Vicinal surfaces :
Morphology and Dynamics at Thermal Equilibrium
Metals and Alloys

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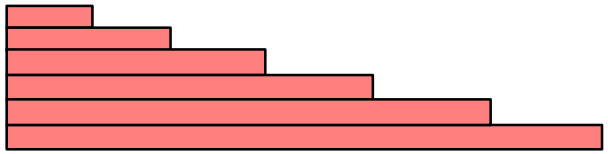
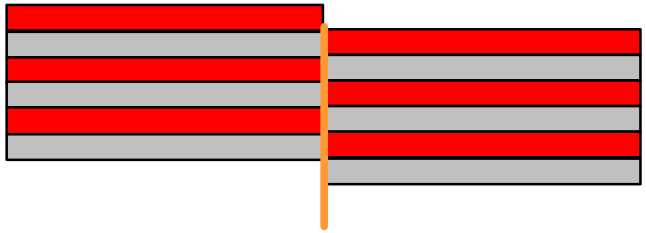
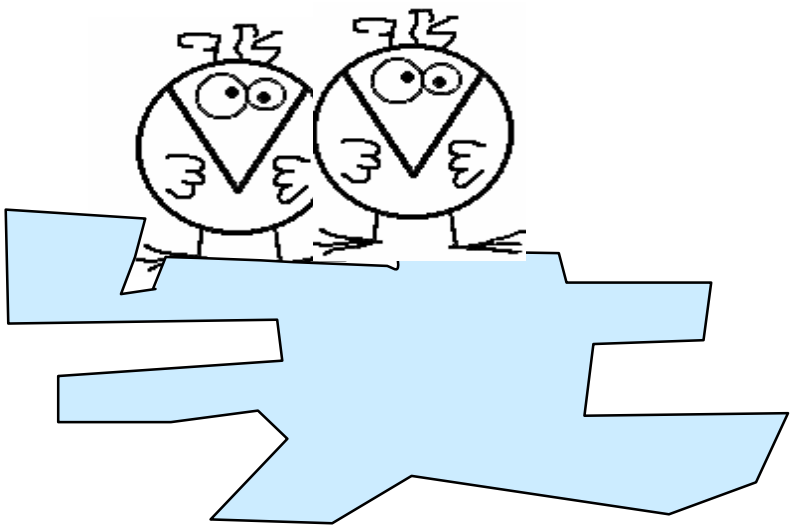
Overview :

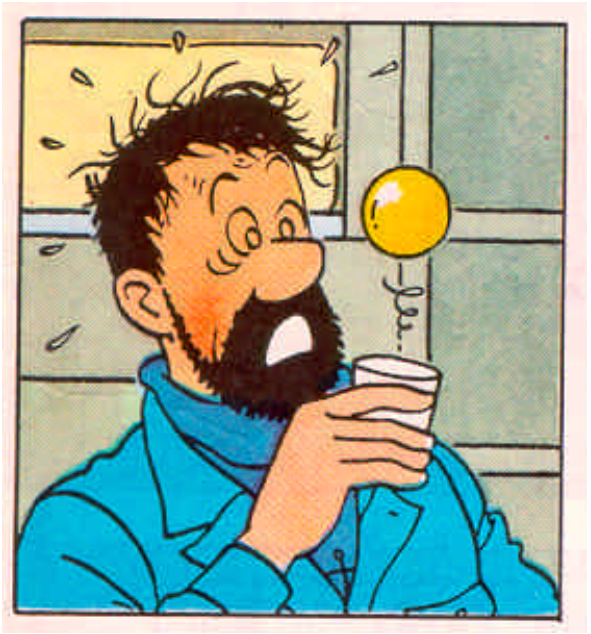
- Introduction to vicinal surfaces
- Morphology at thermal equilibrium
- Statistical analysis : correlation functions
- Dynamics
- Application to vicinals of Cu
- Morphology of vicinals of alloys
- Conclusions





Equilibrium shape of crystals and nanostructures





Without gravity ...

$$\iint_S E(\vec{n})\, d\vec{S} \qquad minimum$$

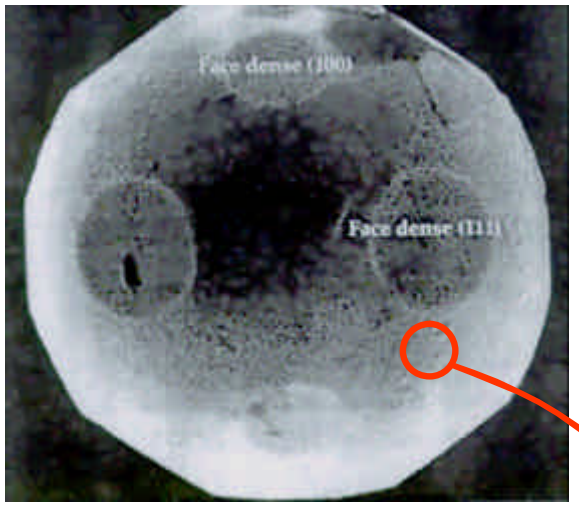
$$Constraint \qquad \iiint_V r(\vec{r})\, d^3(\vec{r}) = cte$$

What are the parameters that govern the shape of a nanostructure ?

Equilibrium morphology of nanostructures

Growth shape

Crystal shape



Equilibrium shape

Au crystallites

Heyraud-Métois (1980)

facet

flat

$T < T_R$

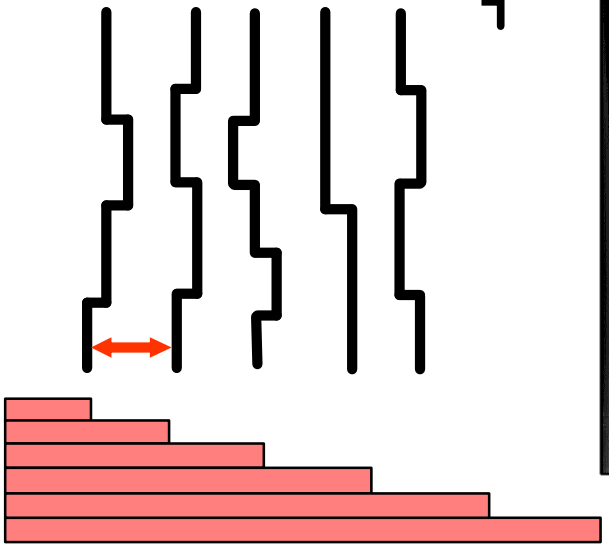
rough

$T > T_R$

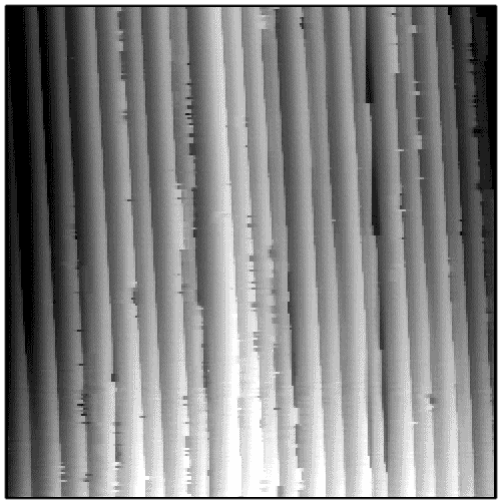
Vicinal orientation
=
close to a dense orientation

Dense plane

Vicinal



Cu(1 1 11) 30 × 30 nm^2

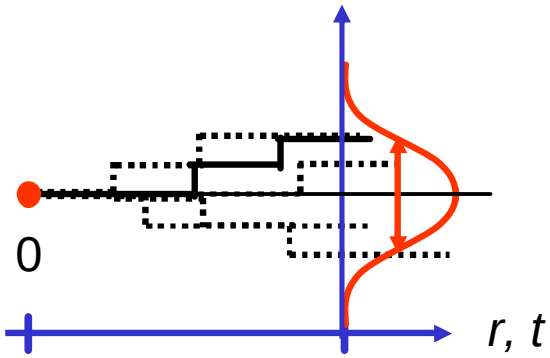


The roughening transition

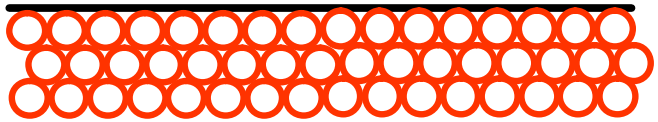
Thermal disorder

$$G(r,t) = \left\langle (h(r,t) - h(0,0))^2 \right\rangle$$

Flat surface:

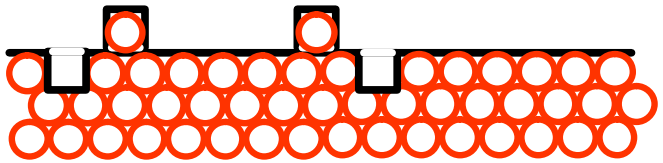


$T = 0$ K



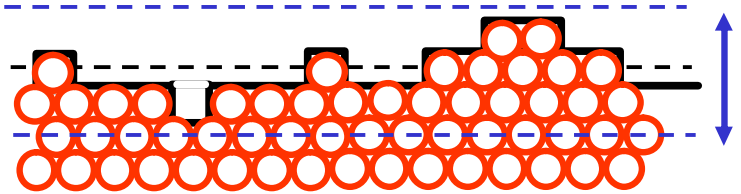
$$\lim_{r\,ou\,t\to\infty} G(r,t) = 0$$

$T > 0$ K



$$\lim_{r\,ou\,t\to\infty} G(r,t) = 4e^{-2J/kT}$$

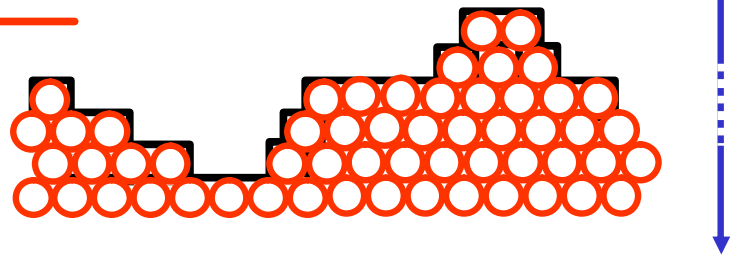
$T < T_R$



$$\lim_{r\,ou\,t\to\infty} G(r,t) = cte$$

Rough surface:

$T > T_R$



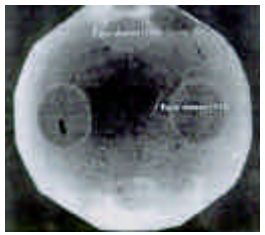
$$\lim_{r\,ou\,t\to\infty} G(r,t) = \infty$$

Surface = 2-d system: $G(r,0) \prec \ln(r)$ $G(0,t) \prec \ln(t)$

Universality class : Kosterlitz-Thouless

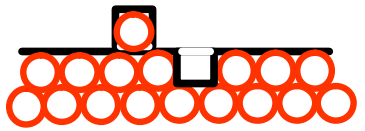
Thermal excitations of solid surfaces

Energy of local defects :

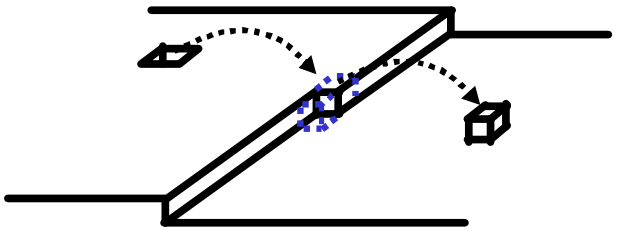


Dense plane : $2J$ = 0.5-0.7 eV

+ activation energy ~ 0.4 eV



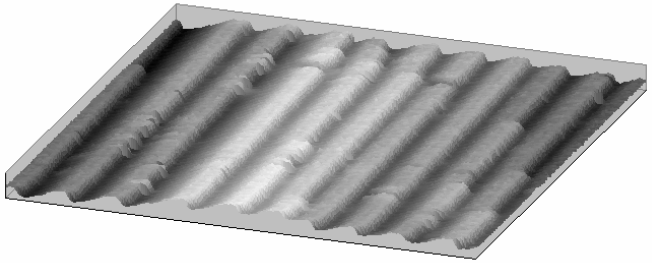
$h(r,t)$

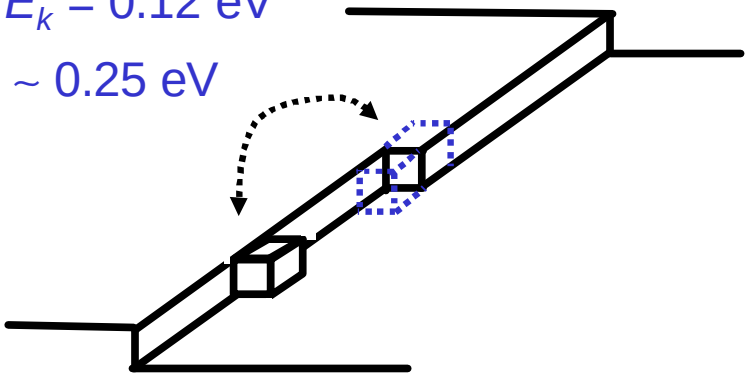


$T_R \gg T_f$

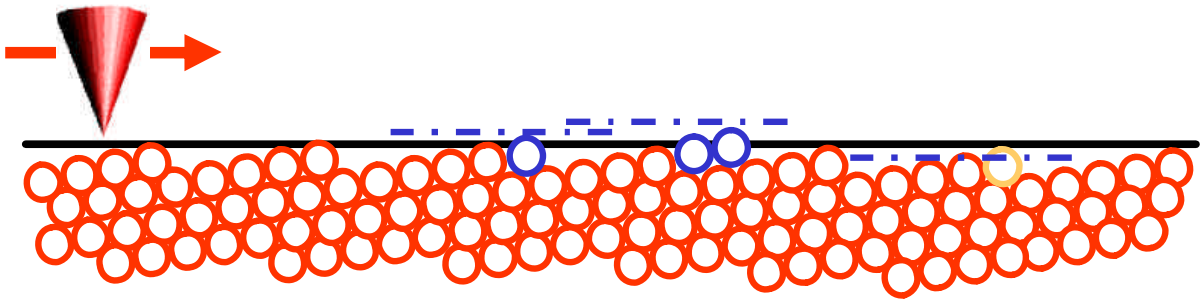
Vicinal surface: creation of kinks at steps E_k = 0.12 eV

+ activation energy ~ 0.25 eV





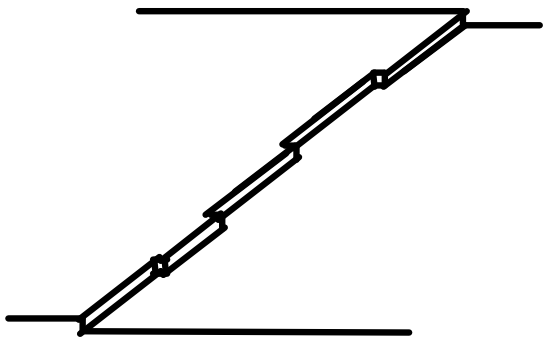
$T_R \gg T_{amb}$

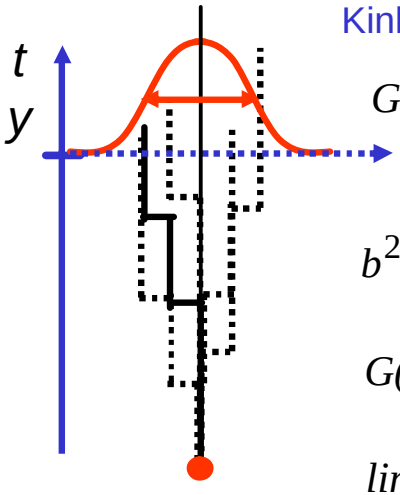


$h(r,t)$

From 1-d to 2-d ...

