Pattern formation by step edge barriers: The growth of spirals and wedding cakes

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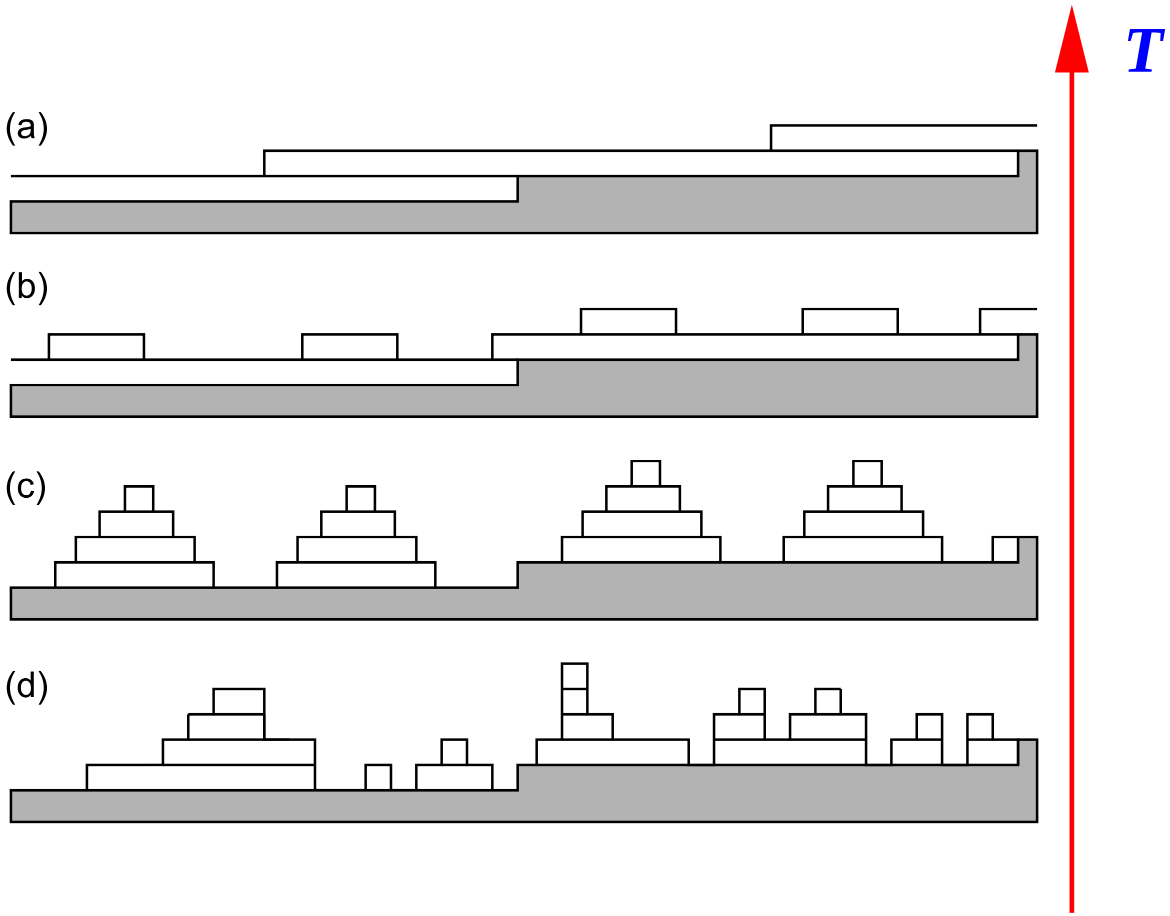
MRS Fall Meeting, Boston, 11/26/2007

Kinetic growth modes

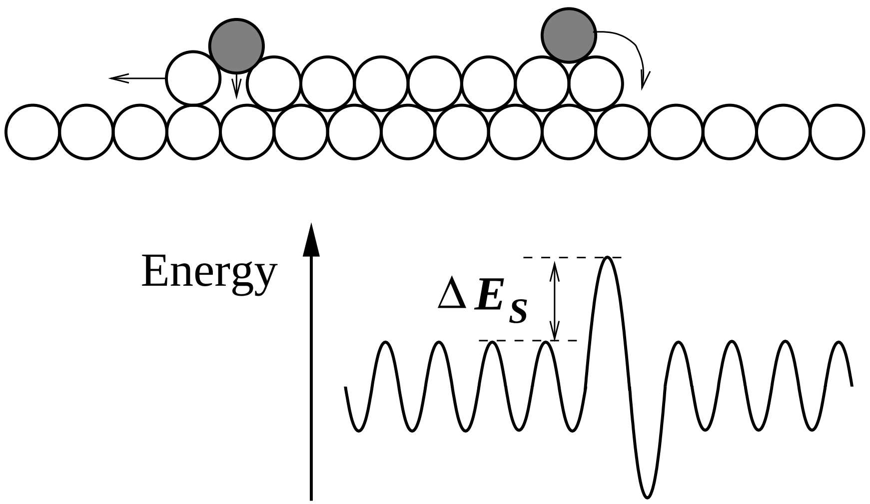


- step flow
- layer-by-layer
- mounds
- self-affine rough

Key factors: In-layer and inter-layer mobility

The Ehrlich-Schwoebel effect

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



D: In-layer diffusion

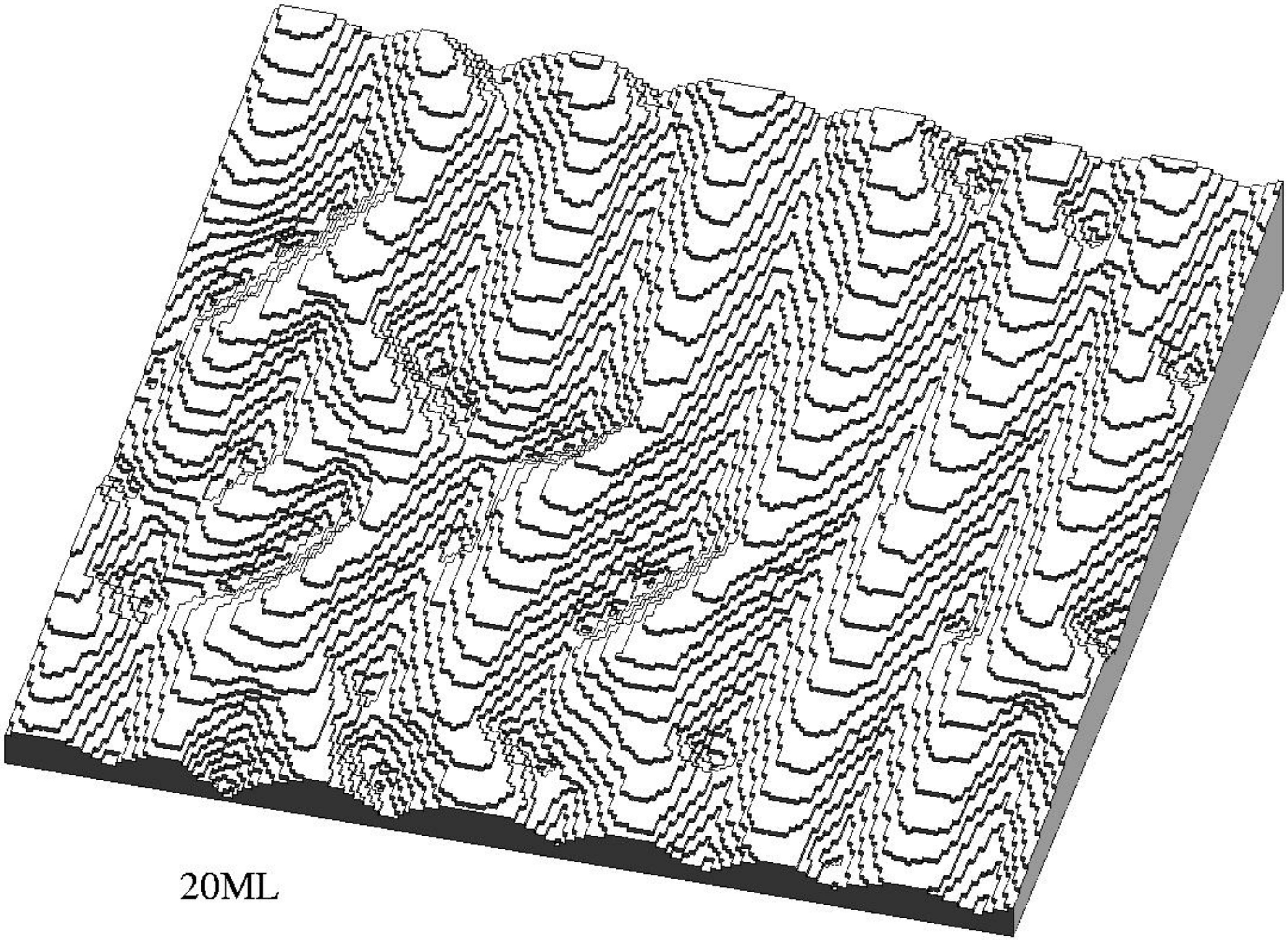
D': Interlayer transport

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

- 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; Tersoff et al., 1994; JK, P. Politi, T. Michely, 2000

