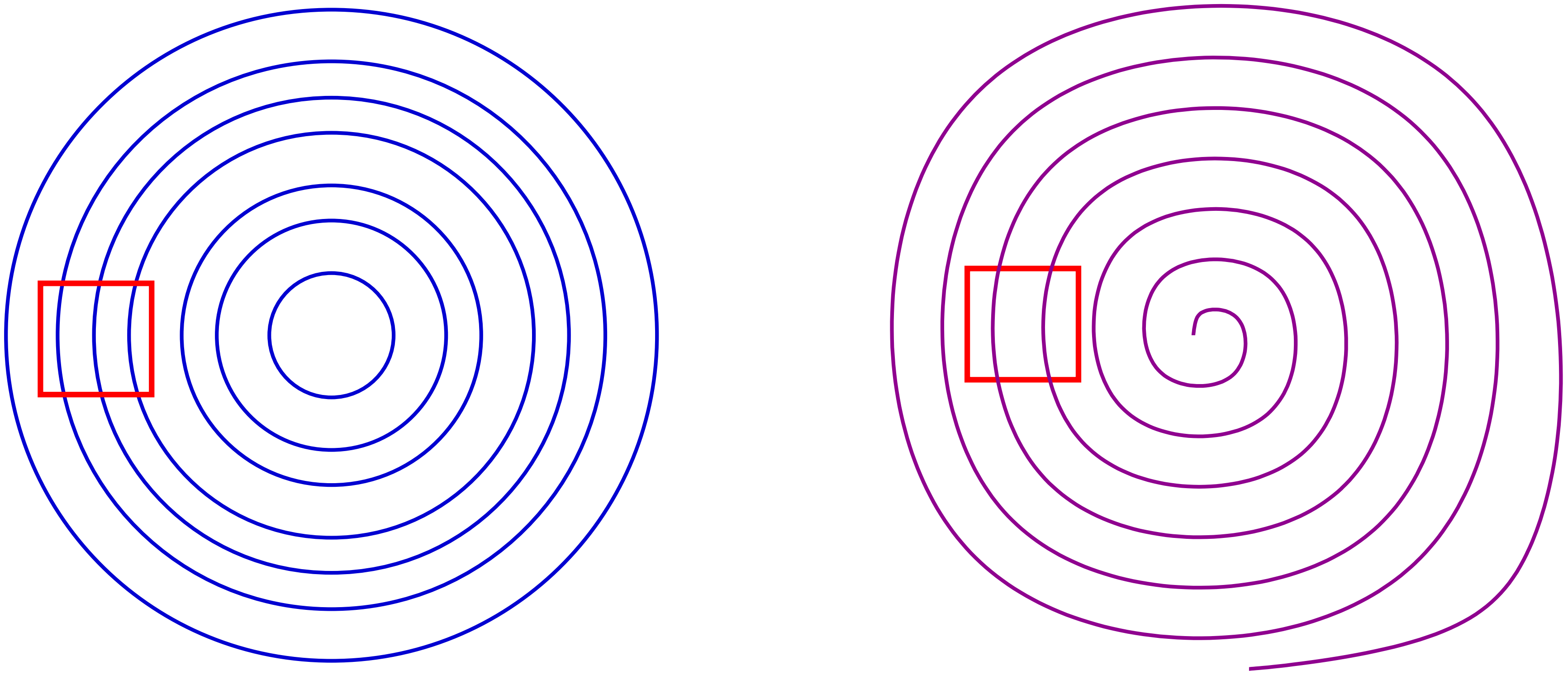
with Ehrlich-Schwoebel barrier

A. Rätz, A. Voigt, caesar Bonn

Mounds versus spirals

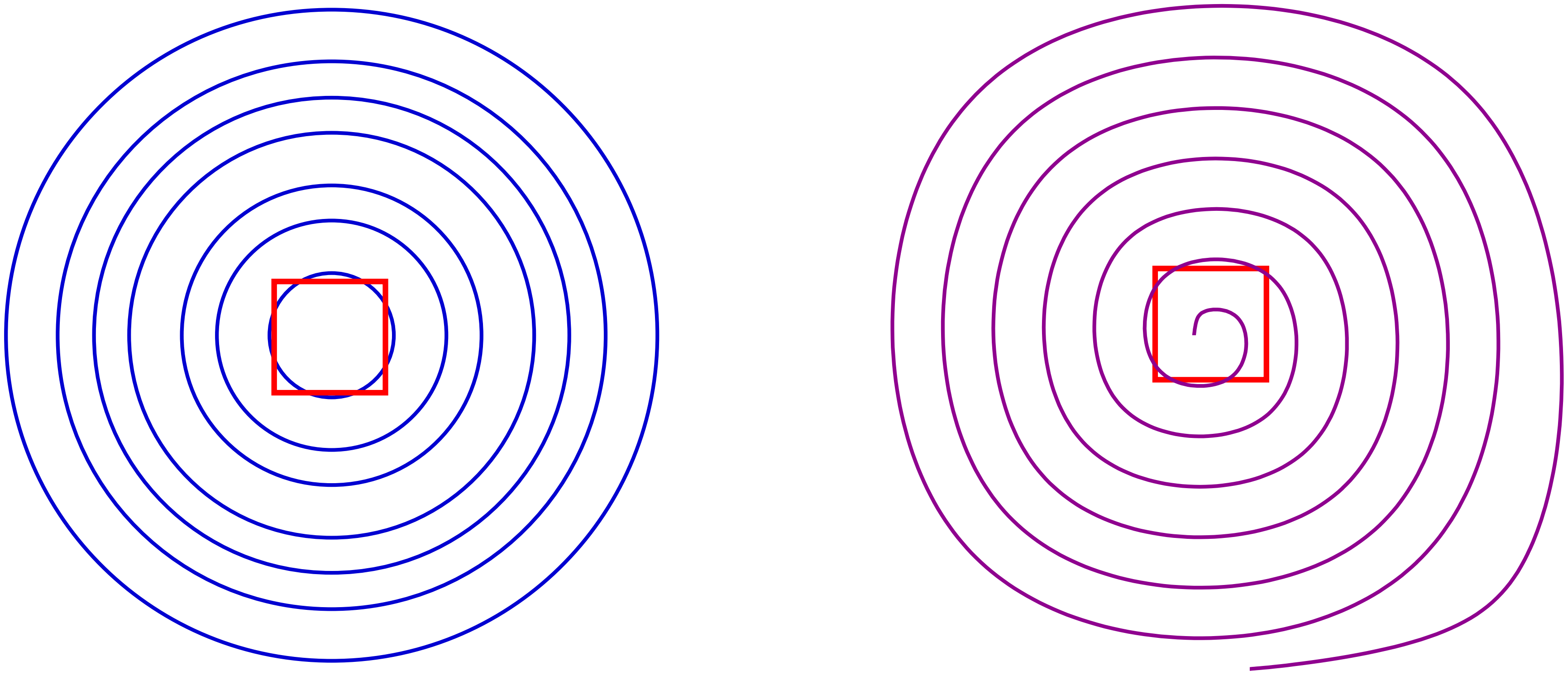


Mounds versus spirals



- **Hillsides**: Steepening due to diffusion bias