Unique step 1-d system





Pour T>0

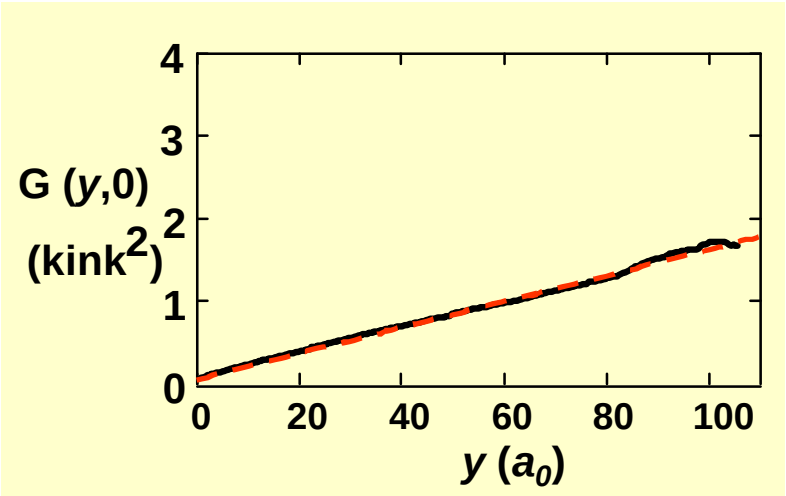
Kink probability : $e^{-\frac{E_k}{k_B T}}$

$$G(y) = b^2 y$$

$$b^2 \approx 2e^{-\frac{E_k}{k_B T}}$$

$$G(t) = a\, t^{1/n}$$

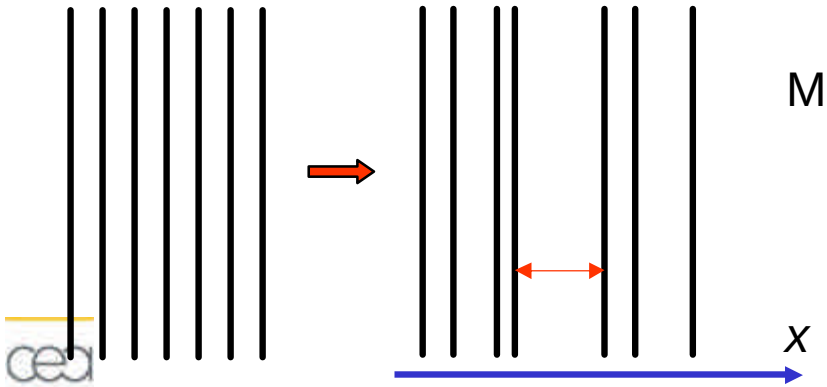
$$\lim_{y,t\to\infty} G(y,t) = \infty$$



b^2 = step diffusivity

1st parameter : the kink energy E_k

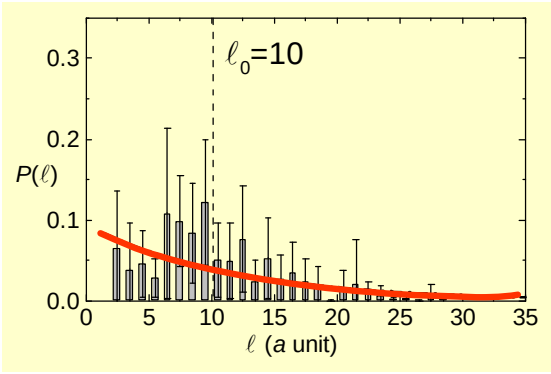
Parallel steps without excitation and interaction



1-d System !
Markovian disorder!

$$G(x) \prec x$$

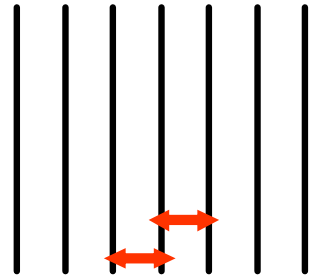
$$G(y) = 0$$



Ex: Cu_3Au (1 1 11) !

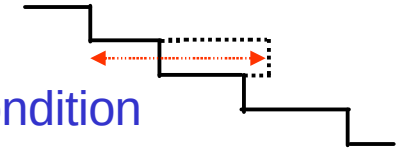
From 1-d to 2-d ...

+ step-step interaction:

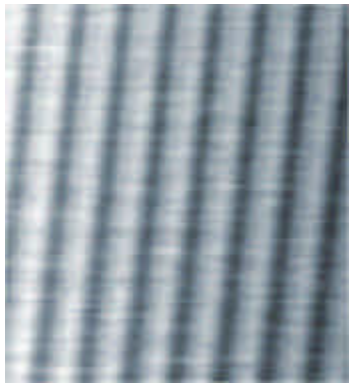


- No step crossing condition
- Elastic like step-step interaction A/L^2

$A \sim 6$ meV/at



Even step distribution →

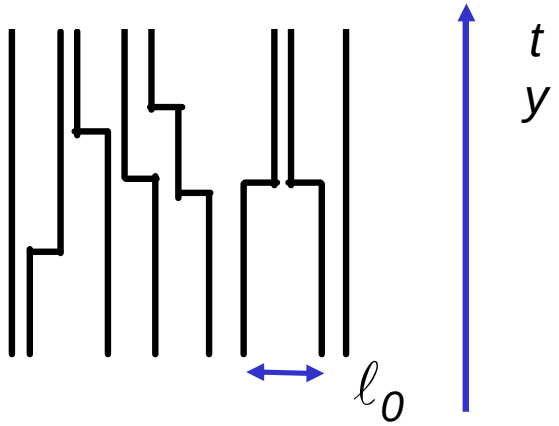


Cu (1 1 5) (5.8 x 5.3 nm²) room T

2nd parameter : the step-step interaction (no crossing + A/L²)

Array of steps + kink excitation

+ step-step interaction:



Beyond:

Collision length

$$G(L_c) = b^2 L_c = (\ell_0 / 2)^2$$

$$L_c = \ell_0{}^2 / 4b^2$$

Collision time

$$G(t) = a\ t^{1/n}$$

$$t_c = \left(\ell_0{}^2 / 4a\right)^n$$

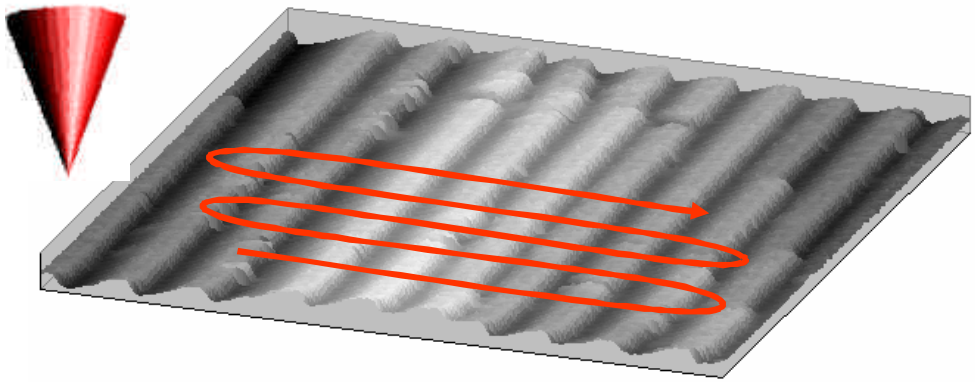
$$dS = -\frac{b^2}{\ell_0{}^2} k_B \ln(2)$$

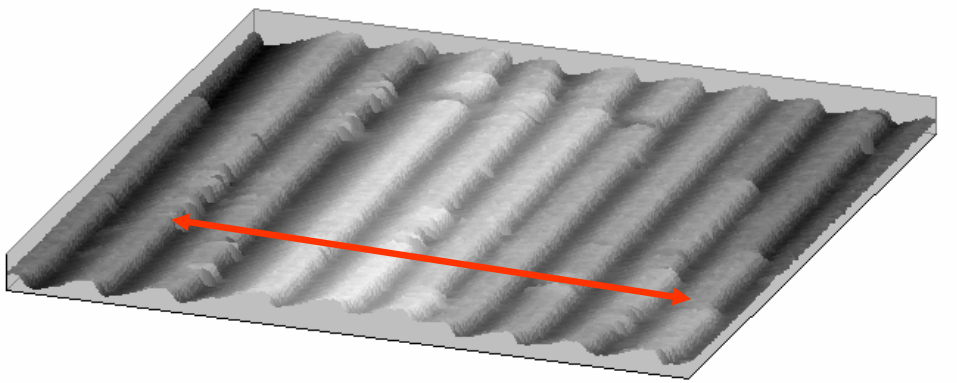
/step $$F = F_0 + \frac{k_B T\, b^2}{\ell_0{}^2} \ln(2)$$

2-d system !

$$G(r,t) \prec \ln(r,t)$$

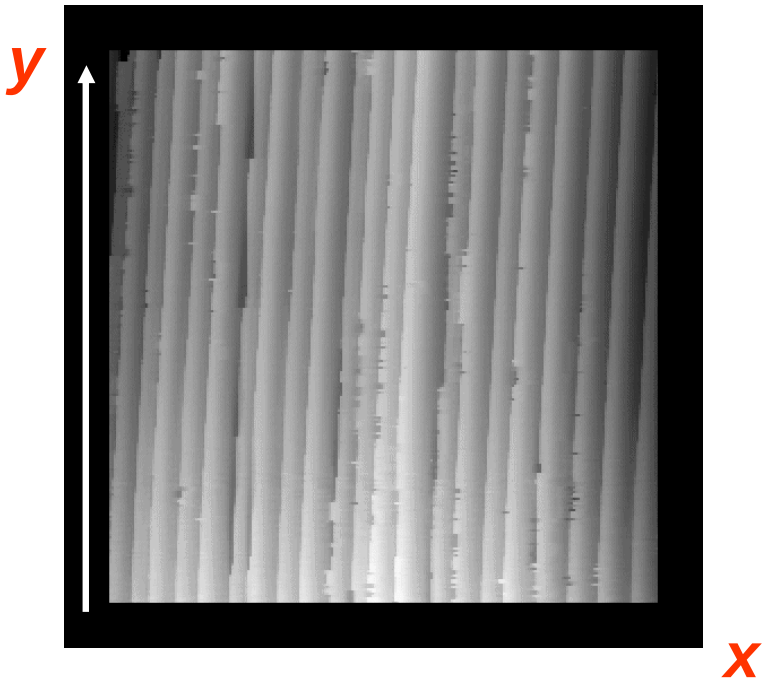
STM observations





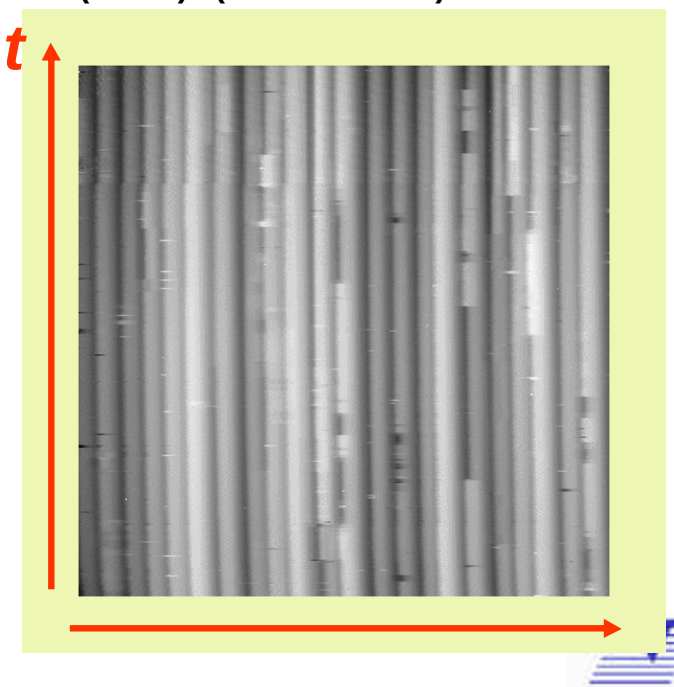
Standard STM Image

Cu(1 1 11) (30 nm ´ 30 nm)



Time STM Image

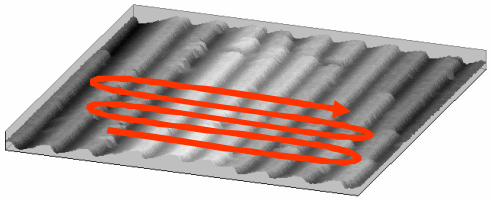
Cu(1 1 11) (30 nm ´ 150 s)



Correlation functions

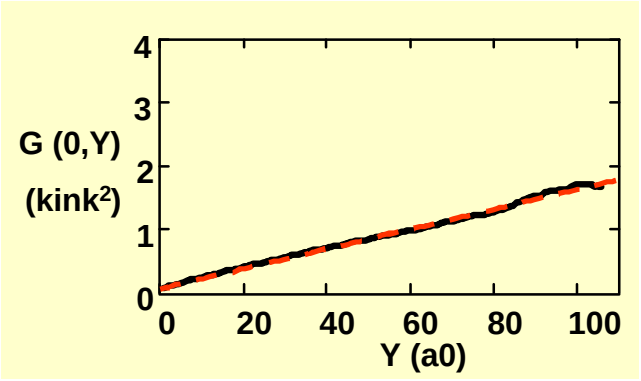
$$G(r,t) = \left\langle (h(r,t) - h(0,0))^2 \right\rangle$$

High scan speed:

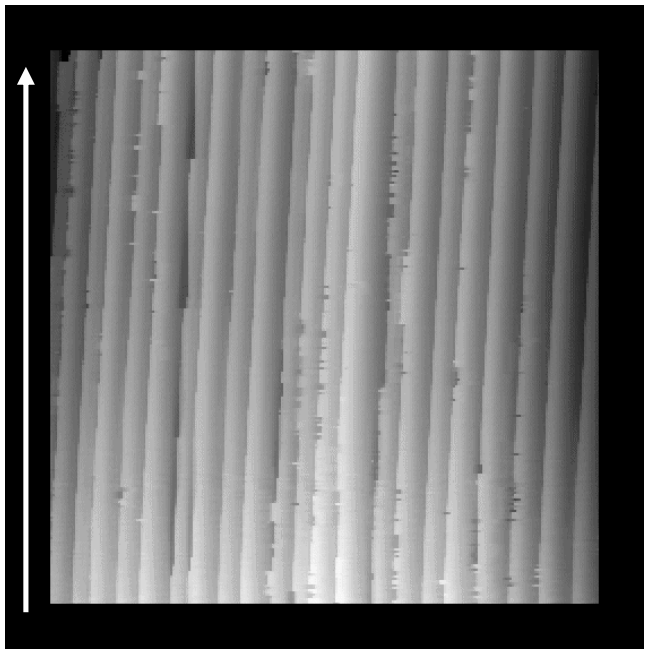


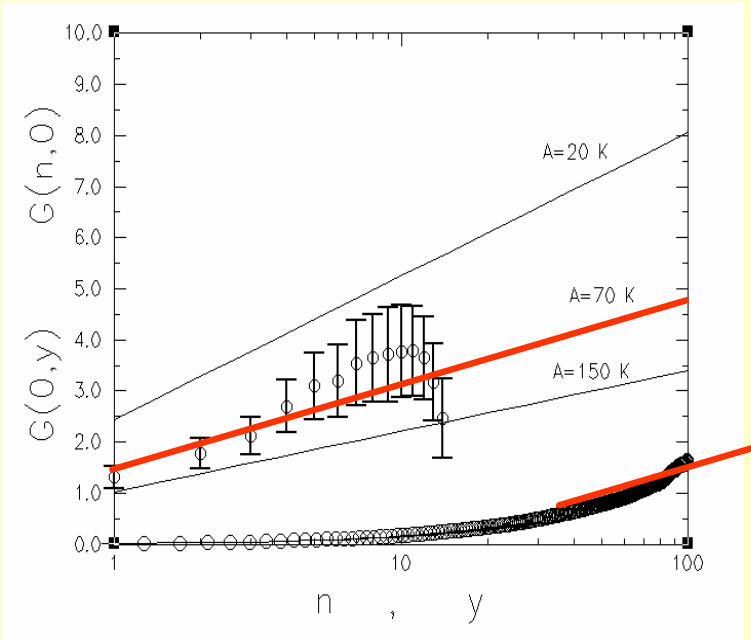
$$G(r) = \left\langle (h_t(r) - h_t(0))^2 \right\rangle$$

Spatial correlation → Roughness



Cu(1 1 11) (30 nm ´ 30 nm)



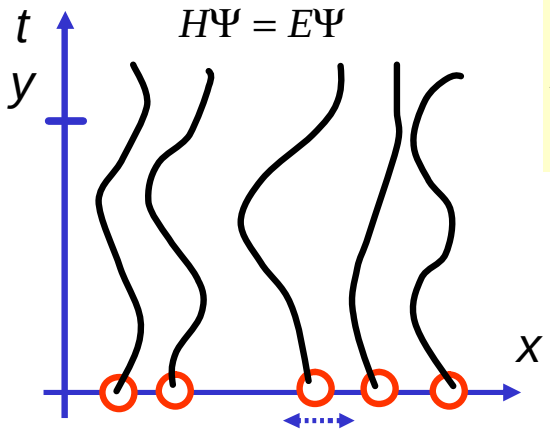


Exact solution for energetics

No step crossing + elastic interaction + …. A/L^2

Exact solution for A/L^2 interactions
(Calogero Sutherland 1970)