Step meandering by the ES effect

J. Kallunki, JK, Europhys. Lett. **66**, 749 (2004)

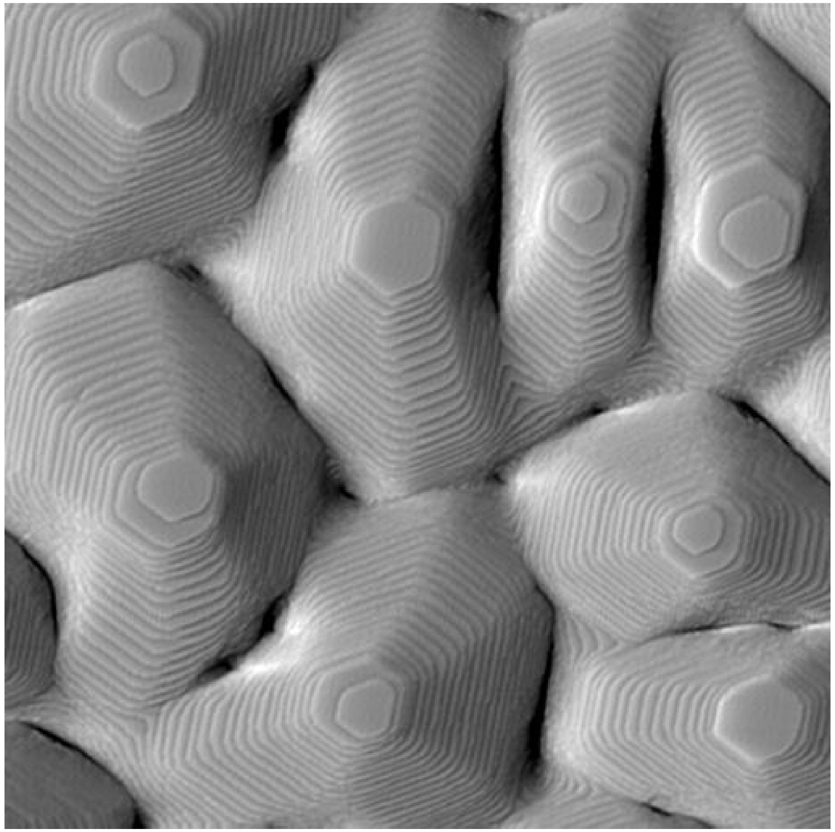


20ML

Wedding cakes on Pt(111)

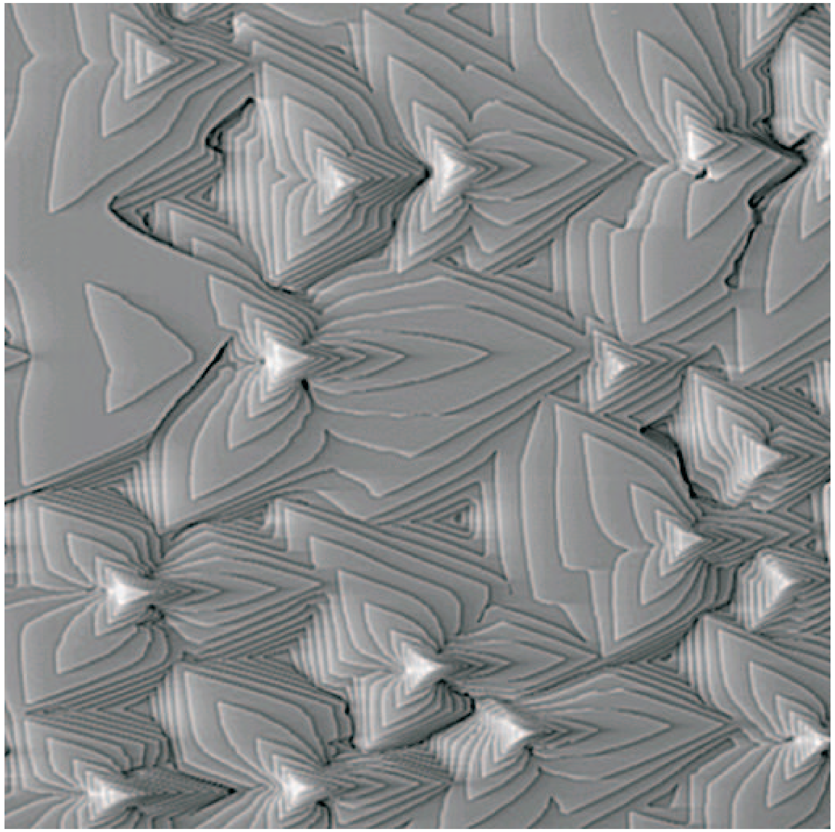
T. Michely, JK: Islands, Mounds and Atoms (2004)

440 K



166 nm

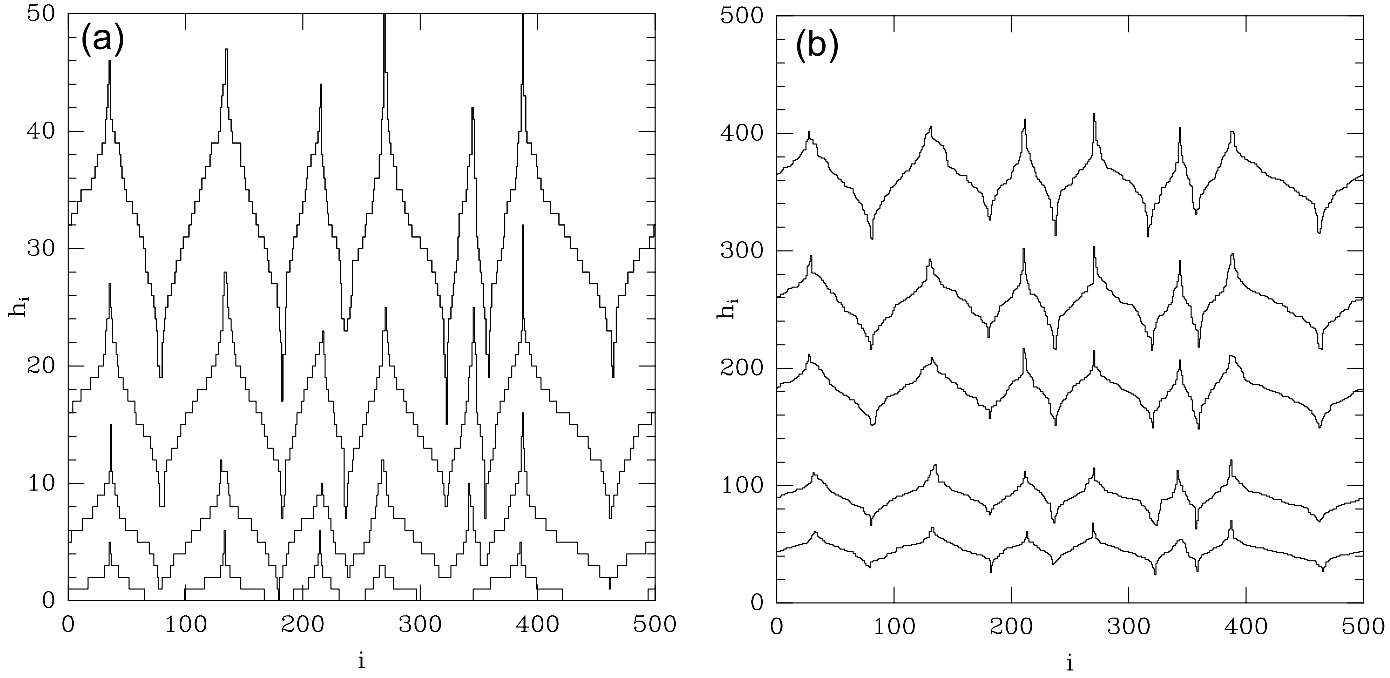
520 K



790 nm

One-dimensional growth simulation with $D' = 0$

JK, J. Stat. Phys. 87, 505 (1997)

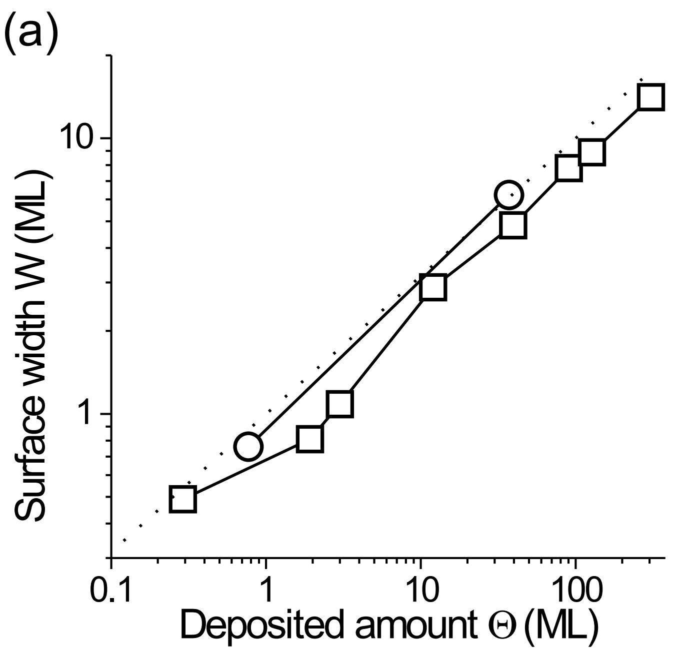


$\Theta = 1 - 32$ ML $\qquad$ $\Theta = 45 - 362$ ML

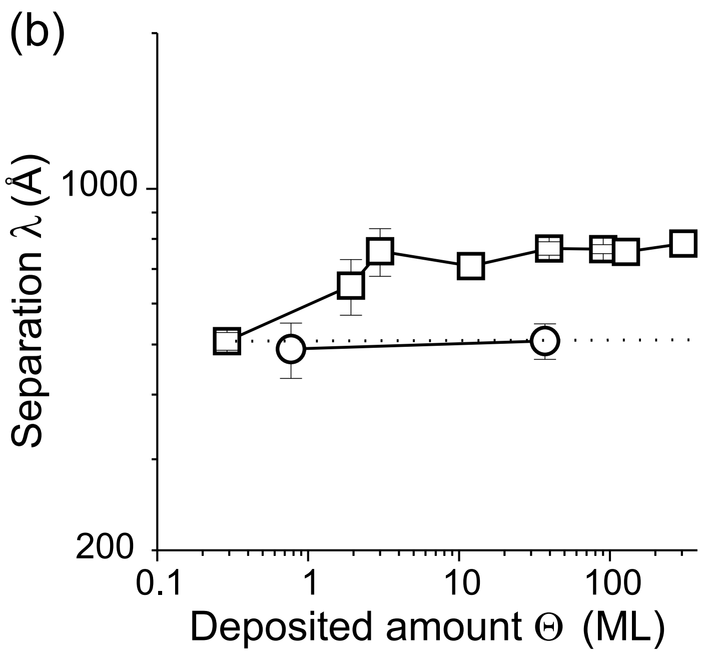
- Pattern with fixed length scale $\sim (D/F)^{1/4}$ $\quad F$: deposition flux
- Roughness $W = \sqrt{\langle (h - \bar{h})^2 \rangle}$ grows as $\sqrt{\Theta}$

Test of the model: Wedding cakes on Pt(111)

Roughness: $W = \sqrt{\Theta}$



Correlation length: $\lambda =$ const.