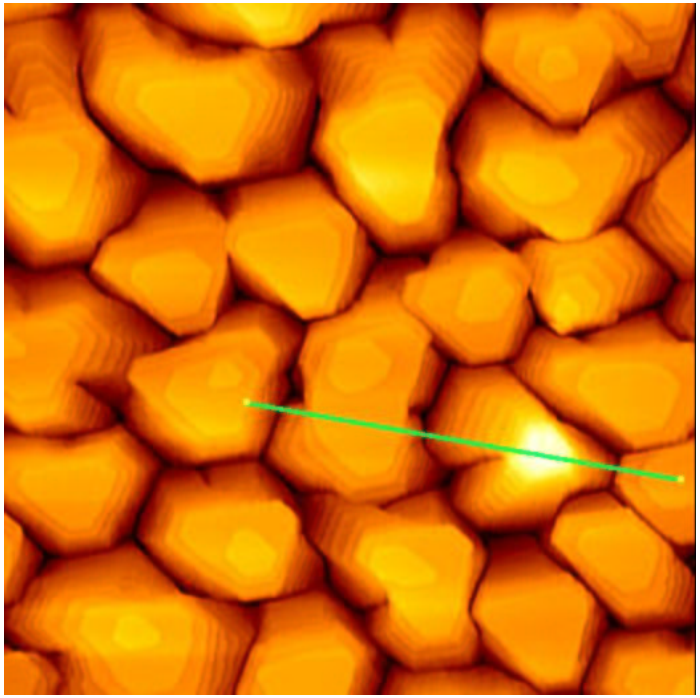
Mounds versus spirals

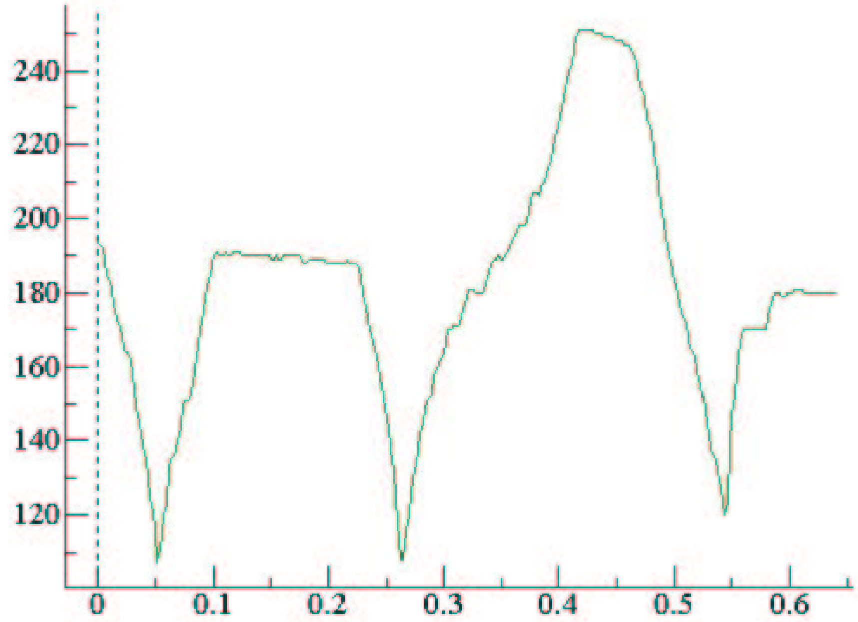


- **Hillsides**: Steepening due to diffusion bias
- **Top**: Atoms near the spiral core feel no confinement