Fermions model

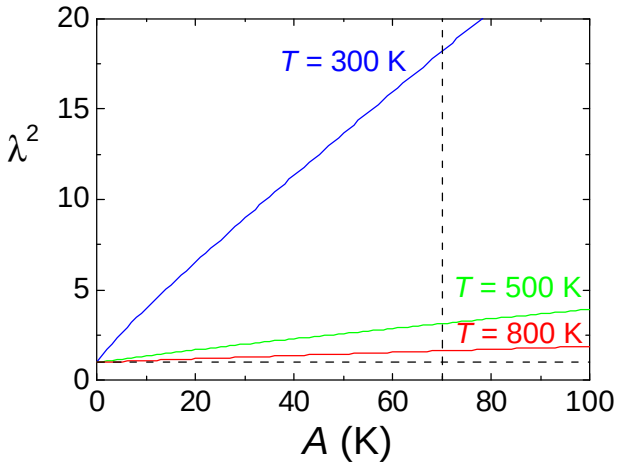


$$H = -\frac{\hbar^2}{2m}\sum_{i=1}^{n}\frac{\partial^2}{\partial x^2} + \sum_{i>j}\frac{g}{(x_i - x_j)^2}$$

$$E = \frac{\hbar^2}{2m}\frac{1}{3}\frac{l^2 p^2}{\ell_0^3}\left(1 - \frac{1}{lN^2}\right)$$

where : $l = \frac{1}{2}\left(1+\sqrt{1+2g}\right)$

Ex : Cu(1 1 11) E_k= 1430 K, A = 70 K



For steps : $m \equiv \frac{k_B T}{b^2} = \tilde{b}$ $\quad \hbar \equiv k_B T$ $\quad t \equiv y$

$$F_{int} = \frac{d}{\ell_0^3} \qquad d = \frac{p^2}{6} k_B T\, b^2 l^2 \qquad l = \frac{1}{2}\left(1+\sqrt{1+\frac{4A}{k_B T\, b^2}}\right)$$

Entropic: (A=0) $\quad l^2 = 1$

Strong elastic interaction: $\quad l^2 = \frac{A}{k_B T\, b^2}$

A = 70 K = 6 meV

T = 300K $\quad l^2 = 18$

T = 500K $\quad l^2 = 3$

Energetics :

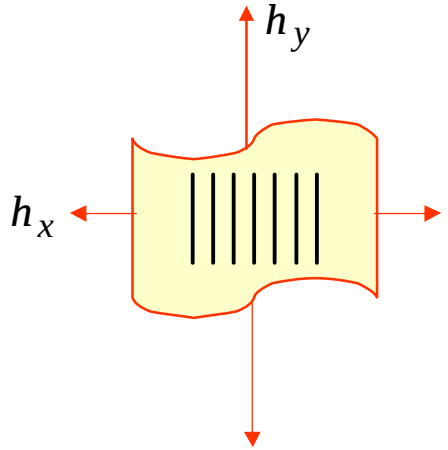
Fermions model
Calogero-Sutherland

$$F = F_0 + \frac{b(E_k)}{h} p + \frac{d(E_k, A)}{{h_0}^3} p^3$$

$T > T_R$

Capillary waves model *(Villain 1985)* : h_y, h_y : Surface stiffnesses

$$F = \sum_{m,y} \left[\frac{h_x}{2} \left(h_{m+1,y} - h_{m,y} \right)^2 + \frac{h_y}{2} \left(h_{m,y+1} - h_{m,y} \right)^2 + V_{loc}\left(h_{m,y} \right) \right]$$



V_{loc} : lattice localization potential (= 0 for $T > T_R$)

One gets :

$$h_x = 6 \frac{d}{{\ell_0}^4}$$

$$h_y = \frac{k_B T}{b^2} + \ldots$$

$$h_x, h_y = f(E_k, A)$$

Fluctuations at thermal equilibrium $\left\langle F_q \right\rangle = \frac{1}{2} k_B T$

$T > T_R$

$$G(m) = \frac{k_B T}{p \sqrt{h_x h_y}} \left(\ln(m) + 2 \right)$$

$$G(y) = \frac{k_B T}{p \sqrt{h_x h_y}} \left(\ln(y) + \frac{3}{2} \right)$$

$T < T_R$

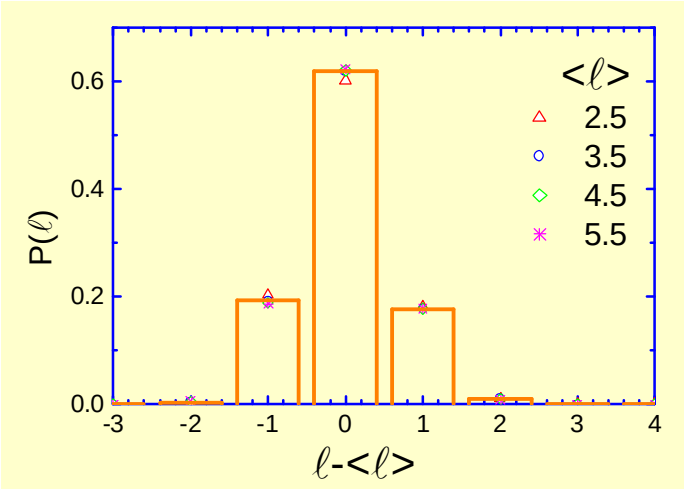
$$G(r \to \infty) = \frac{k_B T}{\sqrt{2 h_y \left(h_x + 4 p^2 V_{loc} \right)}}$$

$h_y, h_y = ? \ldots$

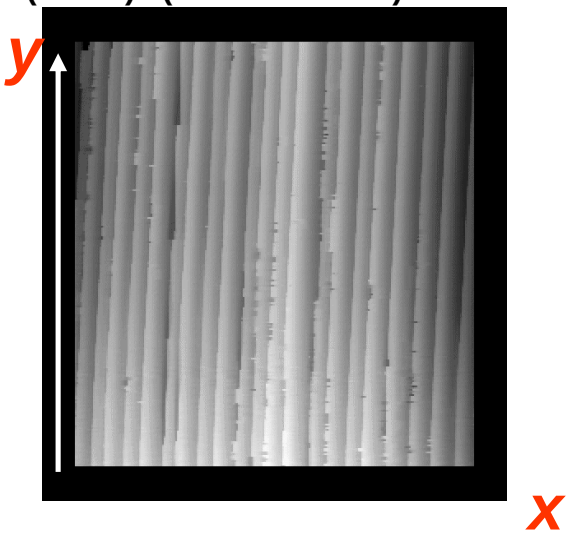
Terrace Width Distribution

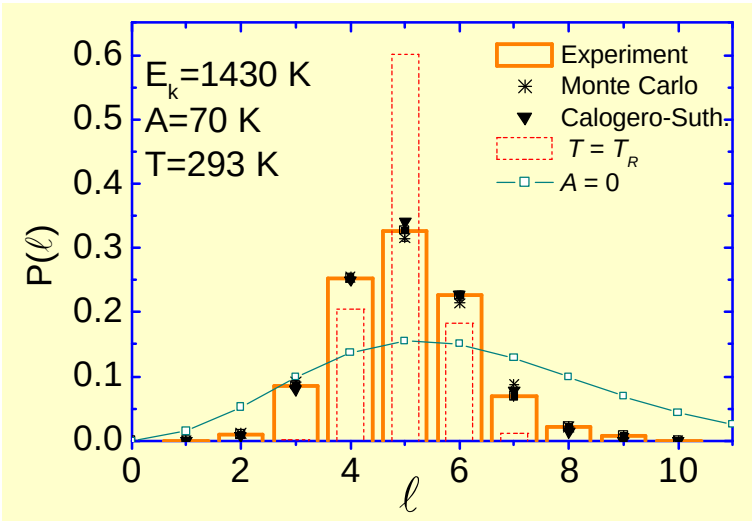
$T = T_R$

$$G(m) = \frac{2}{p^2}\left(ln(m) + 2\right) \qquad G(1) = \frac{4}{p^2}$$



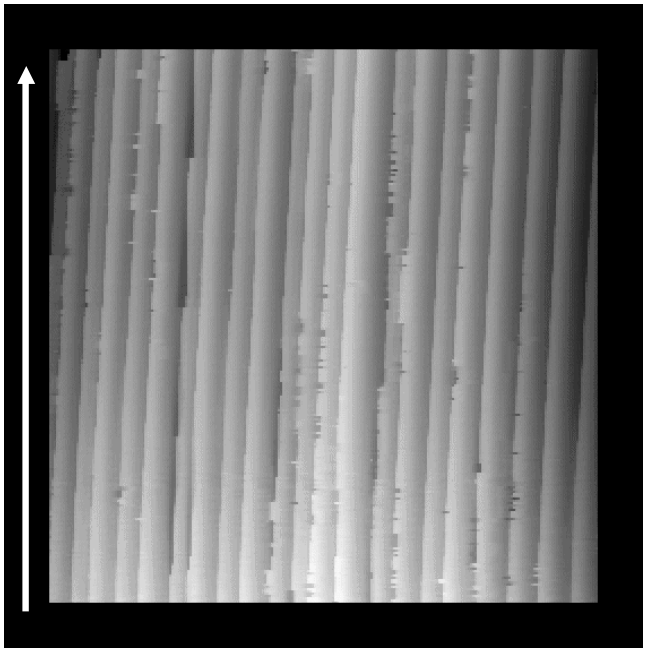
Cu(1 1 11) (30 nm ´ 30 nm)

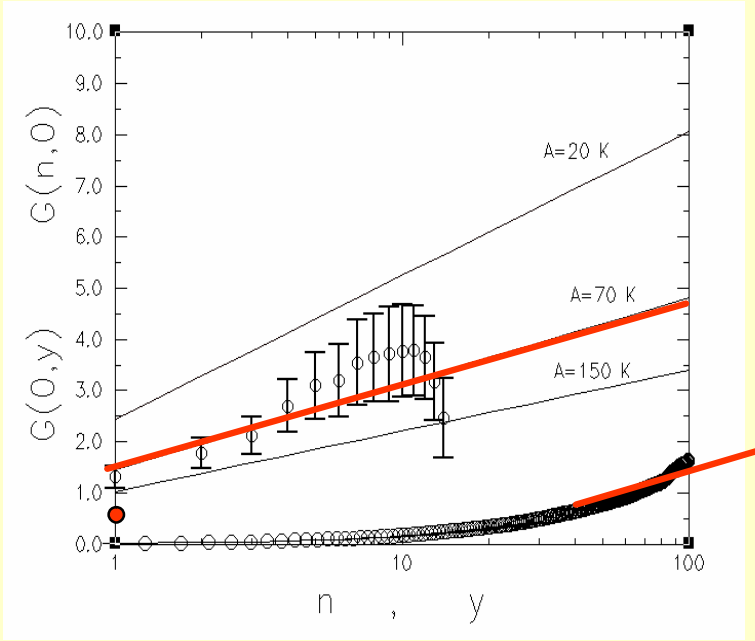




Kink energy, Step-step interaction:

Cu(1 1 11) (30 nm ´ 30 nm)





$$G(1,0) > \frac{4}{p^2}$$

$T = 300K$

$h_y = 19700K$

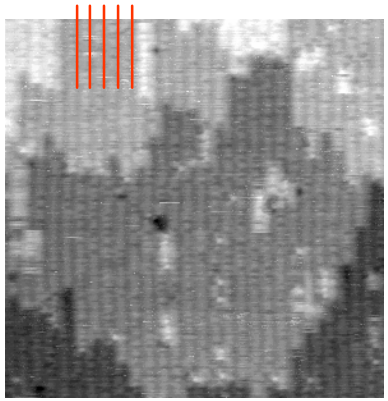
$h_x = 1K$

E_k = 1430 K (0.123 meV)

A = 70 K (6 meV)

T_R = 200 K

The Cu(115) surface

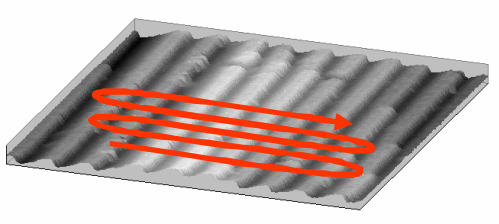


Cu(1 1 5)

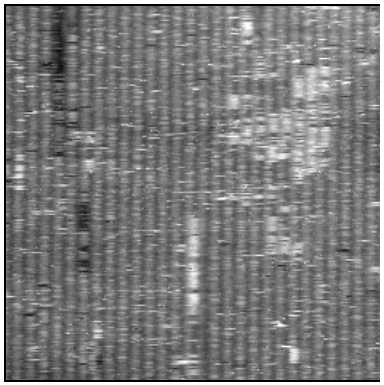
(20 nm ´ 20 nm)

300 K

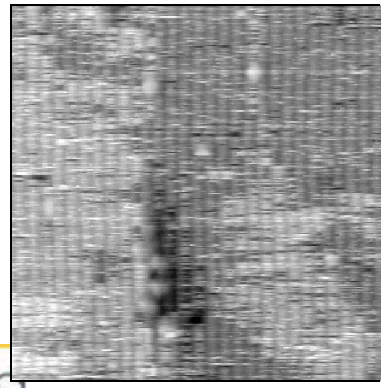
$$G(1,0) < \frac{4}{p^2}$$

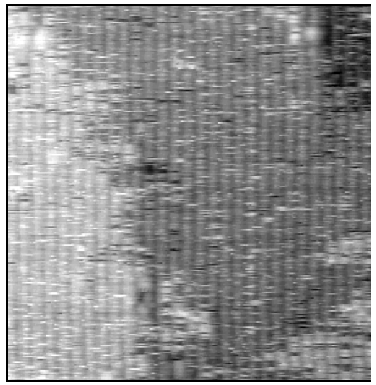


$$G(m,y) = \left\langle (h_m(y) - h_0(0))^2 \right\rangle$$



325 K

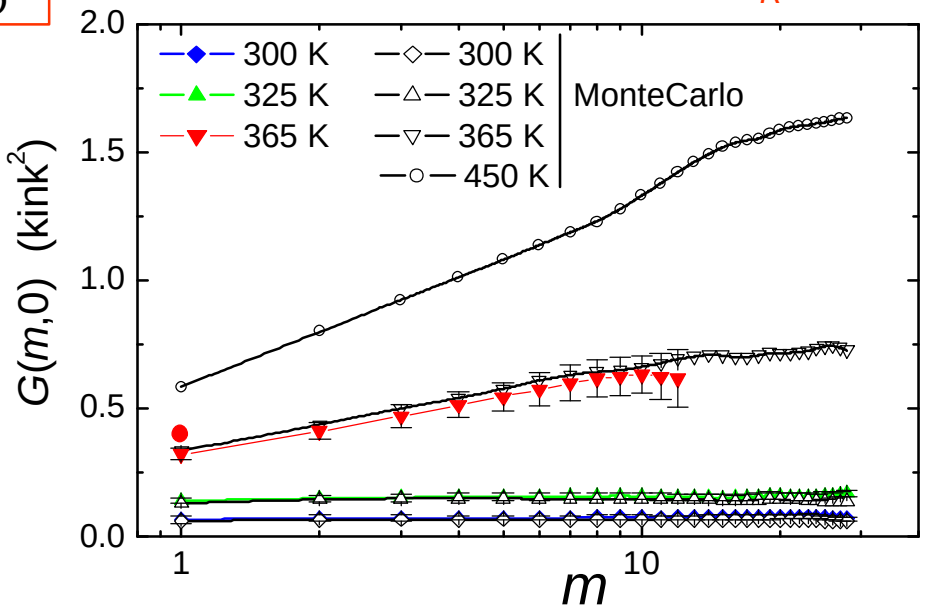




365 K

t + 25s

$G(1,0) < 4 / \pi^2$ $\quad T < T_R$



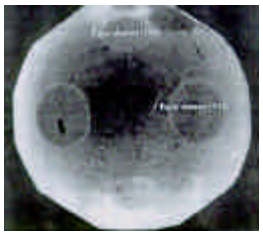
✧, Δ, ∇,○ : Monte Carlo simulation

E_k = 1430 K

A = 65 K

V_{loc} >0

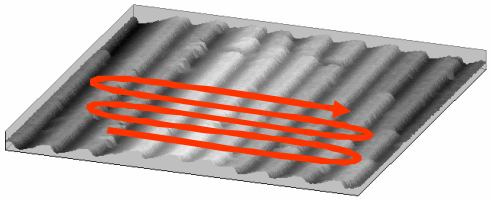
T_R =380 K



t

Time correlation functions $G(r,t)=\left\langle (h(r,t)-h(0,0))^2 \right\rangle$

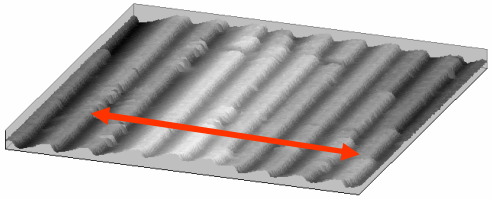
High scan speed:



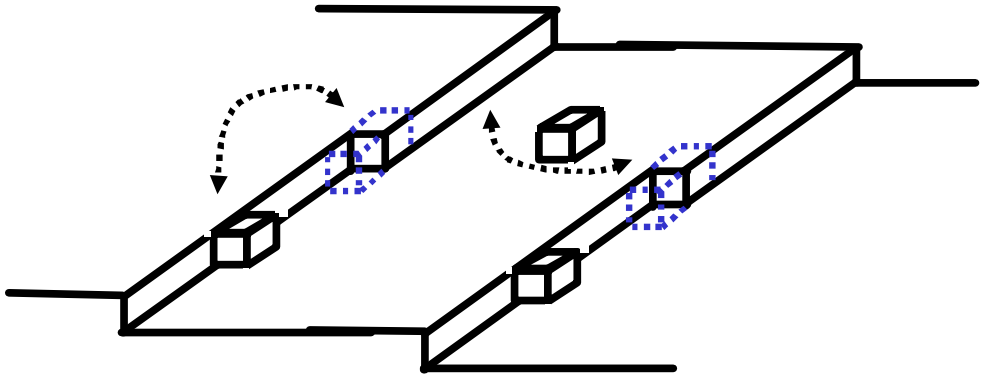
Spatial correlation → Roughness

$$G(r)=\left\langle (h_t(r)-h_t(0))^2 \right\rangle$$

Time fluctuations



$$G(t)=\left\langle (h_r(t)-h_r(0))^2 \right\rangle$$

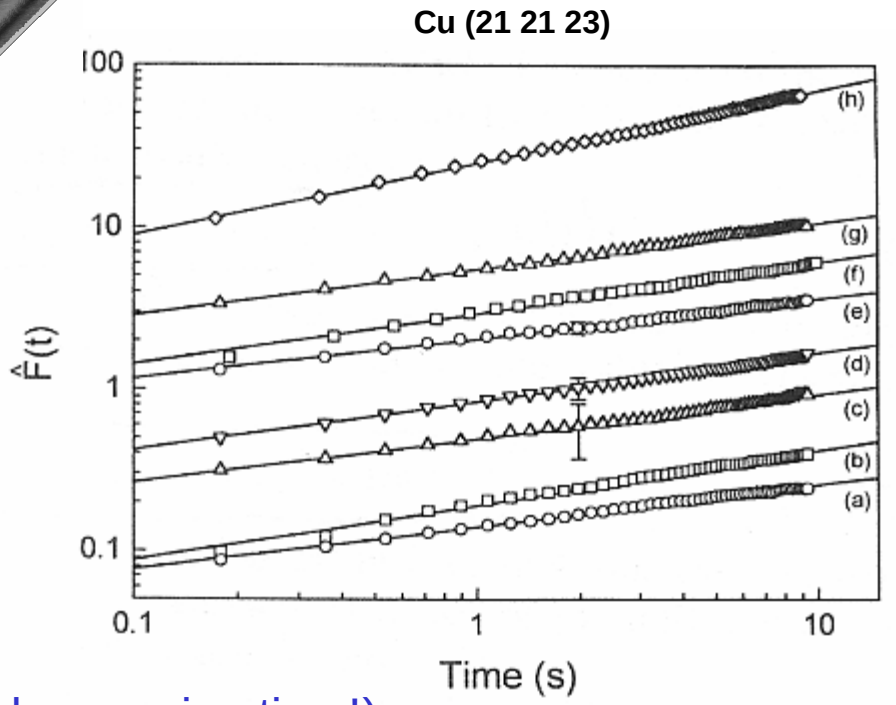


Low *T*

$G(t) \prec t^{1/4}$

High *T*

$G(t) \prec t^{1/2}$

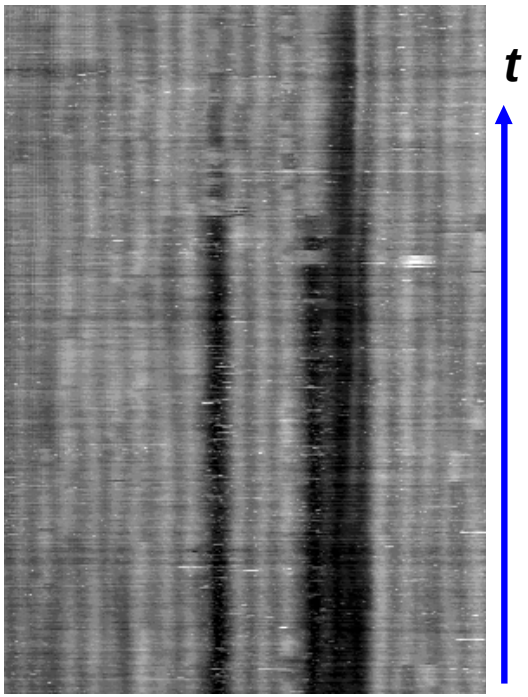


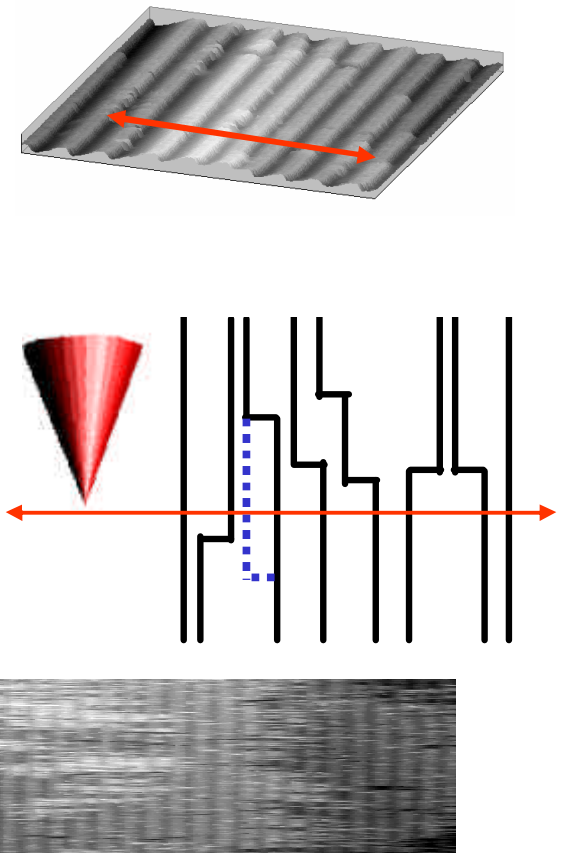
(1-d approximation !)

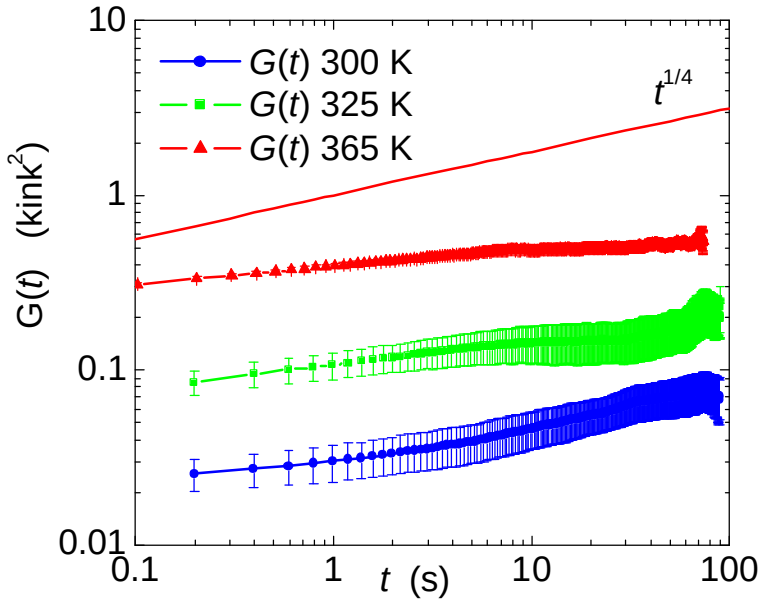
short times

Giesen *et al.* Surf. Sci. (1998)

Cu(115) : time fluctuations on a flat surface







14nm ´ 80 s
152 ´ 400 pixels²

T =300 K

14 nm ´ 20 s
152 ´ 200 pixels²

T =365 K

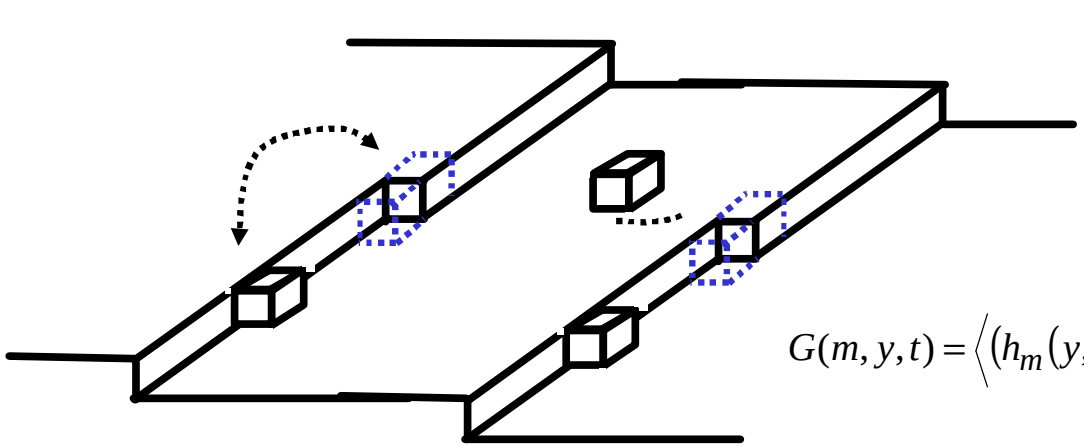
G(t) ?

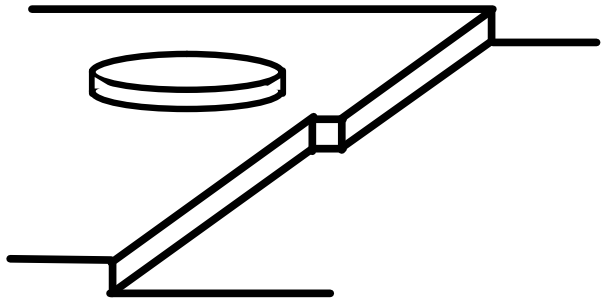
$T < T_R$ =380 K

→ Strong step-step interaction = 2-d approach !

Thermal equilibrium fluctuations of vicinal surfaces

M. Giesen : *Progress in Surface Science 68 (2001) 1*





$$G(m,y,t) = \left\langle \left(h_m(y,t) - h_0(0,0)\right)^2 \right\rangle$$

+ Adatom on terraces

$$G(t) \prec t^{1/2}$$

Langevin equation:

$$\frac{\partial h(y)}{\partial t} = -\frac{\Gamma}{kT}\left(\frac{dH}{dh(y)}\right) + x(y,t))$$

Γ : hopping rate

$$\left\langle x_{y'}(t'))\, x_y(t))\right\rangle = 2\,\Gamma\, d(y-y')\, d(t-t')$$

(Fluctuation dissipation theorem)

+ Adatom along steps (+ matter conservation)

$$G(t) \prec t^{1/4}$$

$$\frac{\partial h(y)}{\partial t} = \frac{\Gamma}{kT}\frac{\partial^2}{\partial y^2}\left(\frac{dH}{dh(y)}\right) + x(y,t))$$

$$\left\langle x_{y'}(t'))\, x_y(t))\right\rangle = -2\,\Gamma\left[\frac{\partial^2}{\partial y^2} d(y-y')\right] d(t-t')$$

2-d Langevin equation

Langevin 2d equation : (+ matter conservation within the surface plane)

$$\frac{\partial h_m(y)}{\partial t} = \frac{1}{kT}\left(\Gamma_x \frac{\partial^2}{\partial m^2} + \Gamma_y \frac{\partial^2}{\partial y^2}\right)\left(\frac{dH}{dh_m(y)}\right) + x(m,y,t))$$

Energetics: capillary wave model: $H = \sum_{m,y}\left[\frac{h_x}{2}\left(h_{m+1,y} - h_{m,y}\right)^2 + \frac{h_y}{2}\left(h_{m,y+1} - h_{m,y}\right)^2 + V_{loc}\left(h_{m,y}\right)\right]$

Parameters:

Energetic: η_x , η_x : surface stiffness

V_{loc} : localization potential (= 0 for $T > T_R$)

2 more parameters:

Hopping rates:

Γ_x , Γ_y

Noise term: $\left\langle x_{m',y'}(t'))x_{m,y}(t))\right\rangle = -2\left(\Gamma_x \frac{\partial^2}{\partial m^2}d(m-m') + \Gamma_y \frac{\partial^2}{\partial y^2}d(y-y')\right)d(t-t')$ (Fluctuation dissipation theorem)

$$G(t) = \frac{kT}{p^2}\int_0^p\int_0^p \frac{1-e^{-a_q|t|}}{b_q}\,dq_x dq_y$$

$$a_q = \frac{4b_q}{kT}\left[\Gamma_x(1-\cos(q_x)) + \Gamma_y(1-\cos(q_y))\right] \qquad b_q = h_x(1-\cos(q_x)) + h_y(1-\cos(q_y)) + 4p^2 V_{loc}$$

Time correlation function for an isotropic surface

h_x, h_y are known Γ_x, Γ_y parameters

$$G(t) = \frac{kT}{p^2} \int_0^p \int_0^p \frac{1 - e^{-a_q |t|}}{b_q} \, dq_x dq_y$$

$$h_x = h_y \quad \Gamma_x = \Gamma_y$$

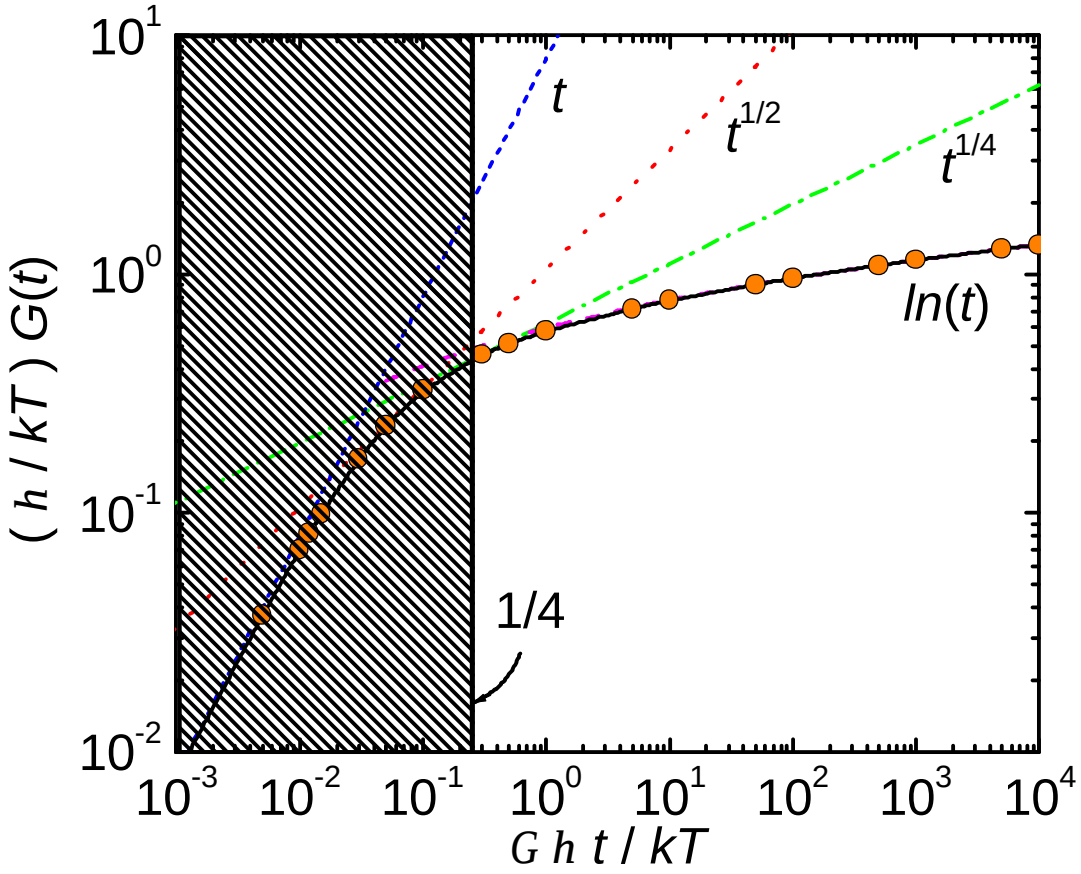
Short times: linear !