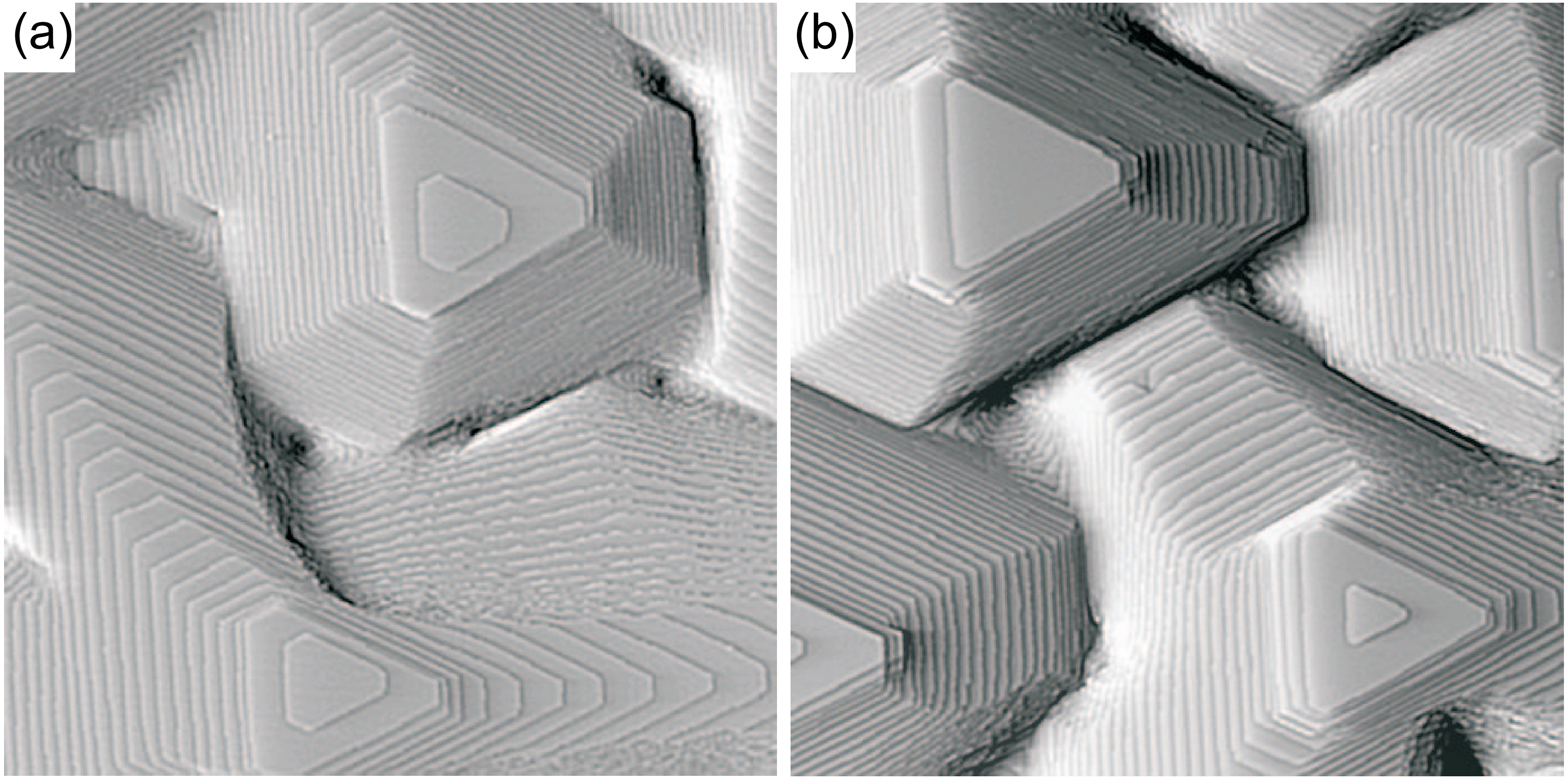


□: clean growth conditions

O: growth in the presence of CO

Kalff et al., Surf. Sci. Lett. 426, L447 (1999)

Mound shape and layer coverages



⇒ mound shapes **visualize** the coverage distribution

A simple model for the shape of wedding cakes

JK, P. Kuhn, 2002

- Layer coverages $\theta_n \in [0,1]$, $n = 0,1,2,..,n_{\mathrm{top}}$

- Interlayer transport is completely suppressed for $n < n_{\mathrm{top}}$:

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

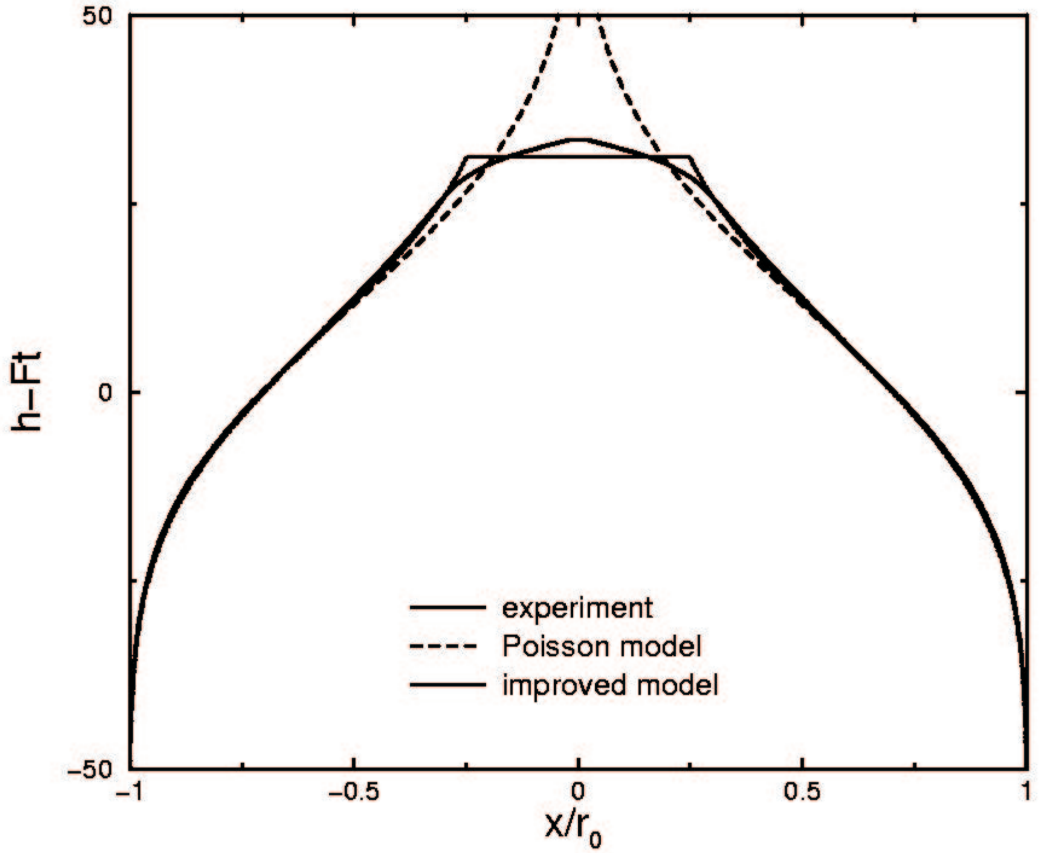
- Top layer grows as $\dot{\theta}_{n_{\mathrm{top}}} = F\theta_{n_{\mathrm{top}}-1}$ and a new top layer nucleates $[n_{\mathrm{top}} \to n_{\mathrm{top}}+1]$ when $\theta_{n_{\mathrm{top}}} = \theta_c$

- Layer distribution for large Θ is a cut-off error function of width $W = \sqrt{(1-\theta_c)\Theta}$ and inflection point at $n = \Theta$

- Microscopic interpretation of θ_c:

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

Comparison with wedding cakes on Pt(111)



- Delayed nucleation on top terraces implies flat plateaux
- Nucleation takes place at coverage $\theta_c \approx 0.22 \quad \Rightarrow \quad \Delta E_S \approx 0.14$ eV

Spiral growth

Paul Klee: Heroische Rosen (1938)

Spirals in the history of crystal growth

LETTERS TO THE EDITORS

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Role of Dislocations in Crystal Growth

THE theory of nucleation in the formation of liquid or solid phases from the vapour, the most detailed treatment of which in any published work is that by Becker and Döring[1,2], is in satisfactory quantitative agreement with experiment with regard to the primary nucleation of liquid droplets[1,3], which requires saturation ratios of from 3 to 6 in typical cases. The theory predicts further that the primary nucleation of a crystal from the vapour requires still larger saturation ratios, so that the critical conditions for nucleation of the liquid are reached first, unless working with very low vapour pressures far below the melting point. This is also in agreement with observation.