due to the Ehrlich-Schwoebel effect, but there is also no need for nucleation!

Spiral growth on Pt(111)

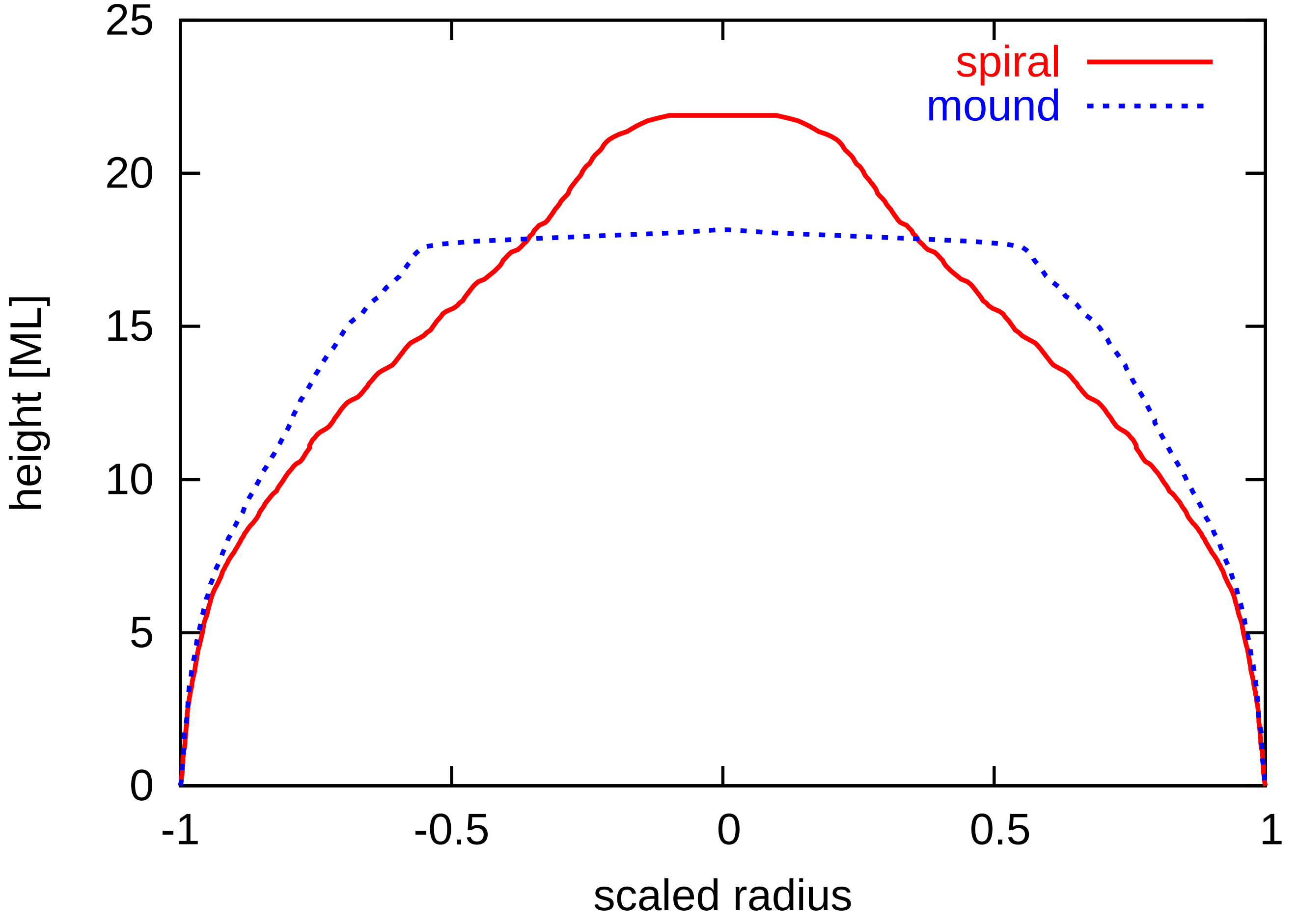
O. Ricken, A. Redinger, T. Michely, Universität zu Köln → poster O 17.64