$$t < \frac{kT}{4\Gamma h}$$

$$G(t) = 8\Gamma t$$

Logarithmic divergence

$$G(t) = \frac{k_B T}{p\, h} \left(\frac{1}{4} ln \left(\frac{p^4 \Gamma h}{k_B T} t \right) + 0.7326 \right)$$



Anisotropic surface

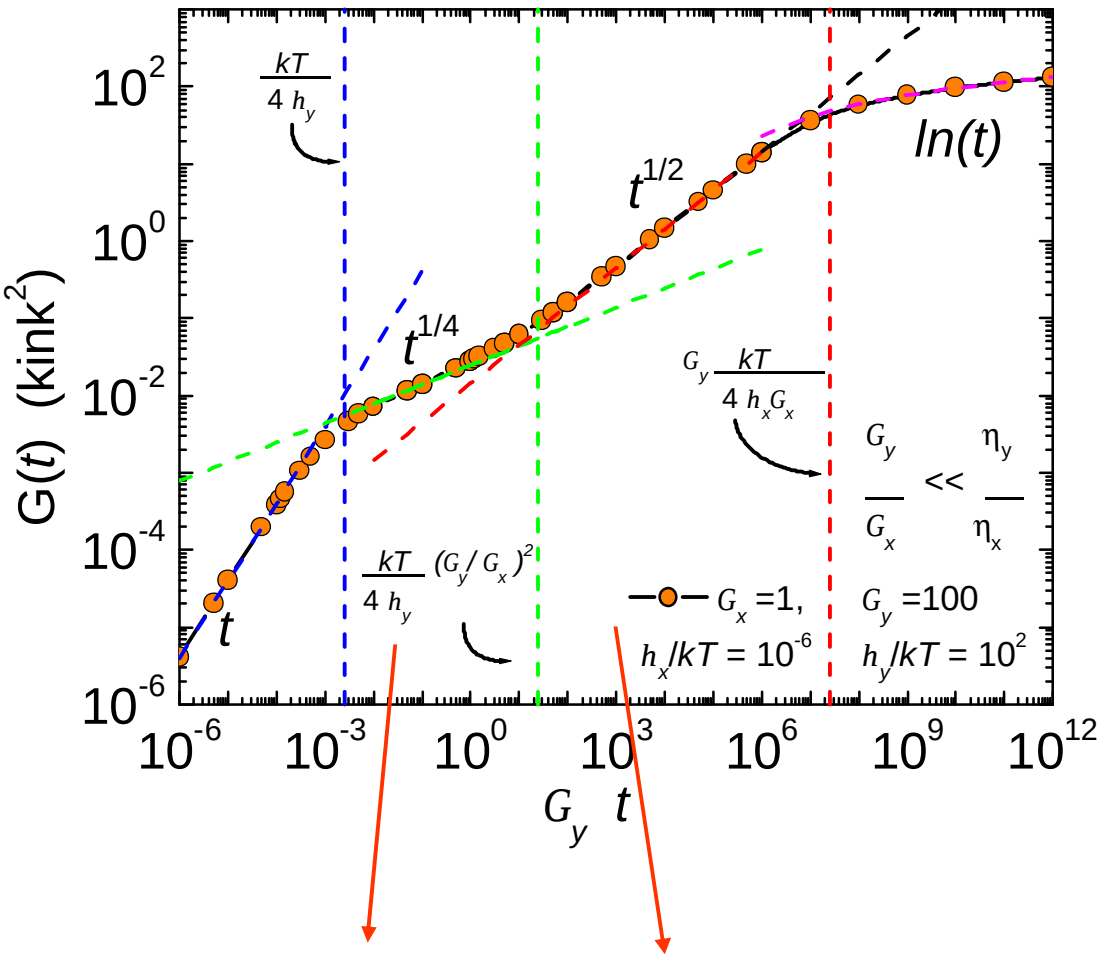
$$G(t) = \frac{kT}{p^2} \int_0^p \int_0^p \frac{1 - e^{-a_q |t|}}{b_q} \, dq_x dq_y$$

1) - Strong energetic anisotropy:

$$\frac{h_y}{h_x} >> \frac{\Gamma_y}{\Gamma_x}$$

+ $t^{1/4}$ regime : id 1-d

+ $t^{1/2}$ regime



Diffusion anisotropy

Energetic anisotropy

Anisotropic surface

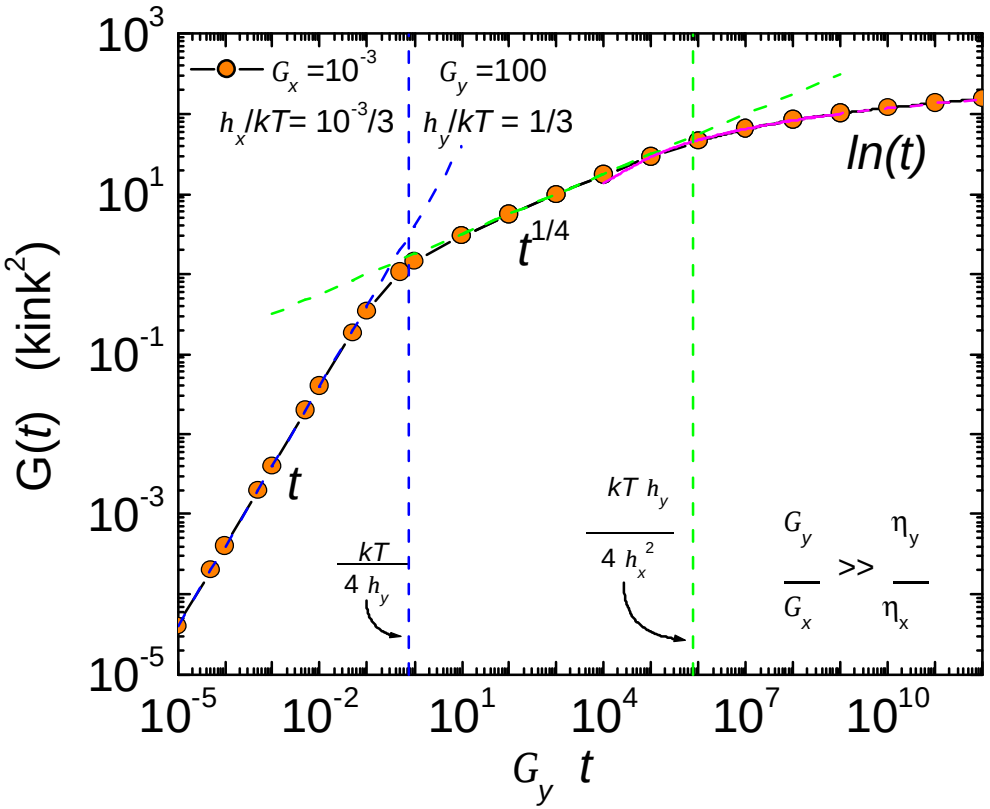
2) -Strong hopping anisotropy:

$$G(t) = \frac{kT}{p^2} \int_0^p \int_0^p \frac{1 - e^{-a_q |t|}}{b_q} \, dq_x dq_y$$

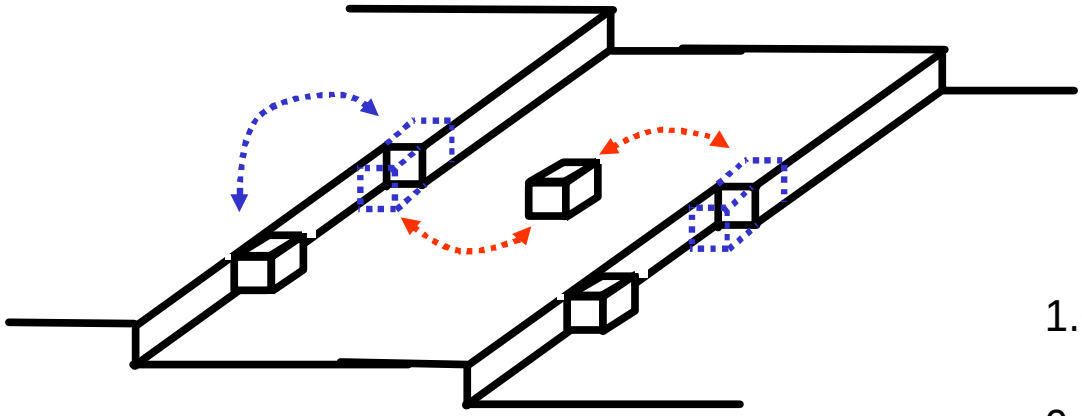
$$\frac{h_y}{h_x} << \frac{\Gamma_y}{\Gamma_x}$$

Régime $t^{1/4}$: id 1-d

No $t^{1/2}$ regime !



Hopping rates



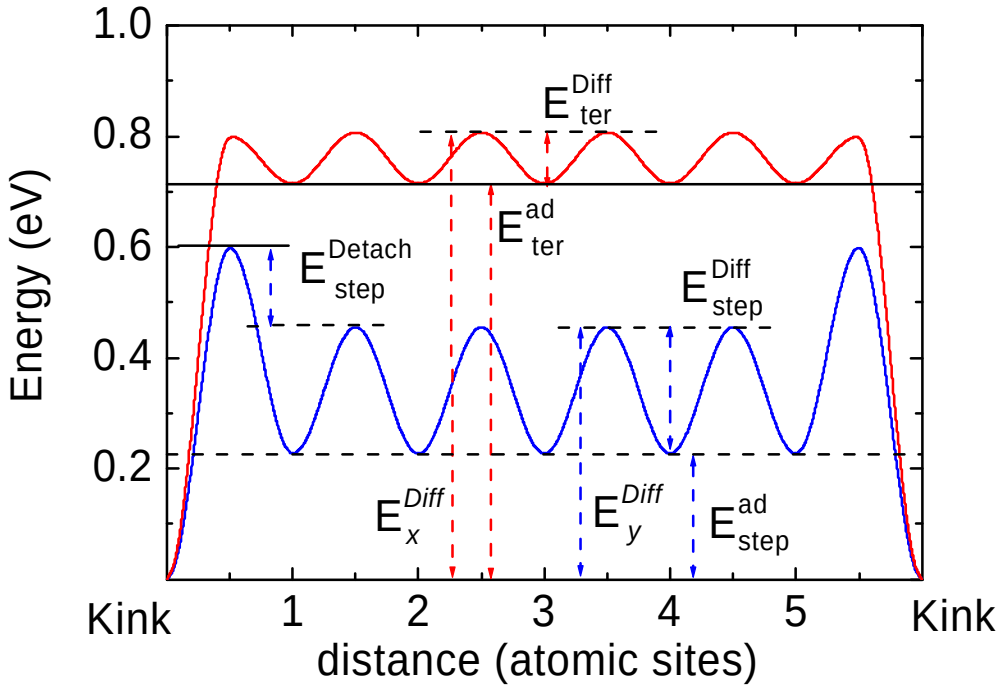
Pimpinelli *et al.* Surf. Sci. 295 (1993) 143 :

$$\Gamma_y = C_k D_y^k = C_k\, n\, e^{-\frac{E_y^{Diff\ k}}{k_B T}}$$

$$\Gamma_x = \frac{C_k}{\ell_0} D_x^k = \frac{C_k\, n\, e^{-\frac{E_x^{Diff\ k}}{k_B T}}}{\ell_0}$$

Other expressions can be used ….

Crude model:
no Schwoebel barriers



$$E^{Diff\ k} = E^{ad} + E_{ad}^{Diff} + \ldots$$

Anisotropies (interaction A/L^2)

Energetic anisotropy

$$h_x = 6\frac{d}{\ell_0{}^4} \qquad h_y = \frac{k_B T}{b^2} + \ldots \qquad \frac{h_y}{h_x} \approx \frac{k_B T\ \ell_0{}^4}{p^2 A\ b^2}$$

Hopping anisotropy

$$\frac{\Gamma_y}{\Gamma_x} \approx \frac{e^{\frac{\Delta E_{Diff}}{k_B T}}}{\ell_0}$$

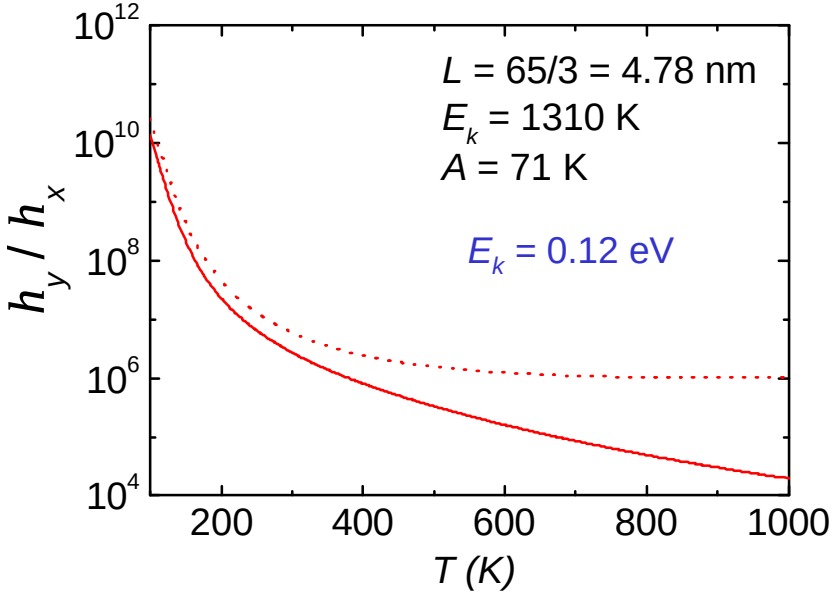
$$\frac{h_y / h_x}{\Gamma_y / \Gamma_x} = \frac{2\,\ell_0{}^5}{p^2 A} T e^{-\frac{E_k - \Delta E_{Diff}}{k_B T}}$$

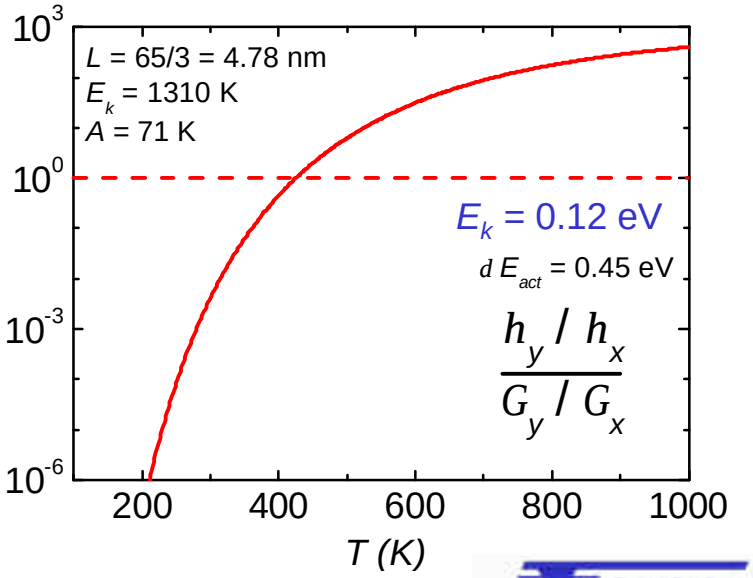
For $E_k > \Delta E_{Diff}$

with T

$t^{1/2}$

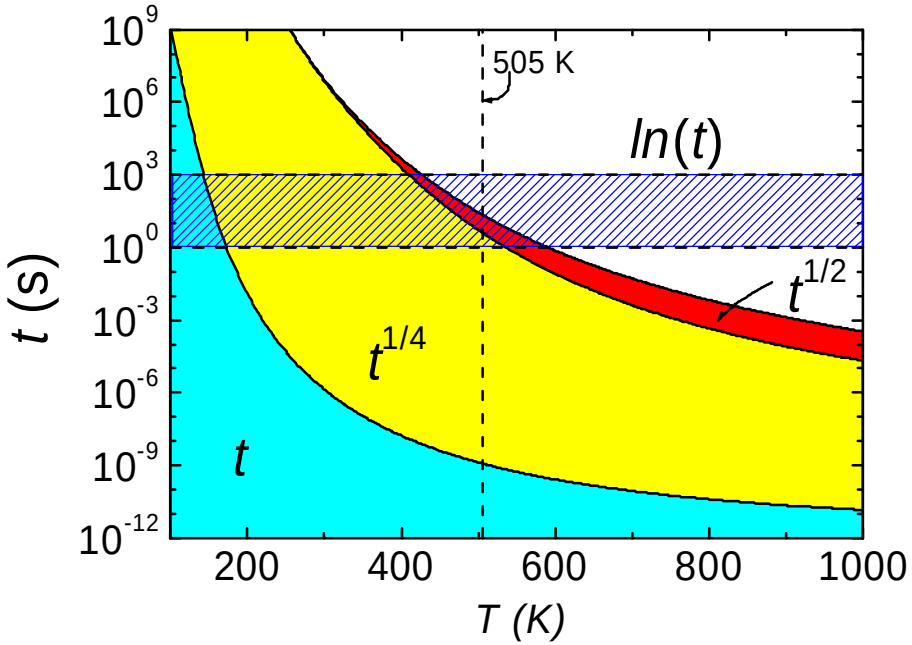
No $t^{1/2}$





$t^{1/2}$ regime appears at high T

(t,T) and (t,L) diagrams (+ A/L^2 interaction)