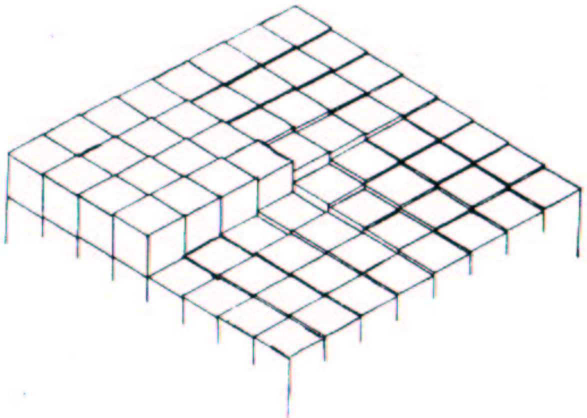

Fig. 2

No one seems to have noticed that the assumption that the growth of crystals from the vapour takes place in this way (by two-dimensional nucleation in the crystal surface) implies a rate of growth which is negligible at small supersaturations.

According to the theory developed by Volmer and Becker and Döring, the number of nuclei formed per second on 1 cm.^{2} of surface is

$$N \sim A \exp\{-\varphi^2/(kT)^2 \log \alpha\}, \qquad (1)$$

where A is of the order of 10^{20}, φ is the interaction energy between two molecules, and α is the saturation ratio, that is, the ratio of the concentration in the vapour to the equilibrium concentration. Experiments by Volmer and Schultze[4] in iodine at 0° C. indicate an observable rate of growth proportional to $\alpha - 1$ when $\alpha \geqslant 1{\cdot}01$. The value of φ/kT for iodine at 0° C. is about 6, so when $\alpha = 1{\cdot}01$, the exponent in (1) is about $-3{,}600$. In fact, the observed growth-rate exceeds the theoretical value by a factor of $e^{3,600}$.

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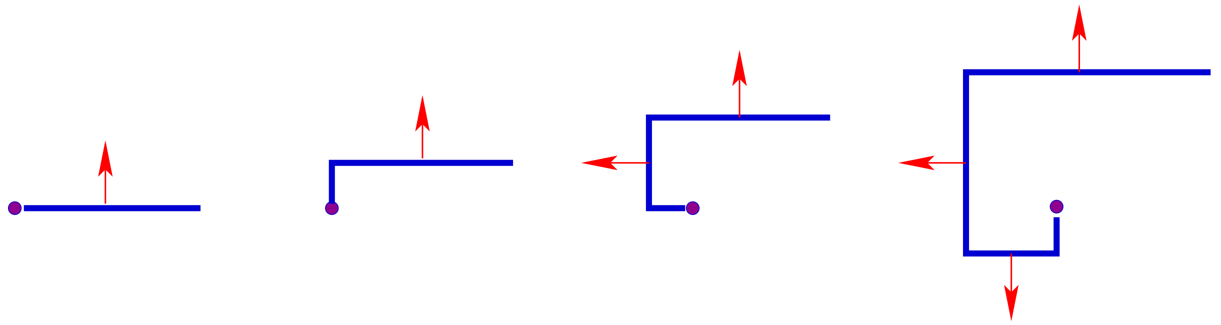
[1] Becker and Döring, *Ann. Phys., Leipzig*, **24**, 719 (1935).
[2] Volmer, "Kinetik der Phasenbildung" (Dresden and Leipzig, 1939).
[3] Volmer and Flood, *Z. phys. Chem.*, A, **170**, 273 (1934).
[4] Volmer and Schultze, *Z. phys. Chem.*, A, **156**, 1 (1931).
[5] Burton and Cabrera (to be published elsewhere).
[6] Frank, *Trans. Farad. Soc.* (in the press).
[7] Burgers, *Proc. Kon. Ned. Akad. Wet.*, **42**, 293 (1939).

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



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

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

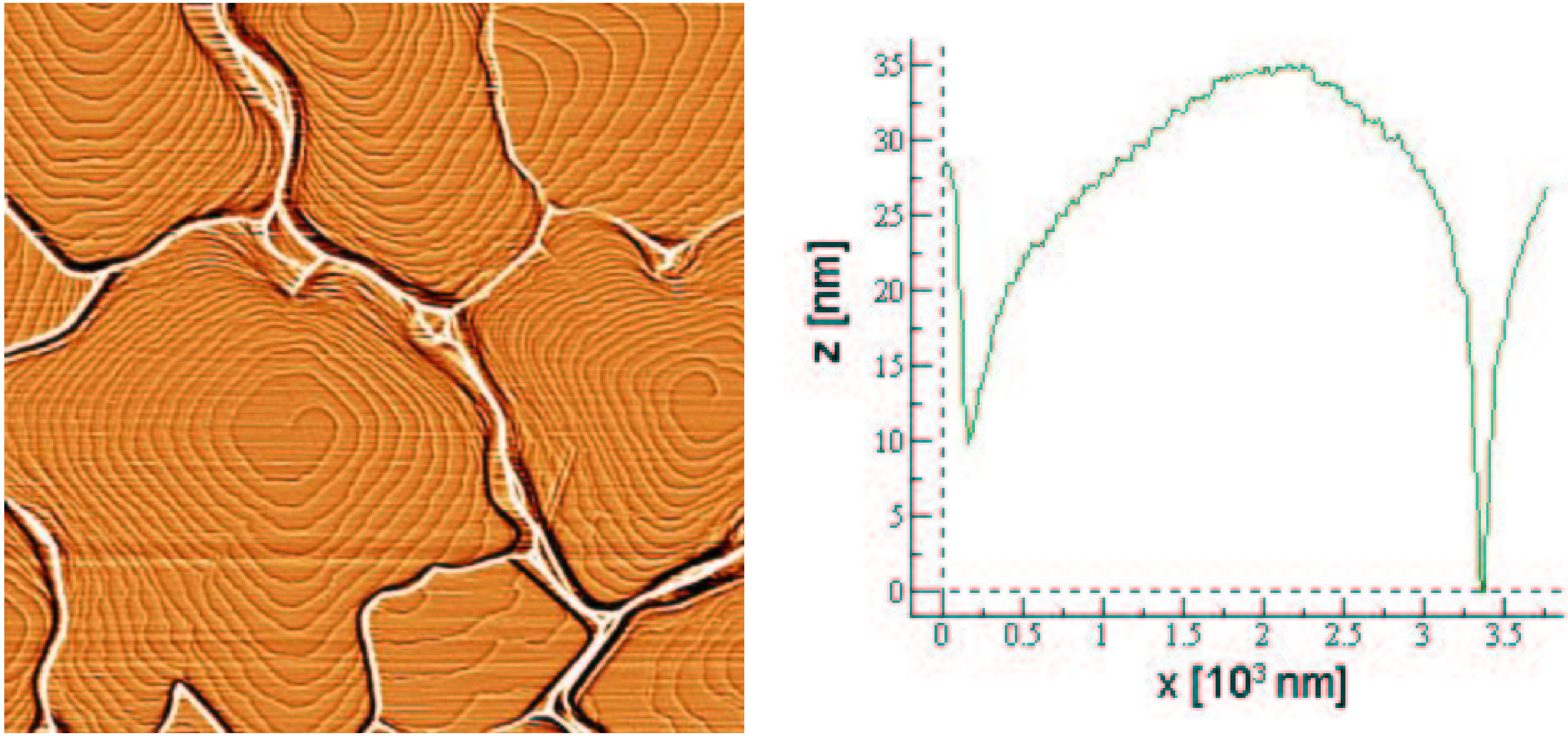
$$v_n = v_0(1 - \kappa R_c) \qquad \kappa: \text{ curvature} \quad R_c: \text{ radius of critical nucleus}$$

$\Rightarrow$ $\kappa = 1/R_c$ at spiral core, asymptotic step spacing $\ell \approx 19 \times R_c \sim F^{-1}$

- Back-force effect: Nonlocal coupling between different turns of the spiral when diffusion length $\gg$ step spacing $\Rightarrow$ asymptotic step spacing $\ell \sim F^{-1/2}$ (attachment limited) or $\ell \sim F^{-1/3}$ (diffusion limited)

- All theories predict close to Archimedean spirals $\equiv$ conical spiral hillocks

Spiral growth in organic thin films



Perylene/Al_2O_3/glass [M. Beigmohamadi et al., Phys. Stat. Sol. (RRL) **2**, 1, 2008]

- ”Nonclassical” spiral hillocks:
  Height profile reminiscent of wedding cakes

Phase field model with Ehrlich-Schwoebel barriers

F. Otto et al., Nonlinearity **17**, 477 (2004)

- Moving boundary value problem for the adatom concentration $\rho(\vec{r},t)$

$$\frac{\partial \rho}{\partial t} = D\nabla^2\rho + F \quad \text{with} \quad \text{b.c.} \quad D\vec{n}\cdot\nabla\rho_\pm = k_\pm[\rho_\pm - \rho^*(1+\gamma\kappa)]$$

$k_\pm$: kinetic coefficients ρ^*: equilibrium adatom concentration γ: step stiffness

- Diffuse interface approximation:

$$\frac{\partial \phi}{\partial t} + \frac{\partial \rho}{\partial t} = \nabla\cdot M_\varepsilon(\phi)\nabla\rho + F, \quad \varepsilon^2\frac{\partial \phi}{\partial t} = \varepsilon^2\nabla^2\phi - \frac{\delta G}{\delta \phi} + \frac{\varepsilon}{\rho^*\gamma}(\rho-\rho^*)$$