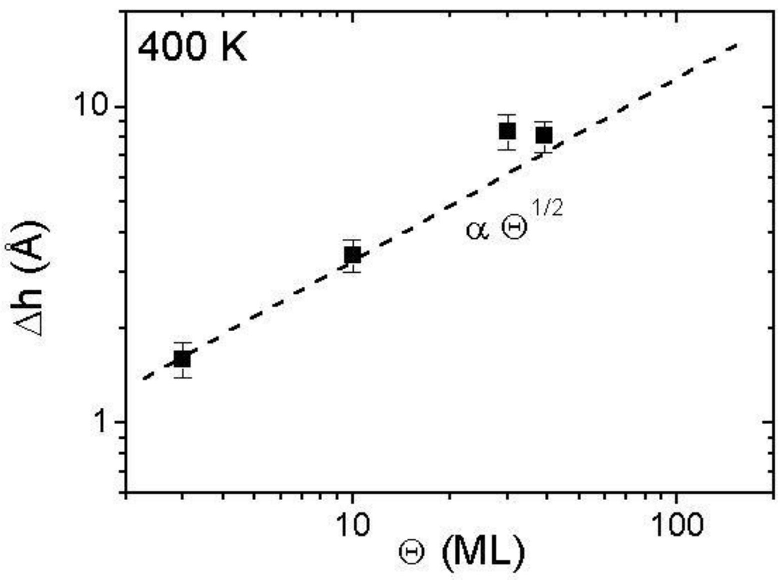
- Screw dislocations induced by He^+ bombardment
- Mounds and spirals coexist, and spiral hillocks are higher

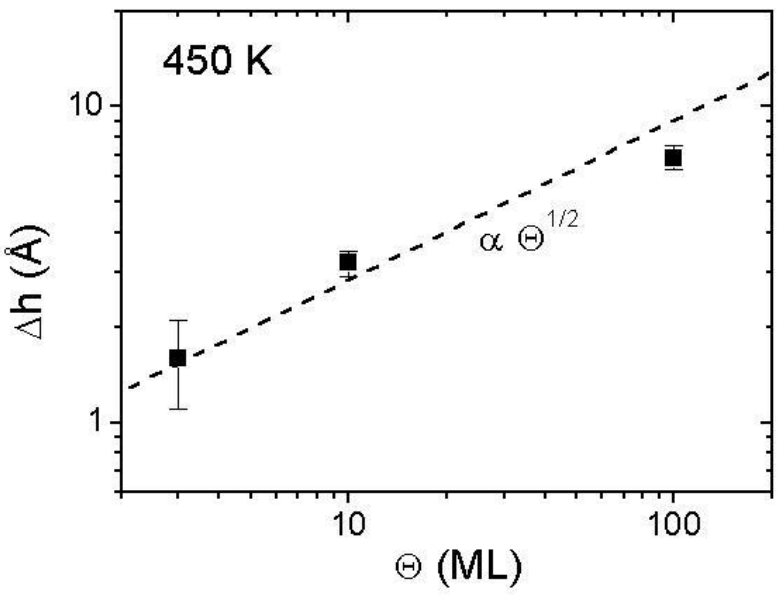
Comparison of shapes at 400 K



$\Rightarrow$ enhanced ”effective Ehrlich-Schwoebel barrier” $\Delta E_S \rightarrow \Delta E_S + 0.13\text{eV}$

Scaling with film thickness





- Δh: Height difference between spiral hillocks and mounds
- Scaling form of the coverage profile

$$\theta_n(t) = \mathscr{F}[(n - \Theta)/\sqrt{\Theta}]$$

implies $\Delta h \sim \sqrt{\Theta}$

Is the Ehrlich-Schwoebel effect relevant for organic thin film growth?