Versus temperature :

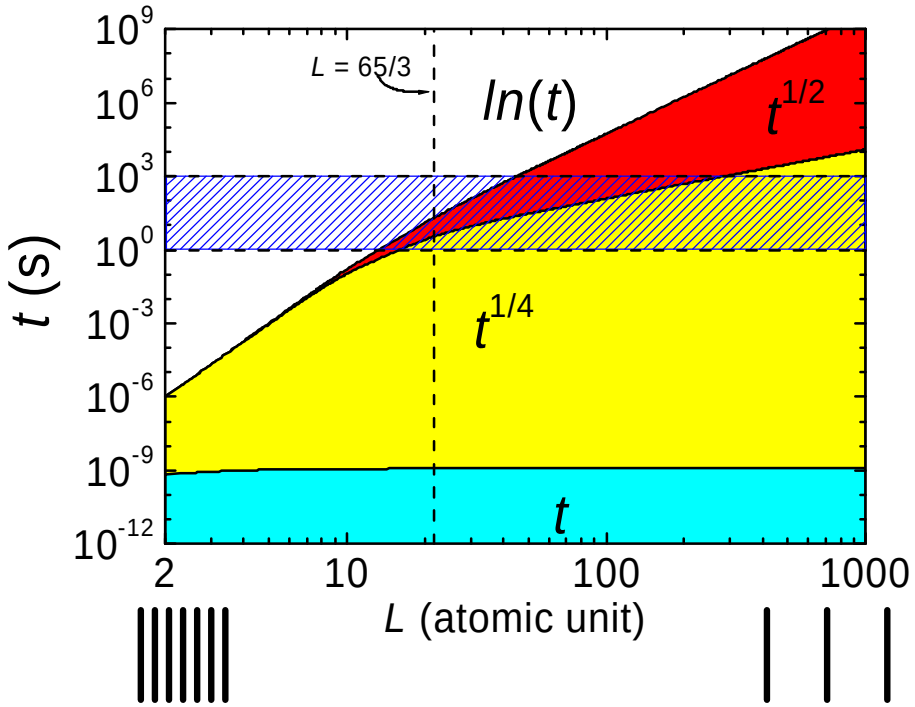
E_k = 1310 K
A = 71 K
L = 65/3 = 4.78 nm = Cu(21 21 23)

$$E^{Diff\ k} = E^{ad} + E_{ad}^{Diff}$$

EMT calculation (Stoltze) :
J. Phys. Cond. Matter 6 (1994) 9495.

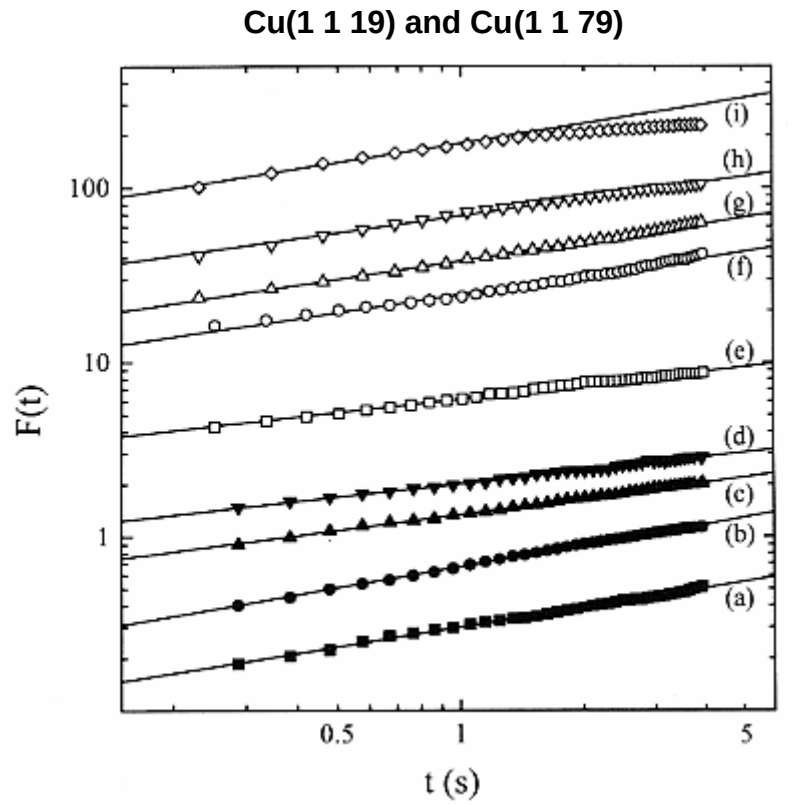
Versus terrace width:

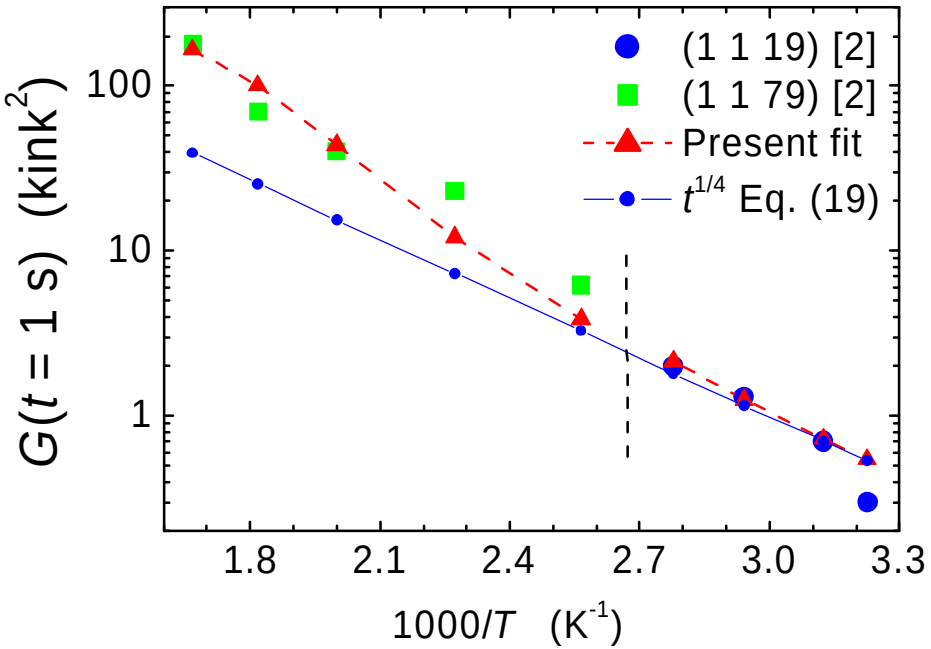
T = 505 K



Application to vicinals of Cu(001)

Giesen *et al.* Surf. Sci. 329 (1995) 47





E_k = 1430 K =0.123 eV

A = 70 K

Γ_y E^{diff}_y = 0.43 eV

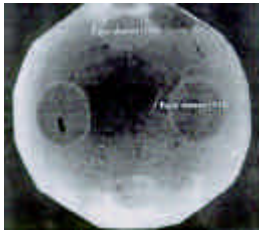
Γ_x E^{diff}_x = 0.67 eV

According to EMT calculation (Stoltze 1994) :

$2\ E_k + E^{diff}_{step} = 0.49$ eV

$E^{ad}_{terr} + E^{diff}_{terr} = 0.93$ eV

In summary ...

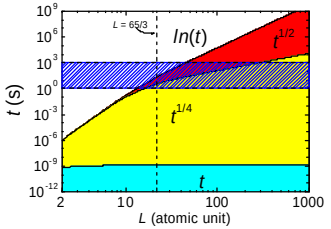


At thermal equilibrium,
Morphology at the nanoscale is related to roughening

Energetics:
Investigation of vicinal surfaces : measurement of atomic parameters
For regular surfaces, 2 main parameters : E_k and A

Dynamics :
2 more parameters : hopping rates G_x , G_y

Complex time behavior (t, $t^{1/4}$, $t^{1/2}$, $ln(t)$)
depending on the energetic and diffusion anisotropies



Alloy surfaces

Surface morphology ⟷ **Chemical order**

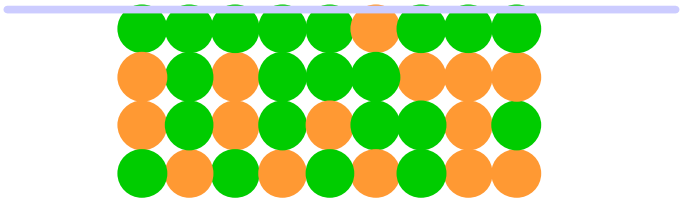
model systems : Cu_3Au , $Cu_{83}Pd_{17}$, Fe_3Al , Quasicrystals (AlPdMn)

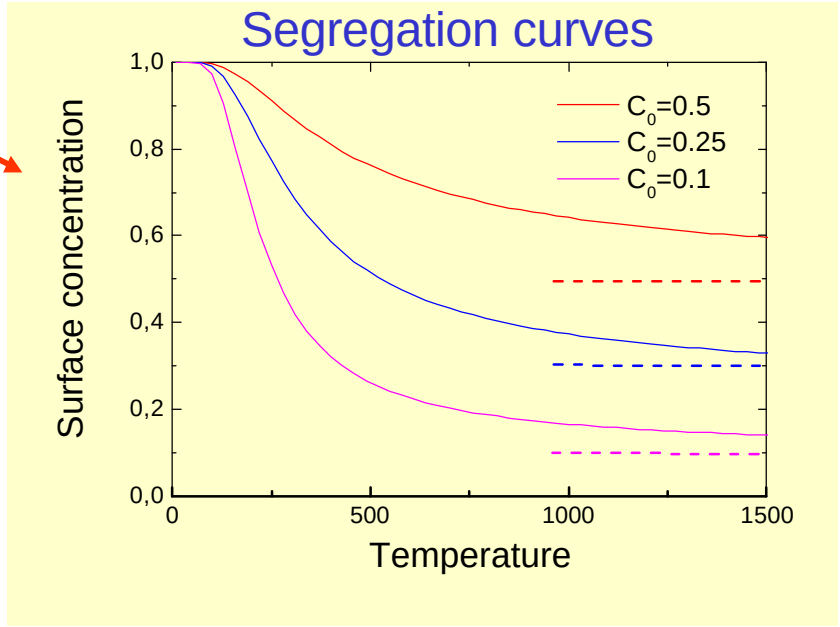
Solid solution:

Surface segregation

A-B alloy **DE = 0.05 eV**

$$E_S(A) < E_S(B)$$

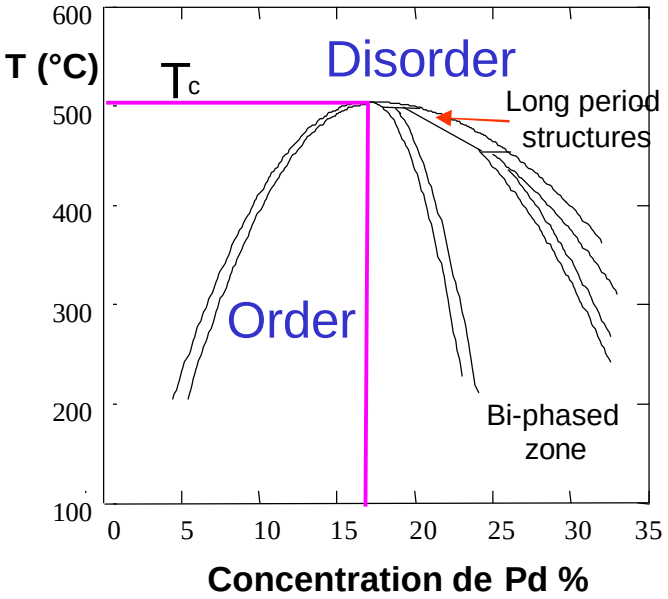


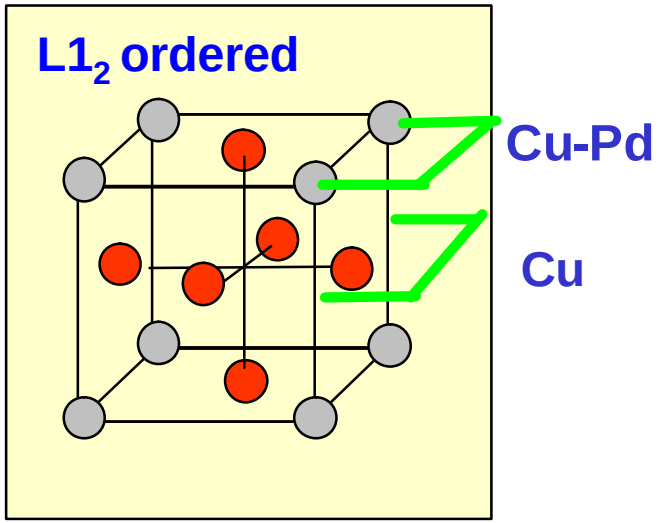


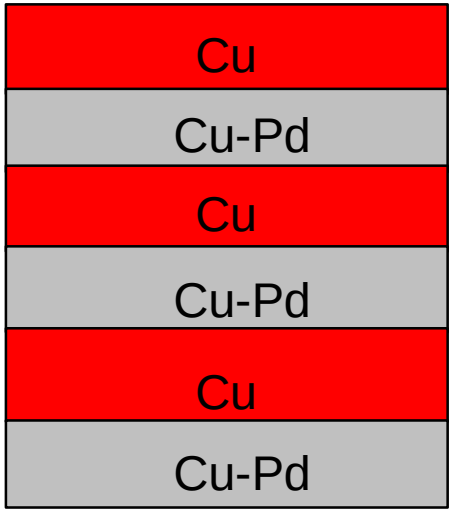
Ordered alloys: + long range chemical order

Much more complex !...