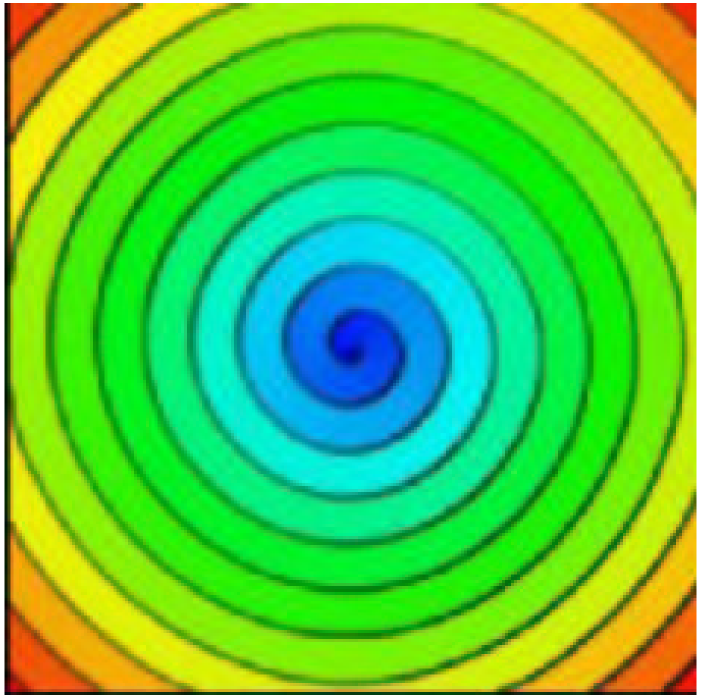
$G(\phi)$: multiwell potential $M_\varepsilon(\phi)$: asymmetric mobility function

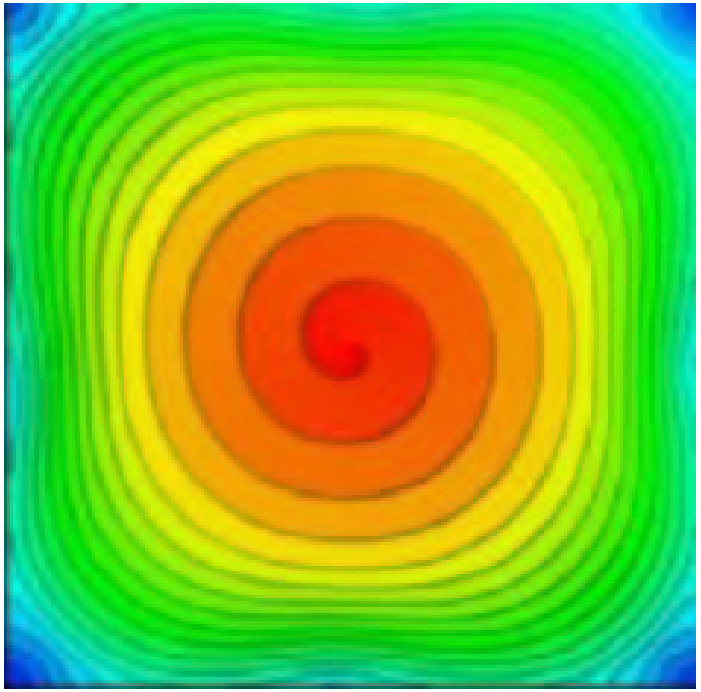
reduces to sharp interface problem with $\varepsilon \to 0$

- Spiral is introduced through $\phi \to \phi - \theta(\vec{r})/2\pi$ A. Karma & M. Plapp, 1998