- PTCDA on Ag(111): 2D $\rightarrow$ 3D transition and slope selection
  Krause, Schreiber, Dosch, Pimpinelli & Seeck, EPL **65**, 372 (2004); Kilian, Umbach & Sokolowski, Surf. Sci. **573**, 359 (2004)

- Non-classical spiral hillocks on pentacene
  Ruiz et al., Chem. Mater. **16**, 4497 (2004)

- Fractal mounds on pentacene
  Zorba, Shapir & Gao, PRB **74**, 245410 (2006)

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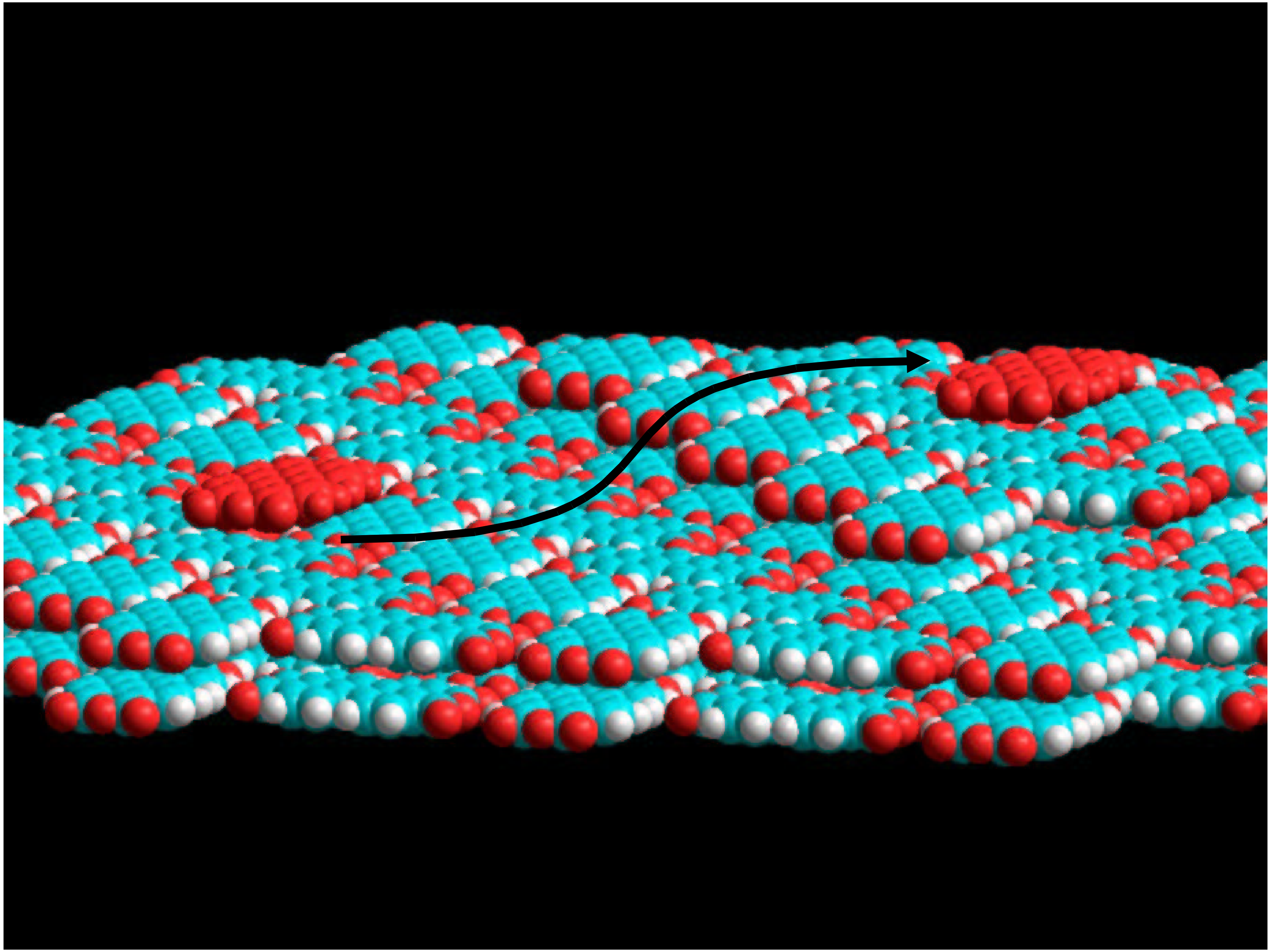
Microscopic calculation: M. Fendrich, University of Duisburg-Essen

- Molecular statics calculation for α-phase of PTCDA ($C_{24}\,O_6\,H_8$)