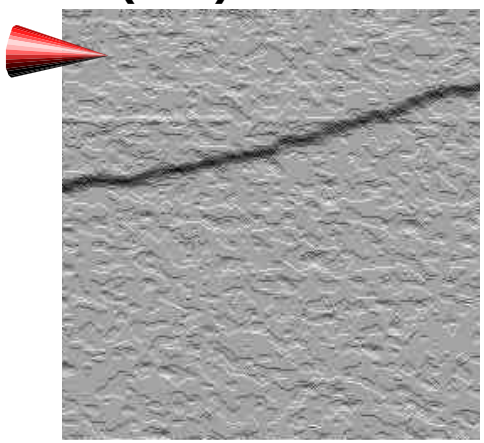
Ordered alloys Cu-Pd (17 %)





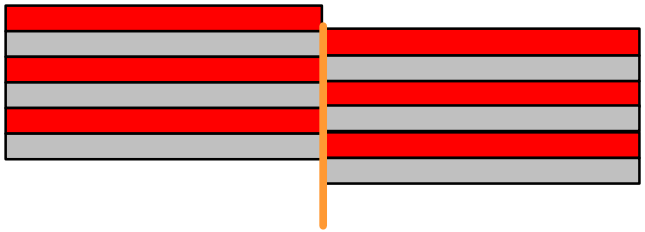


(001) surface



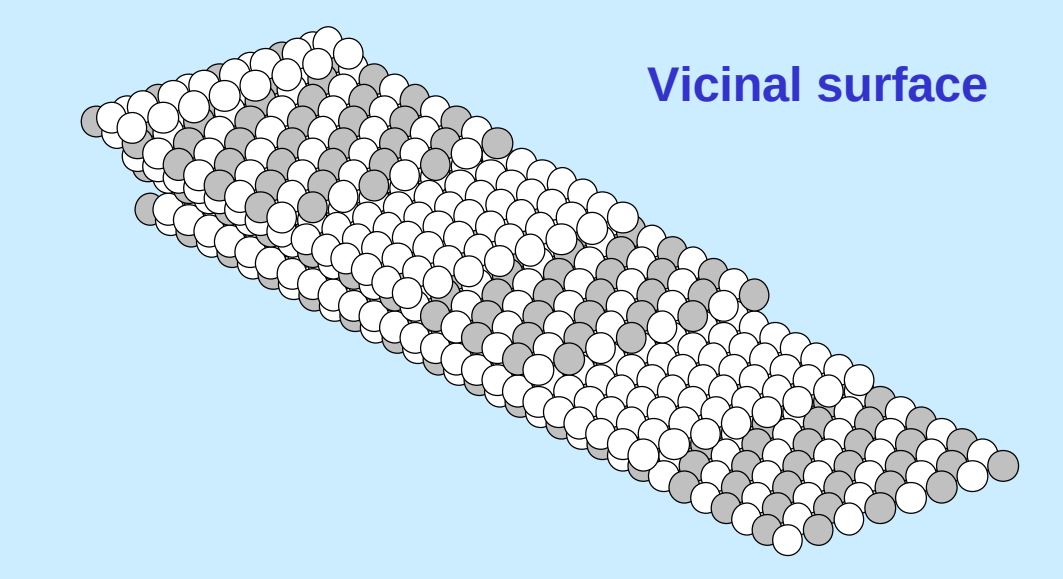
84 nm x 84nm

Cu terraces



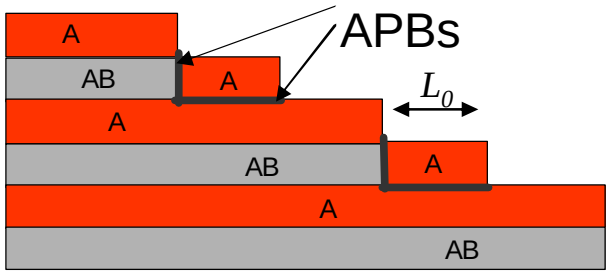
Emergence of
Bulk Antiphase Boundary (APB)

Vicinal surfaces Cu-Pd (17 %)

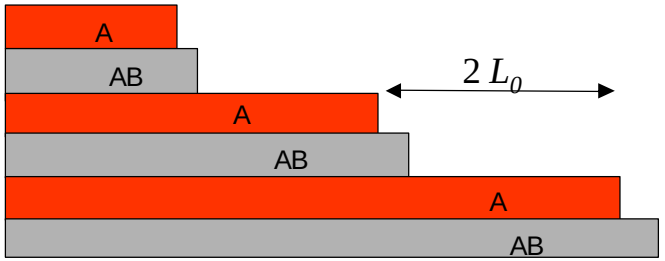


$$F = F_0 + \frac{b(E_k)}{h} p + \frac{d(E_k, A)}{h_0^3} p^3$$

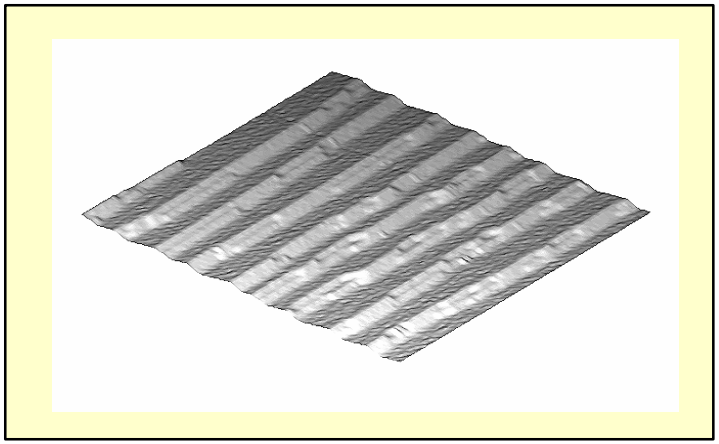
Or …. Cu terraces + single steps or



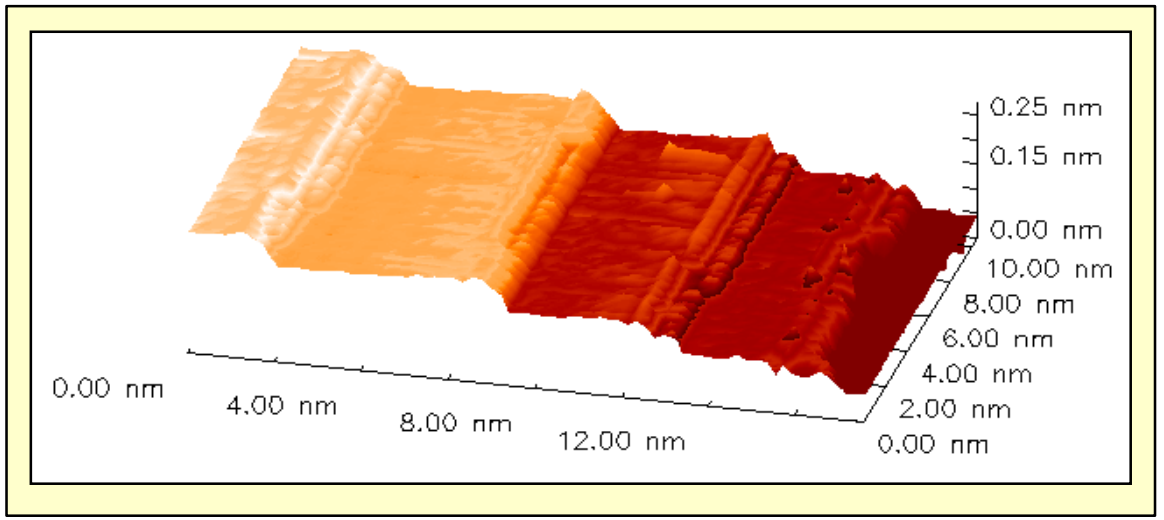
Cu terraces + paired steps ?

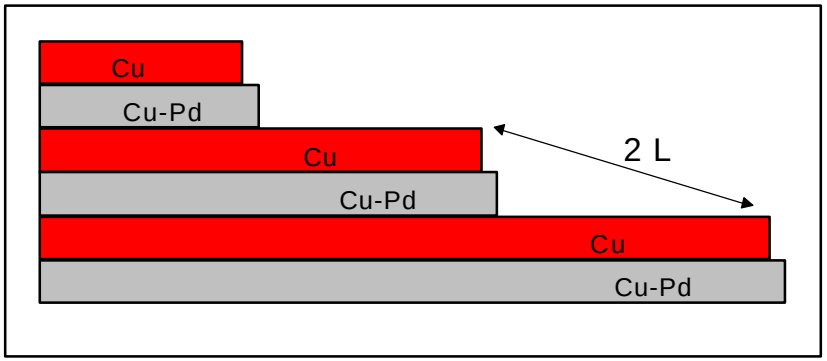


Ordered alloy : Double step structure

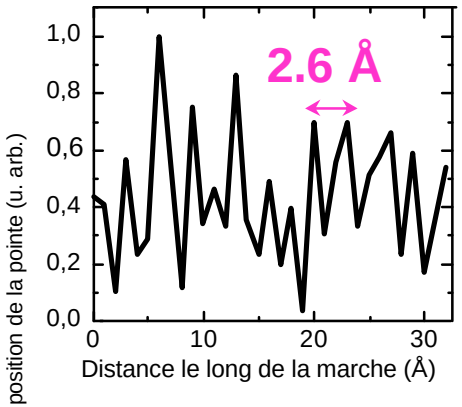


Cu-Pd 17% (1 1 11) 30 x 30 nm^2

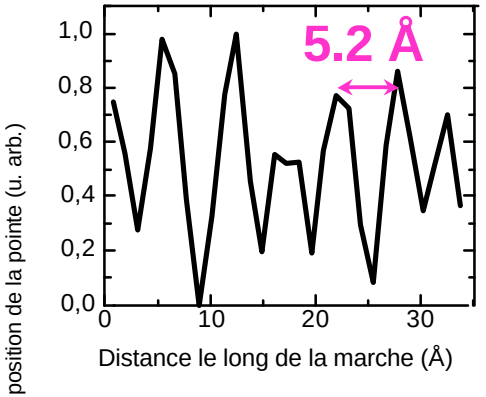




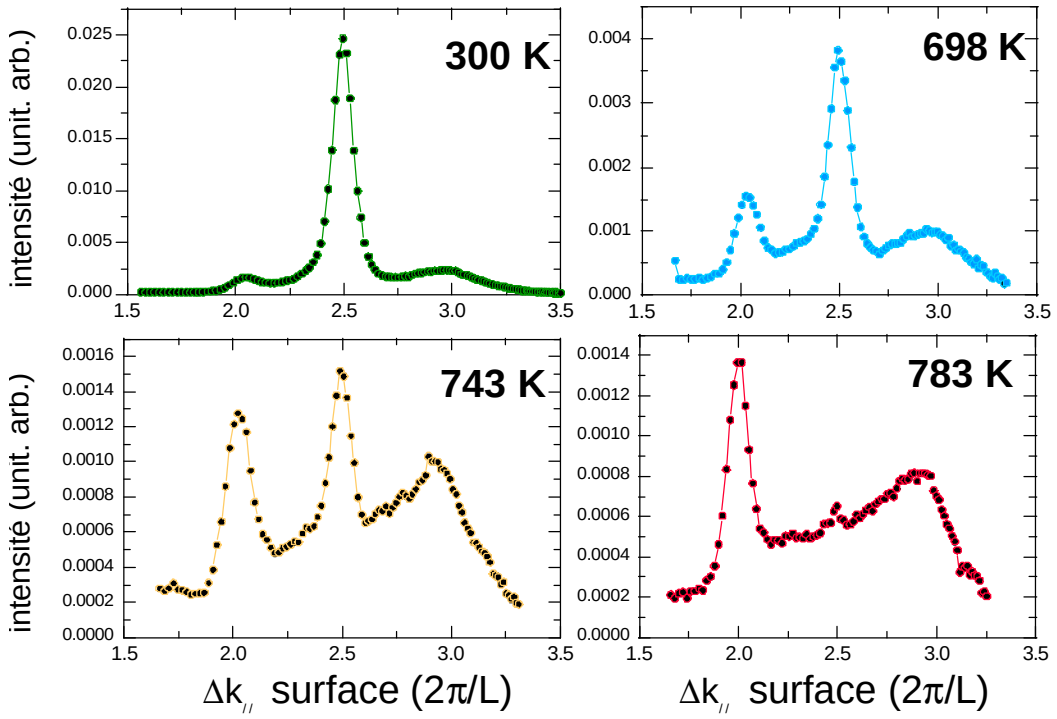
upper step

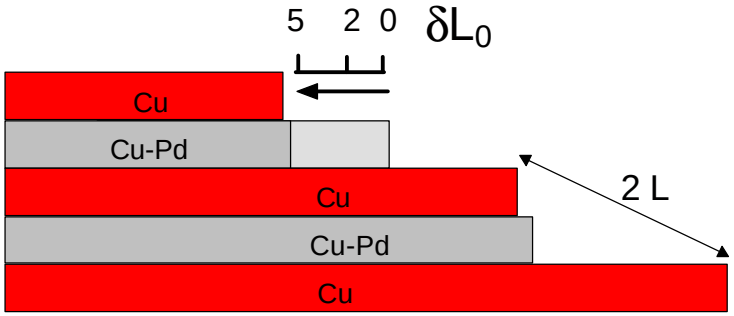


lower step



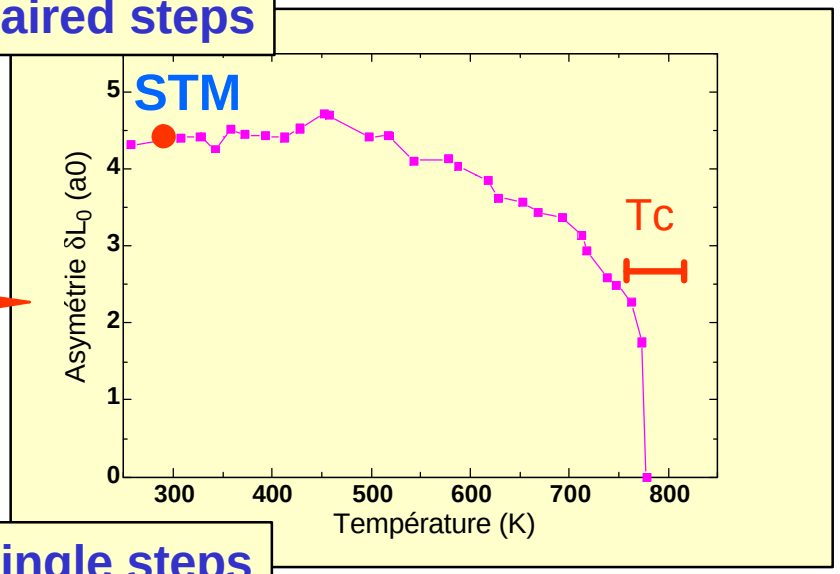
Temperature evolution: Paired steps ⟷ Single steps structure



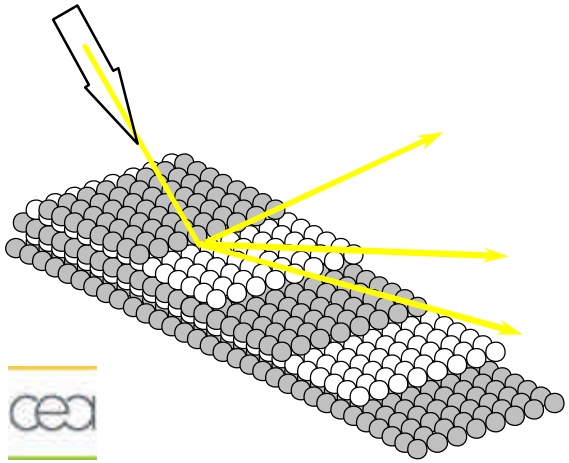


Terrace asymmetry

Paired steps

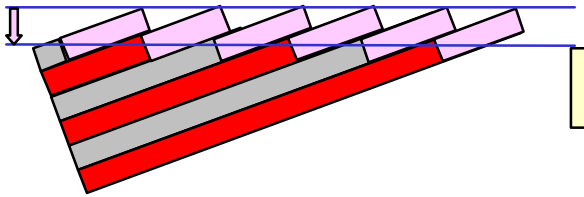


Single steps

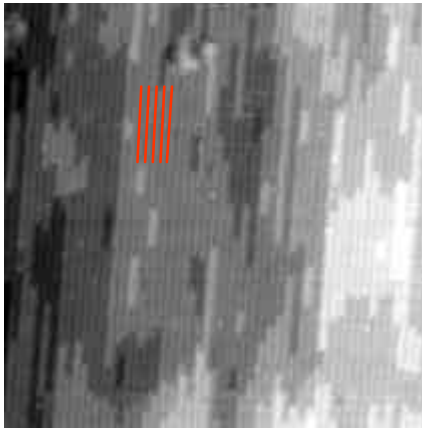


Continuous transition (Bulk 1st order)

disorder

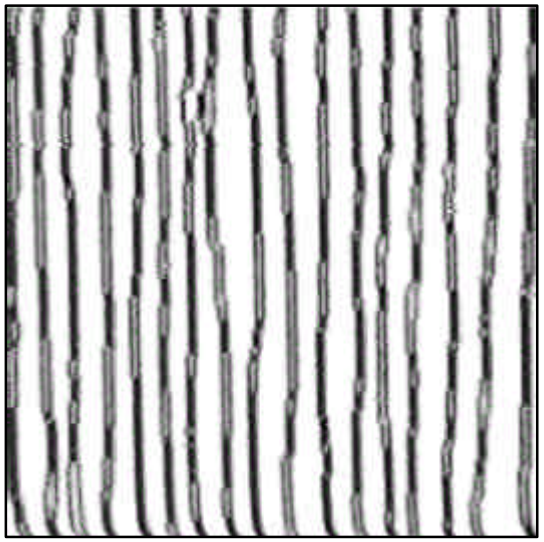


Cu-Pd(17%) (115)



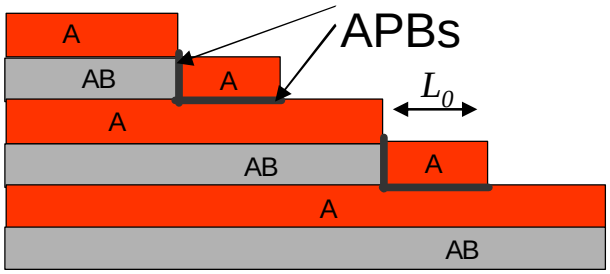
40 x 40 nm²

Cu-Pd(17%) (1 1 11)

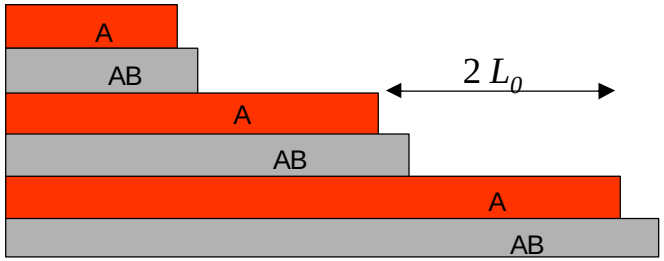


51 x 51 nm²

Single steps !