Phase field modeling of spiral growth

$F = 0.2, D = 10, \rho^* = 0.1, \gamma = 1, \varepsilon = 1$





$k_+ = k_- = \infty$

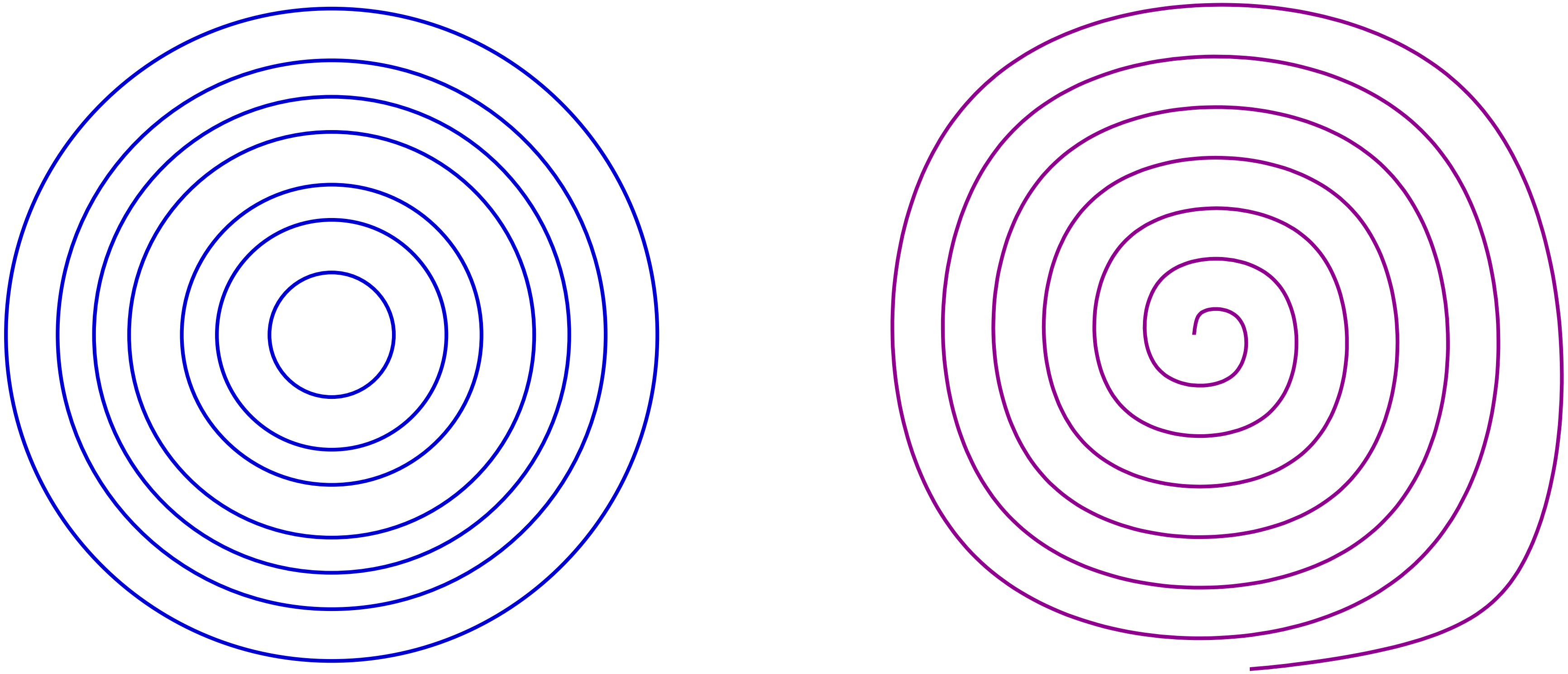
classical

$k_+ = 10, k_- = 1$

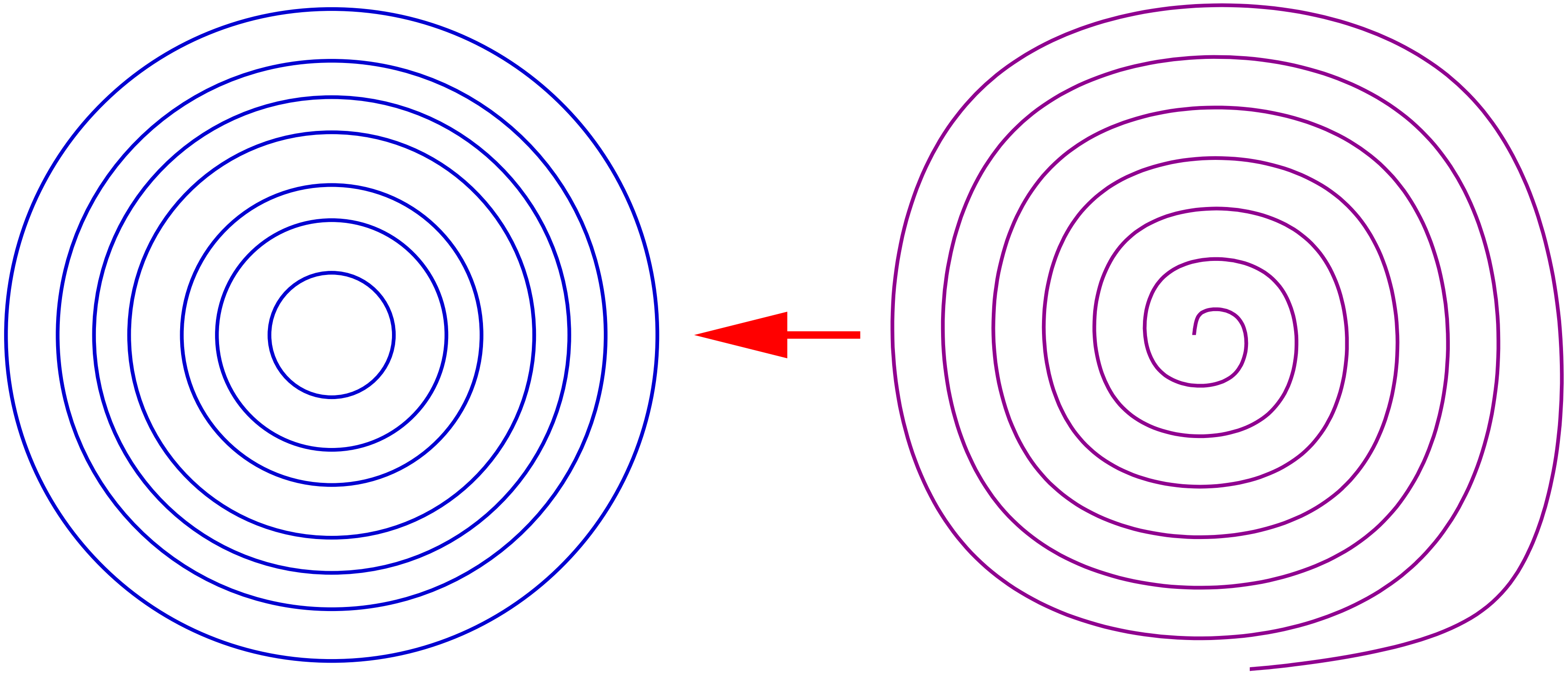
with Ehrlich-Schwoebel barrier

A. Rätz, A. Voigt, caesar Bonn /TU Dresden

Wedding cakes versus spirals



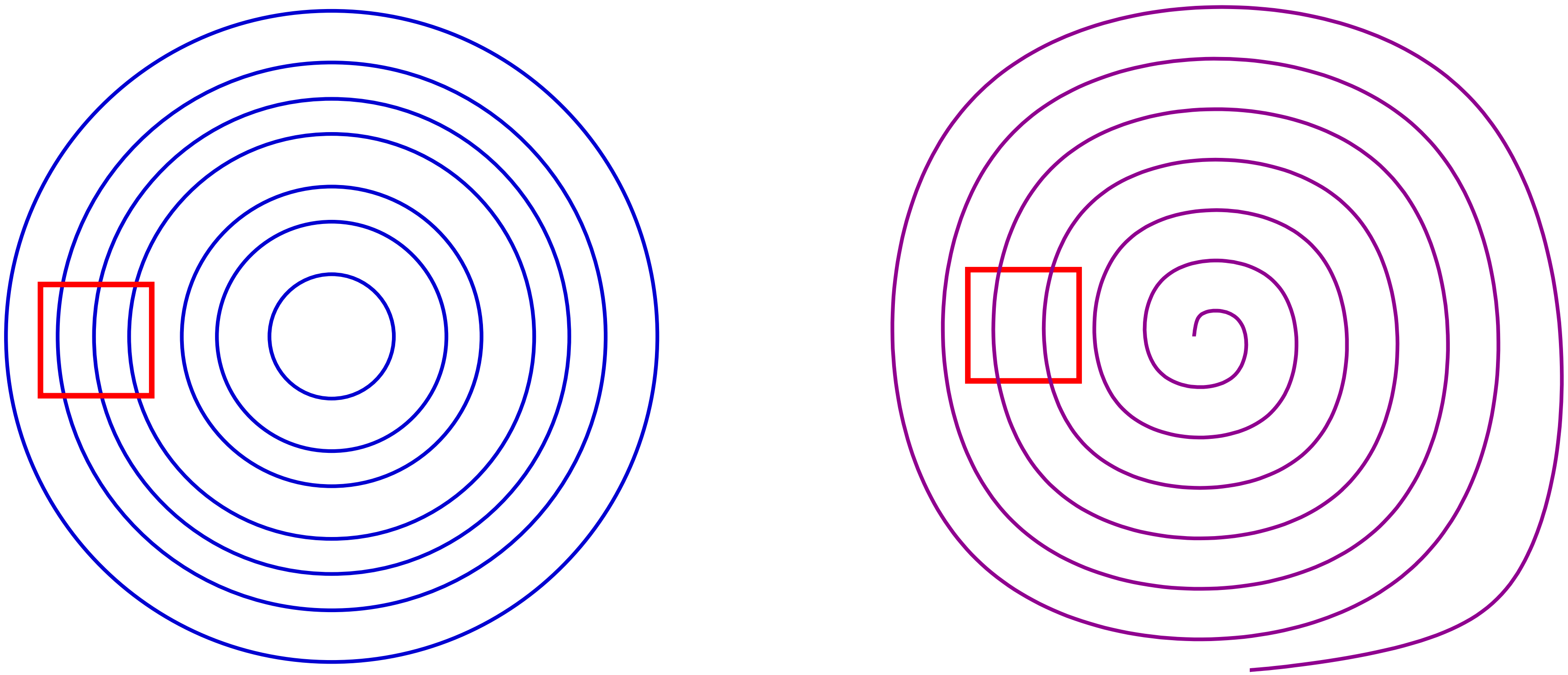
Wedding cakes versus spirals



- Basis of approximate analytic theory of the back-force effect

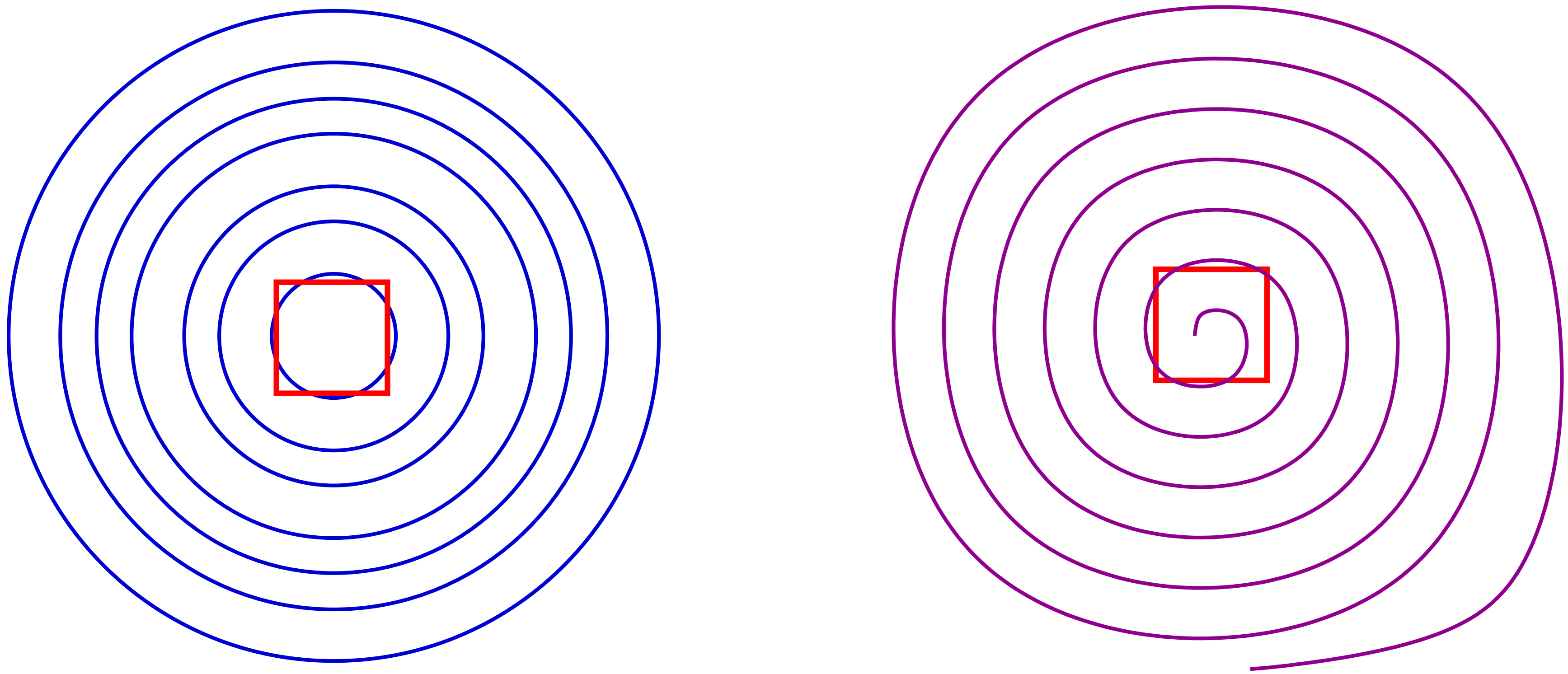
  T. Surek, J.P. Hirth, G.M. Pound, J. Crystal Growth **18**, 20 (1973)

Wedding cakes versus spirals



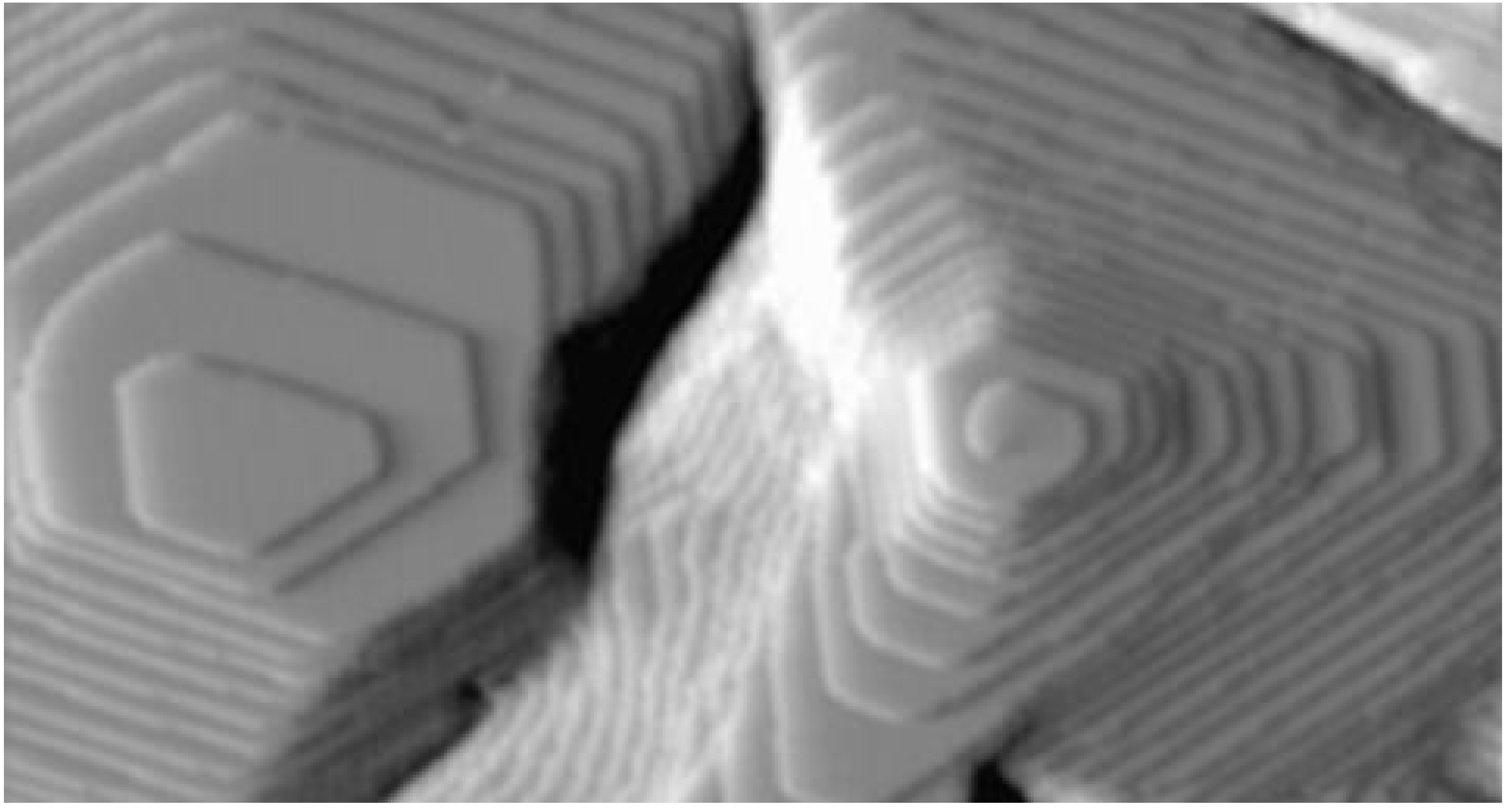
- **Hillsides**: Steepening due to diffusion bias