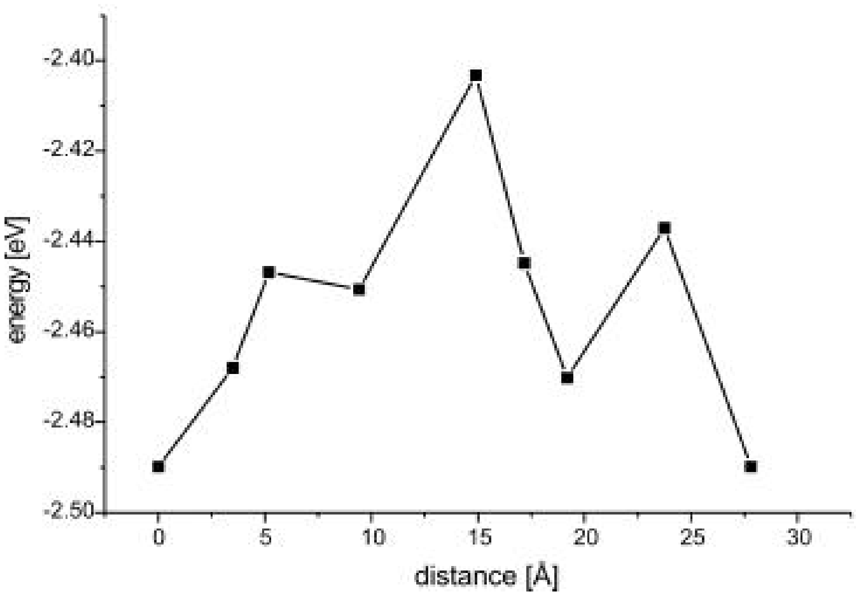
- AMBER force field + electrostatics, 2 rigid layers, NEB algorithm