Paired steps !



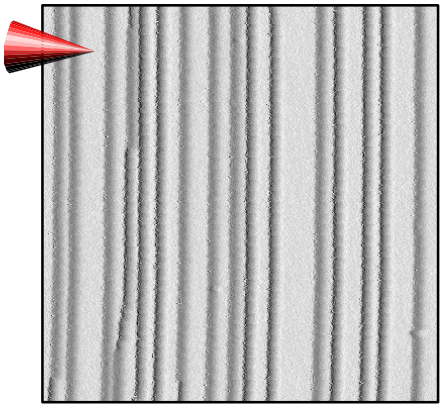
Energetic balance:

- **Step-step interaction (elastic interaction: A/L^2)** **$6A/L^4$** **F_{ds}-F_{ss}**
- **Cost of APBs** **F_{APB}**

$$3.34\ meV < F_{APB} < 6.58\ meV$$

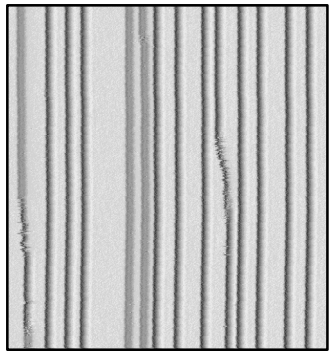
$$F = F_0 + \frac{b(E_k)}{h}\,p + \frac{d(E_k, A)}{{h_0}^3}\,p^3$$

Evolution en T : Cu_3Au



52 nm x 52 nm

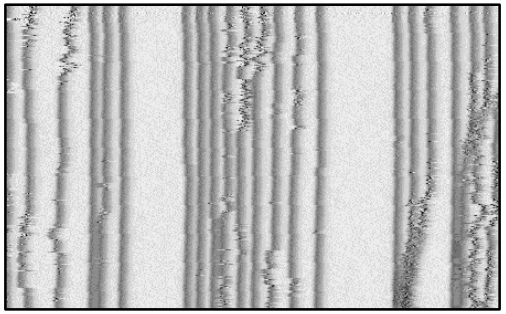
T = 300 K<< T_C



42 nm x 45 nm

T = 500 K < T_C

65 nm x 40 nm

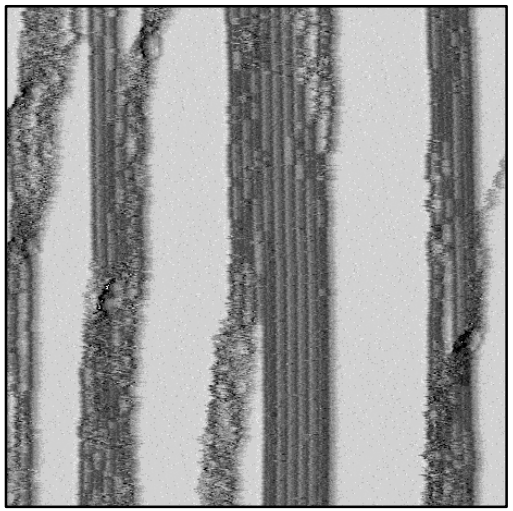


T = 650 K < T_C

ordonné

Reversible

T_c=663 K

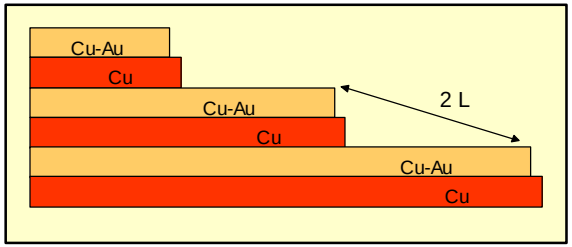


66 nm x 66 nm

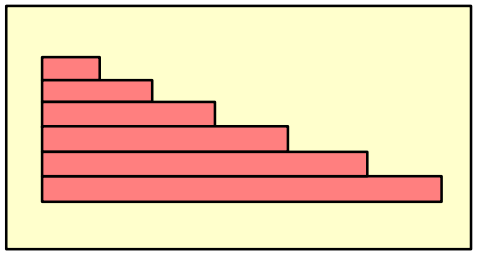
T=700 K > T_C disordered

$T<T_c$:

paired steps !



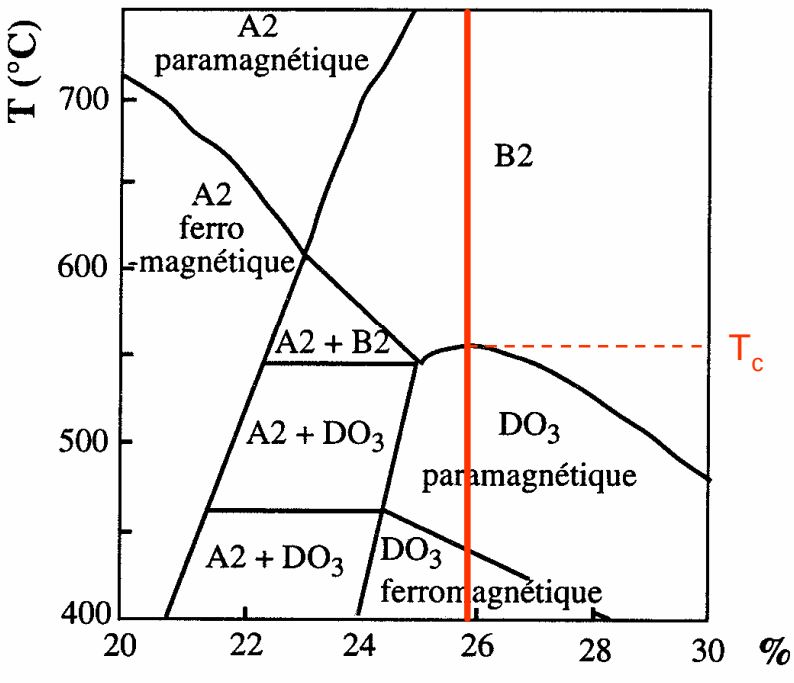
$T>T_c$: Single steps + facetting !



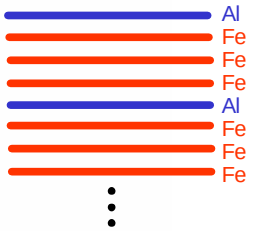
Fe_3Al (778)

Second order transition T_c = 823 K

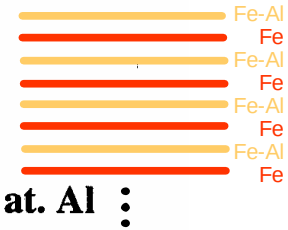
Phase diagram:

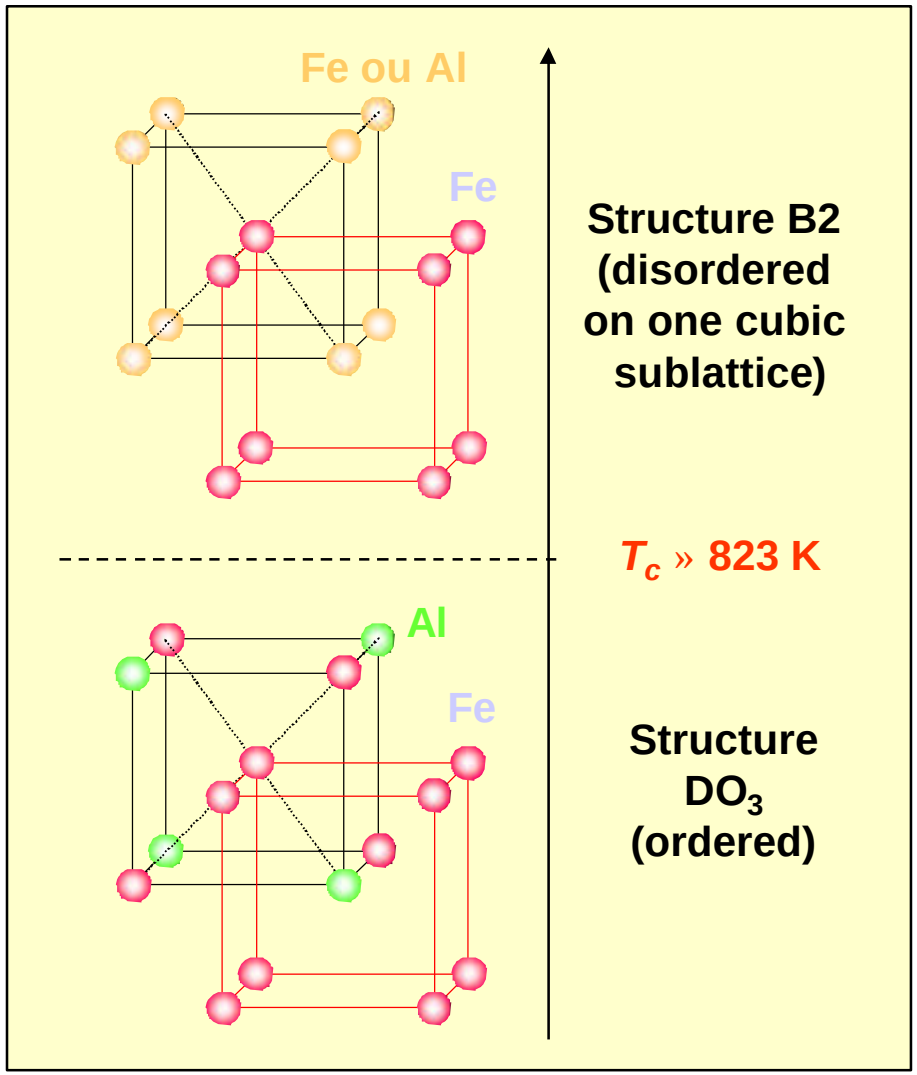


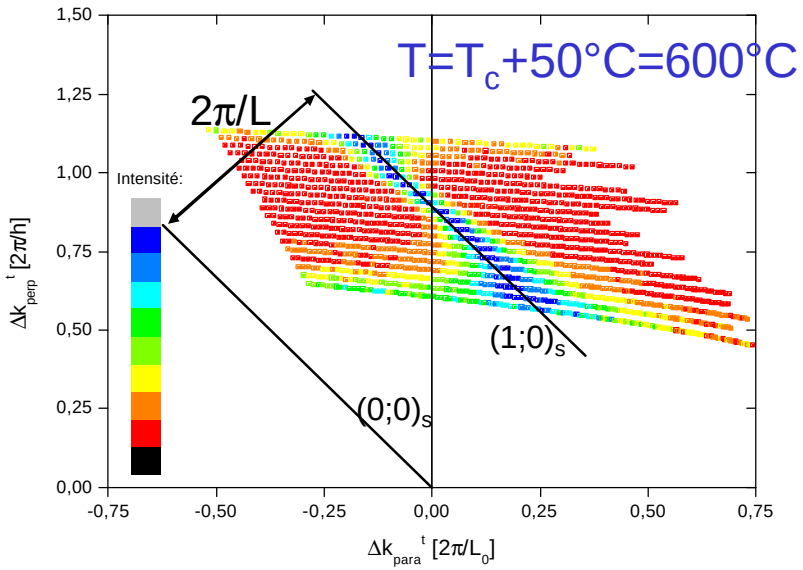
ordered

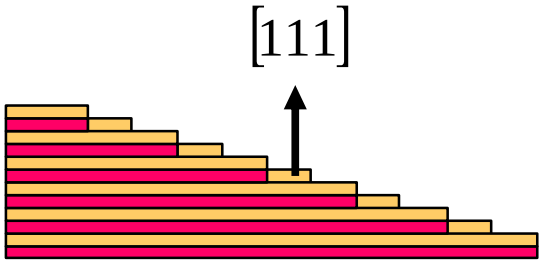


disordered

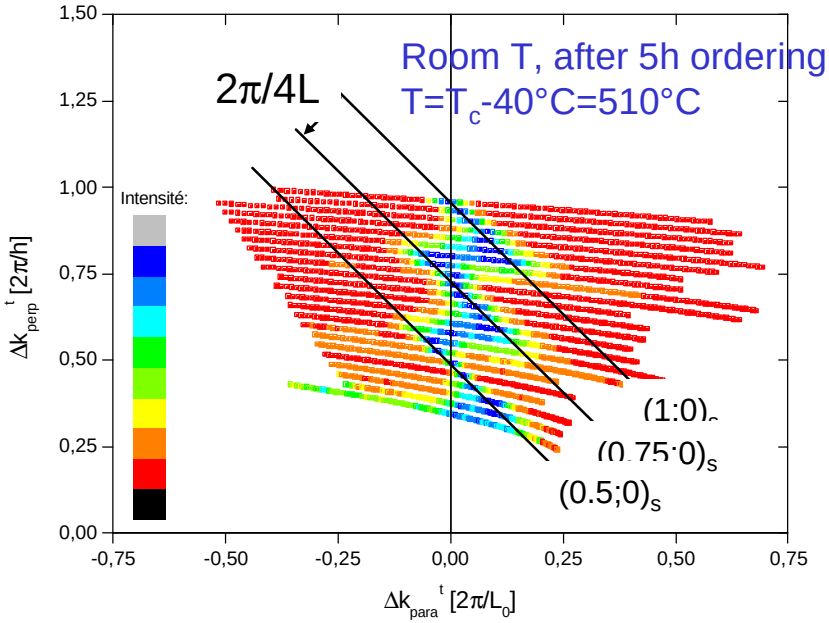


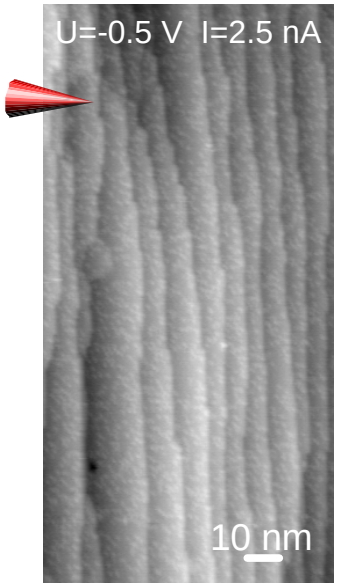






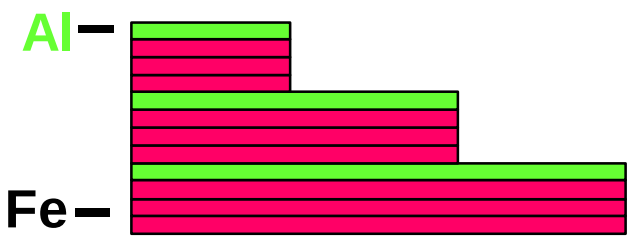
$T > Tc$: single steps !





170 nm x 90 nm

$T < T_c$: 4x steps !



Surface morphology ⟷ Chemical order

In conclusion ...

Thermal behavior of pure metal vicinal surfaces is now well known.
Kink energy, step-step interactions are the main parameters
(and hopping rates for dynamics).

Vicinal of alloys : **Cu_3Au , $Cu_{83}Pd_{17}$, Fe_3Al**

Terrace energy (surface segregation)
APBs energy

$$F = F_0 + \frac{b(E_k)}{h} p + \frac{d(E_k, A)}{{h_0}^3} p^3$$

Terraces — Steps — Step-step interaction

Single steps/Paired steps

High T anisotropic substrates

Surface morphology ⟷ **Chemical order**