Wedding cakes 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!

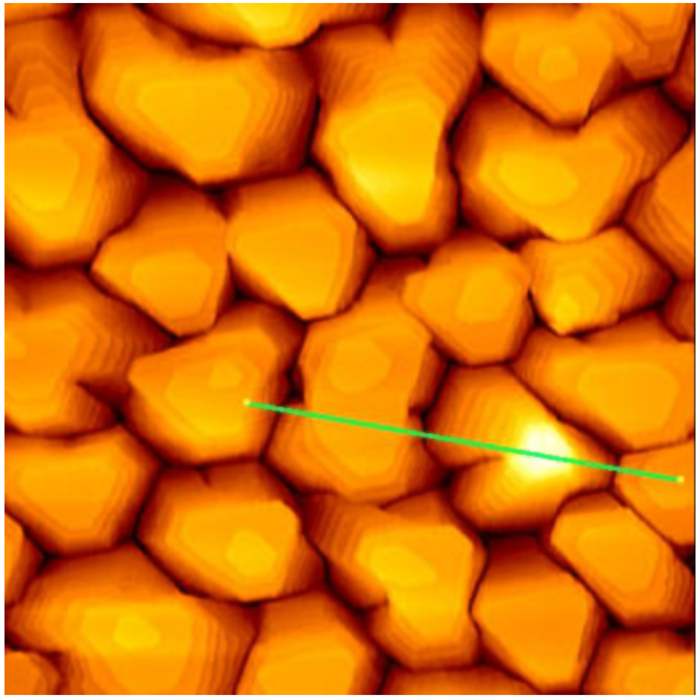
Wedding cakes and spirals on Pt(111)

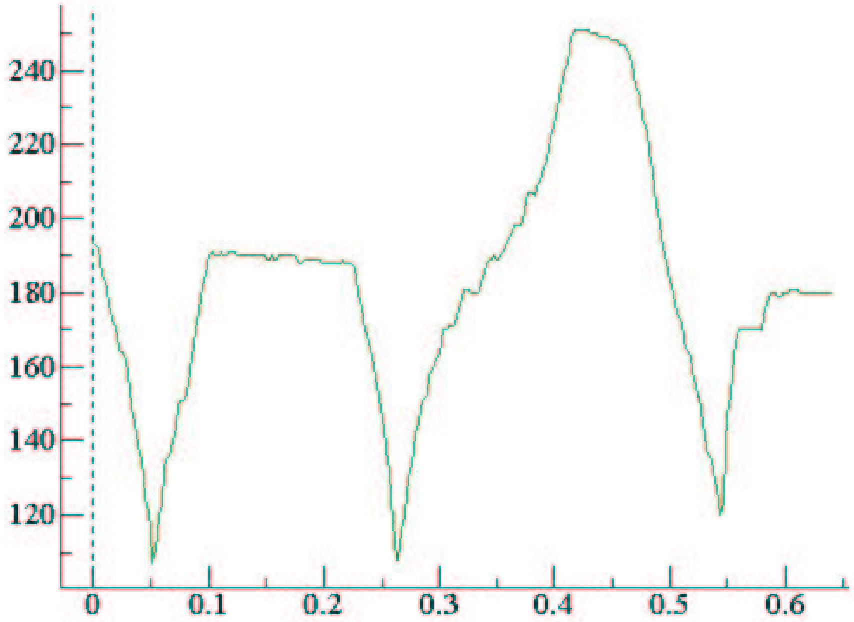


O. Ricken, A. Redinger, T. Michely

Spiral growth on Pt(111)

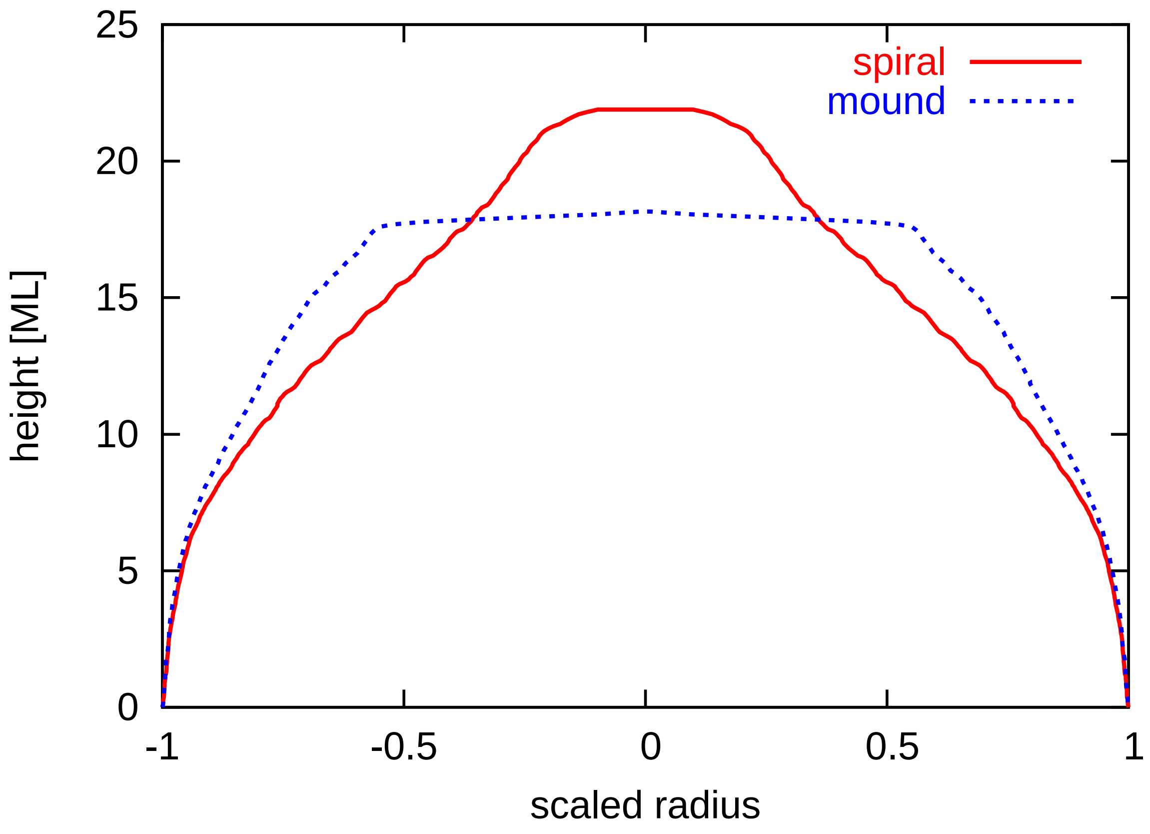
A. Redinger, O. Ricken, P. Kuhn, A. Rätz, A. Voigt, JK, T. Michely, arXiv:0709.2327





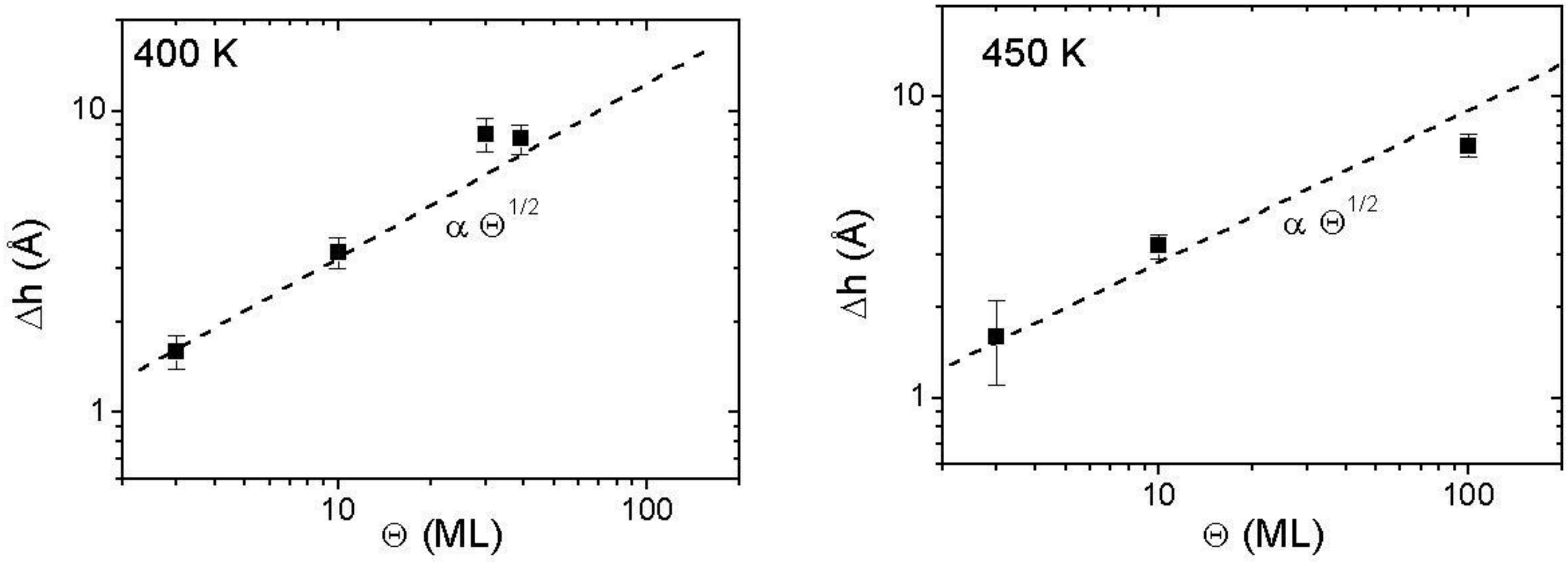
- Screw dislocations induced by He^+ bombardment
- Wedding cakes and spirals coexist, and spiral hillocks are higher