Computational setup

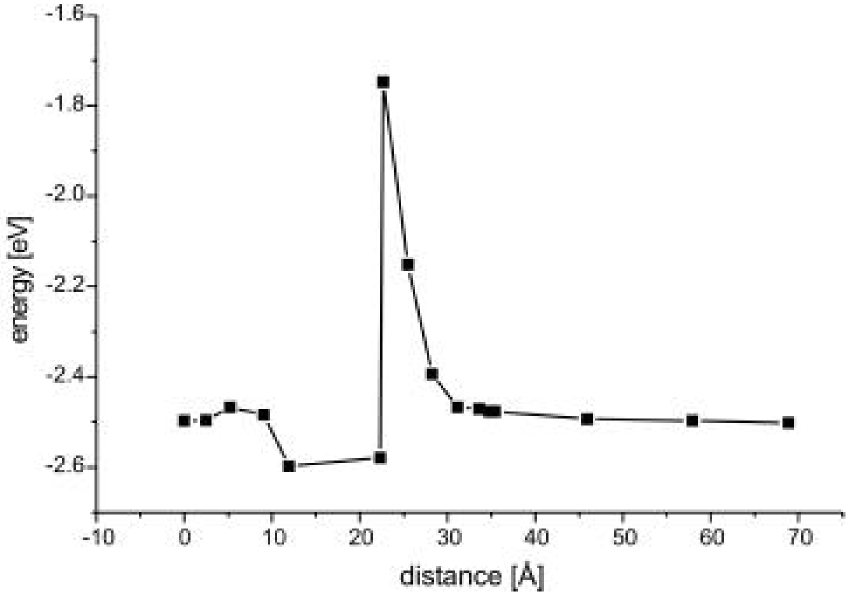


Results

diffusion on the terrace

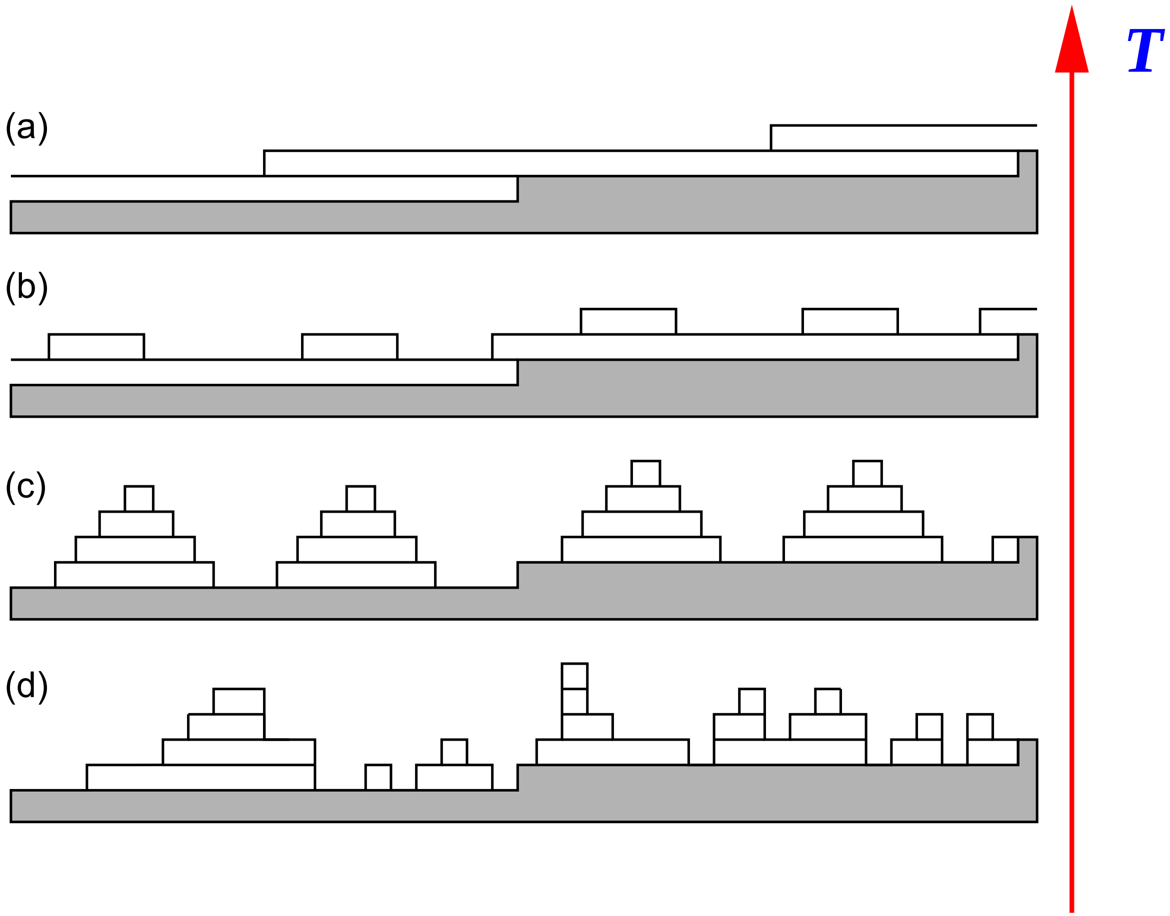


over the step edge



- diffusion barrier $E_D \approx 0.08$ eV, additional ES-barrier $\Delta E_S \approx 0.67$ eV
- complete suppression of interlayer transport at room temperature

Kinetic growth modes



- step flow
- layer-by-layer
- mounds
- self-affine rough

Anomalous scaling and rapid roughening

JK, Adv. Phys. **46**, 139 (1997)

- Scaling theory of surface roughness evolution

$$G(r,t) = \langle [h(\vec{r},t) - h(0,t)]^2 \rangle = a^2(t)\, r^{2\alpha}\, \mathscr{G}(r/\xi(t))$$

$$\xi(t) \sim t^{1/z}, \quad a(t) \sim t^{\lambda}, \quad G(r \to \infty, t) = 2W^2(t) \sim t^{2\beta}$$

- **Anomalous scaling**: Steepening exponent $\lambda = \beta - \alpha/z > 0$

- **Rapid roughening:** $\beta > 1/2$ asymptotically $\Rightarrow W > W_{\mathrm{stat}}$

- Stochastic and deterministic roughening mechanisms generally lead to $\beta \leq 1/2$ and $W < W_{\mathrm{stat}}$

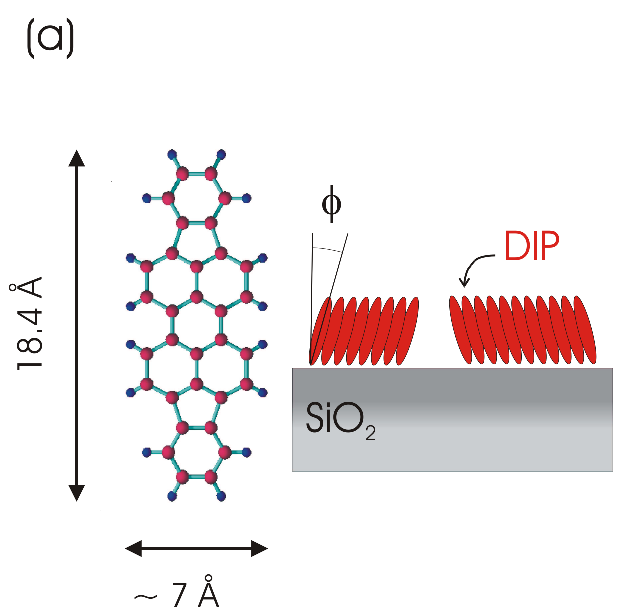
  $\Rightarrow$ rapid roughening (probably) requires thermodynamically driven true uphill mass transport or quenched disorder