Comparison of shapes at 400 K



- enhanced "effective Ehrlich-Schwoebel barrier" $\Delta E_S \rightarrow \Delta E_S + 0.13\text{eV}$
- reflects length of innermost spiral segment $l_c = 23 \pm 6\text{Å}$
- similar results at $T = 300$ K and 500 K

Scaling with film thickness



- Δh: Height difference between spiral hillocks and wedding cakes
- 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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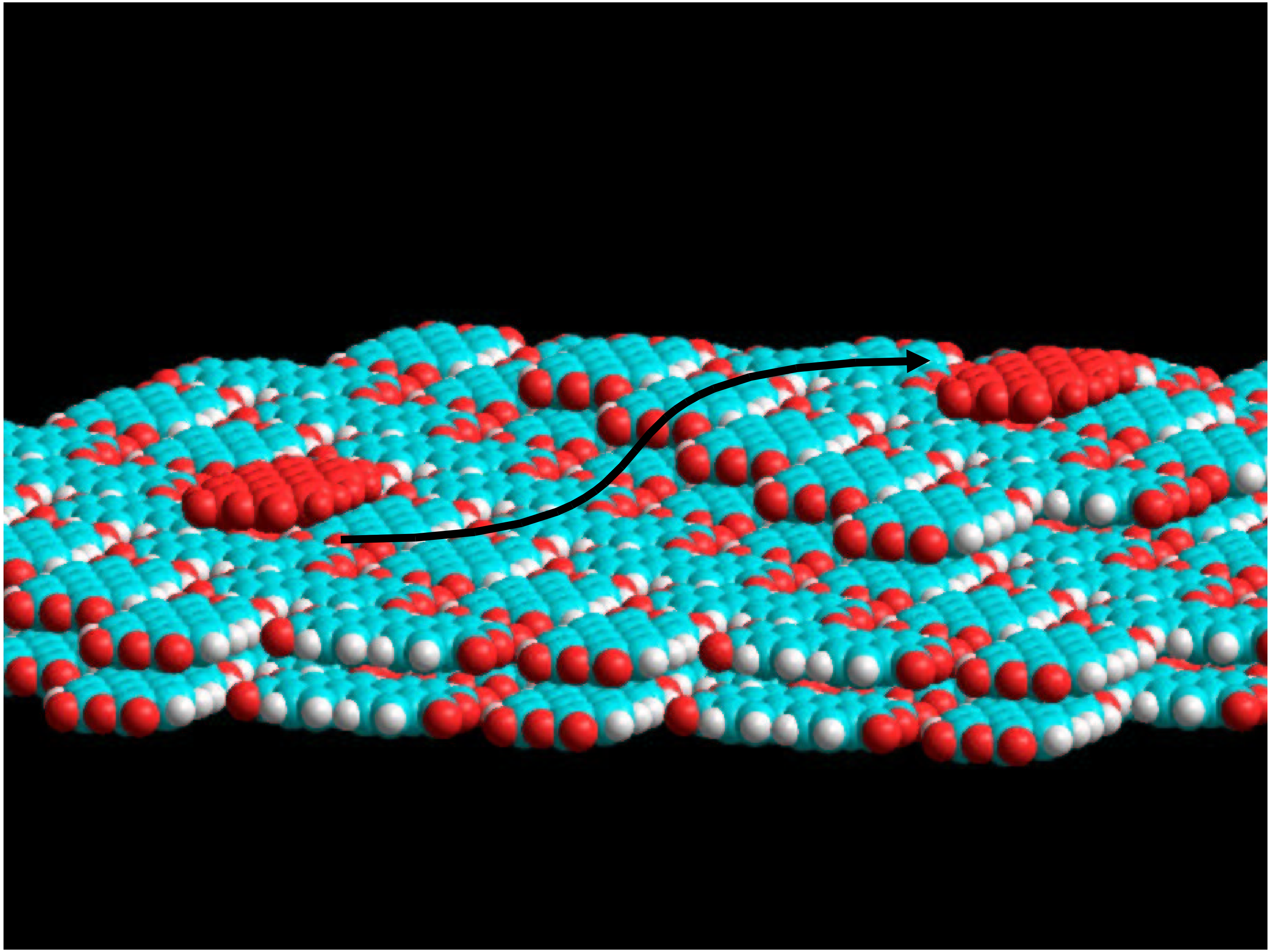
Microscopic calculation: M. Fendrich, University of Duisburg-Essen

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

- Lennard-Jones (AMBER) force field + electrostatics, 2 rigid layers, NEB algorithm

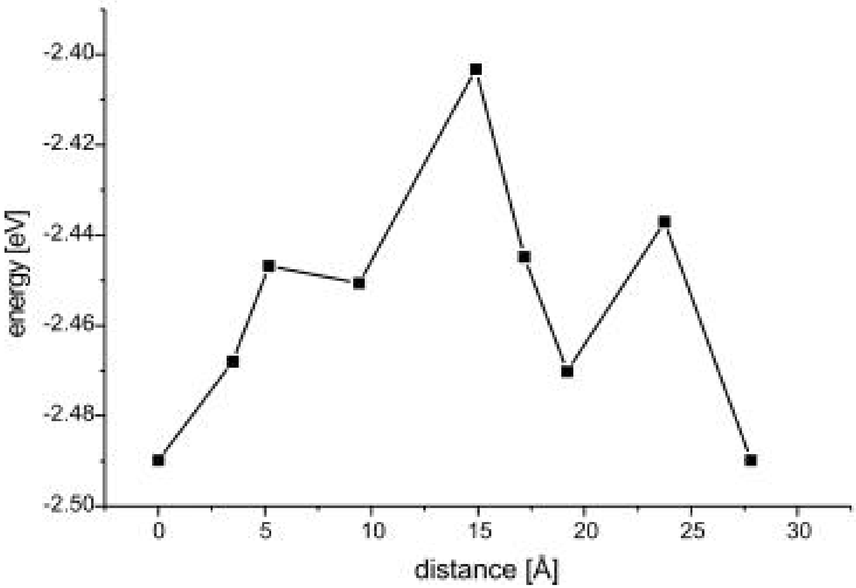
Computational setup



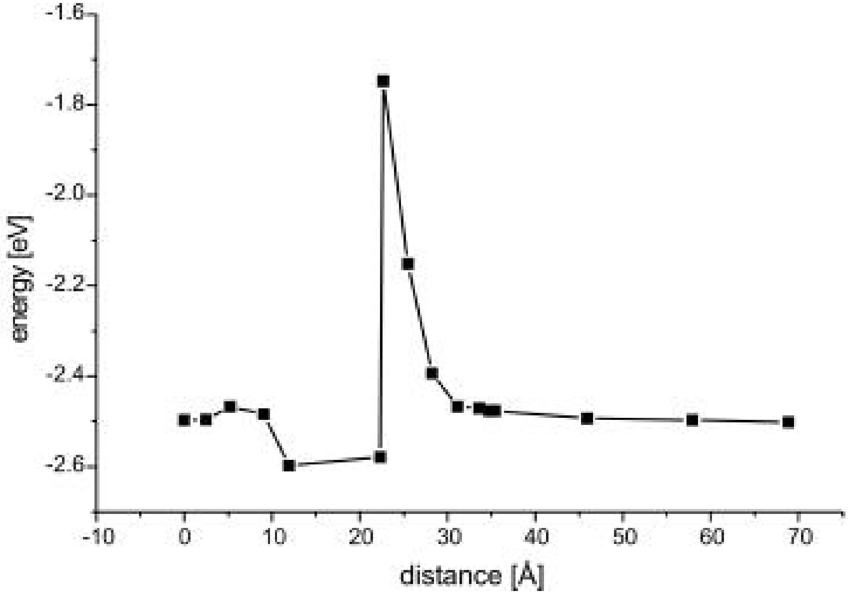
Results

M. Fendrich, JK, PRB **76**, 121301(R), 2007

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
- high in-layer mobility but complete suppression of interlayer transport at room temperature: $D'/D = 5.5 \times 10^{-12}$

Conclusions

- Experiments and modeling combine two key effects shaping the morphology of growing crystalline films: Frank meets Ehrlich & Schwoebel!
- Bimodal distribution of plateau heights due to coexistence of two growth mechanisms
- ES-effect is important for the growth of organic films

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Thanks to:

- Philipp Kuhn, Thomas Michely, Alex Redinger, Oliver Ricken (Köln)
- Markus Fendrich (Duisburg)
- Andreas Rätz & Axel Voigt (Bonn/Dresden)