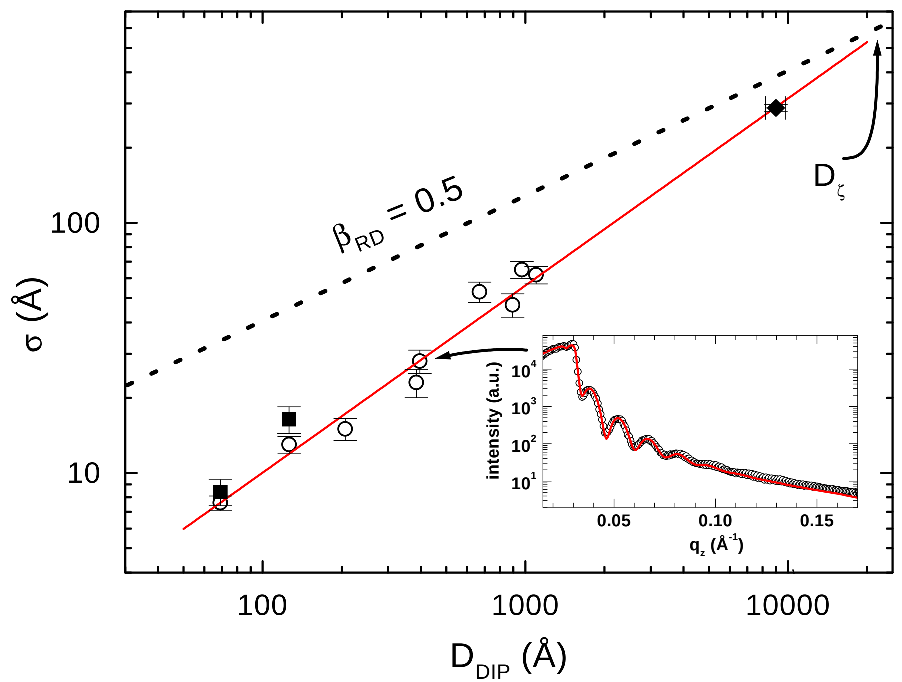
- **Caution**: $\beta > 1/2$ does not necessarily imply $W > W_{\mathrm{stat}}$

Rapid roughening in organic thin film growth

- DIP on SiO_2: $\beta \approx 0.75$, $\alpha \approx 0.68$, $1/z \approx 0.92$, but $W < W_{\mathrm{stat}}$

Dürr et al., PRL **90**, 016104 (2003)



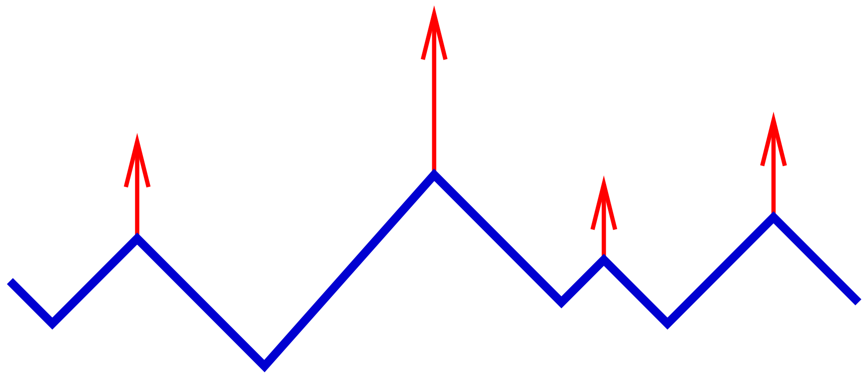


- Phthalocyanine on glass: $\beta \approx 1.02,\ \alpha \approx 0.61,\ \ 1/z \approx 0.72$

Yim, Jones, PRB **73**, 161305(R) (2006)

Rapid roughening induced by disorder

- Kardar-Parisi-Zhang equation with **quenched random growth rates** yields $W \sim t/[\ln t]^{\phi} \Rightarrow$ asymptotically $\beta = 1$ JK, PRL **75**, 1795 (1995)



- Kinetic Monte Carlo simulations of deposition with **quenched random diffusion** yields $\beta \approx 0.6$

  F. Eisholz, E. Schöll and A. Rosenfeld, APL **84**, 4167 (2004)

- Both mechanisms require lateral disorder that **persists vertically** throughout the thickness of the film

Conclusions

- Broad range of concepts available for the analysis of morphology evolution during thin film growth
- Combine insights from **real space** and **real time** probes
- Expect novel effects in organic films from internal degrees of freedom

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Thanks to:

- Philipp Kuhn (Köln)
- Thomas Michely & group (Köln)
- Markus Fendrich (Duisburg)
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