



Centre Interdisciplinaire de Nanoscience de Marseille

Introduction aux contraintes de surface

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P. Muller and A. Saul Surf. Sci Rep. 54, 157 (2004).

Plan

I/ Contraintes de surface versus énergie de surface

II/ Adsorption et courbure spontanée

III/ Description d'une surface non plane

IV/ Elasticité et auto-organisation de surface

V/ Méthodes de mesures des contraintes de surface

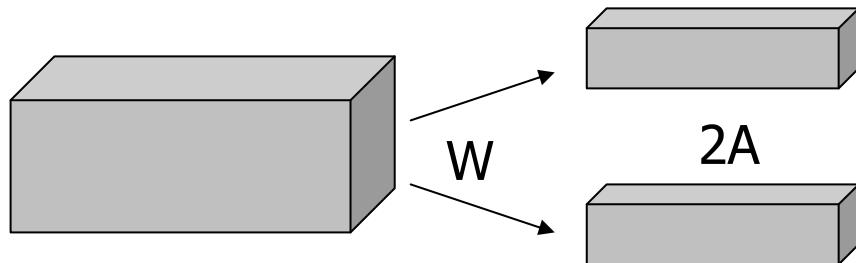
Choix: approche non thermodynamique

Notions de base:

Energie de surface versus contraintes de surface

The usual concept of surface energy

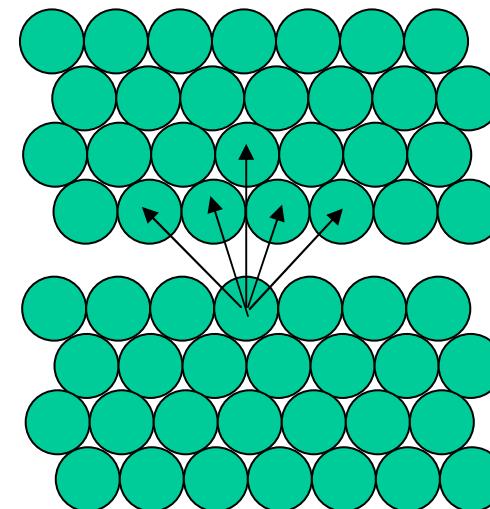
Increase area upon creation
(cleavage)



Surface energy

- Work per surface area :
- $\gamma \text{ [J/m}^2\text{]} = W/2A$
- Scalar, anisotropic
- Origin : missing neighbors

γ connected to broken bonds
is the excess of grand potential



$$\gamma = \frac{W}{2A} = \frac{1}{2A} [n_1 \varphi_1 + n_2 \varphi_2 + \dots]$$

It is a scalar

Plays each time a surface is created

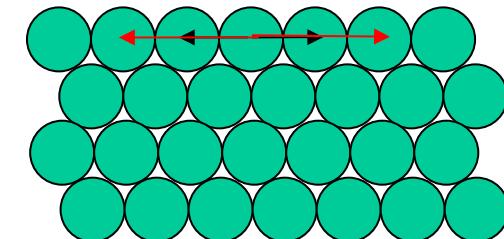
Surface stress: a simple approach

Increase area upon stretching
(deformation)

A δA



s connected to surface forces
is the excess of bulk stress



Surface stress

- Work per surface area

$$s_{ij} \text{ [mJ/m}^2\text{]} = W/\delta A$$

- Tensor, anisotropic

- Origin : modification of the bond strength

$$s_{\alpha\beta} = \frac{1}{A} \frac{\partial(\gamma A)}{\partial \epsilon_{\alpha\beta}}$$

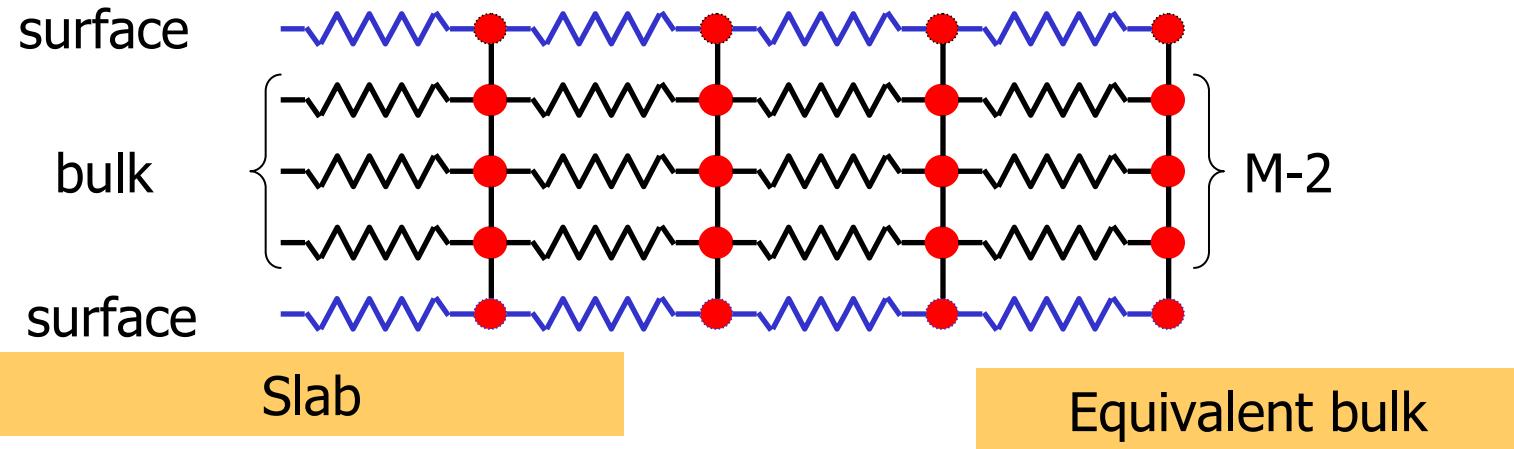
$$\begin{pmatrix} s_{xx} & s_{xy} & 0 \\ s_{yx} & s_{yy} & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

It is a 2D tensor

Plays each time a surface is deformed

P. Muller and A. Saul Surf. Sci Rep. 54, 157 (2004).

Surface stress and surface energy : toy model



$$E_{slab} = \frac{N}{2} \left[(M-2)k(\Delta x - a)^2 + 2k_s(\Delta x - a_s)^2 \right] \quad E_{vol} = \frac{NM}{2} k(\Delta x - a)^2$$

$$\sigma_{slab} = \frac{1}{M\Delta x} [(M-2)k(\Delta x - a) + 2k_s(\Delta x - a_s)] \quad \sigma_{vol} = \frac{k}{\Delta x}(\Delta x - a)$$

Contribution of the surface

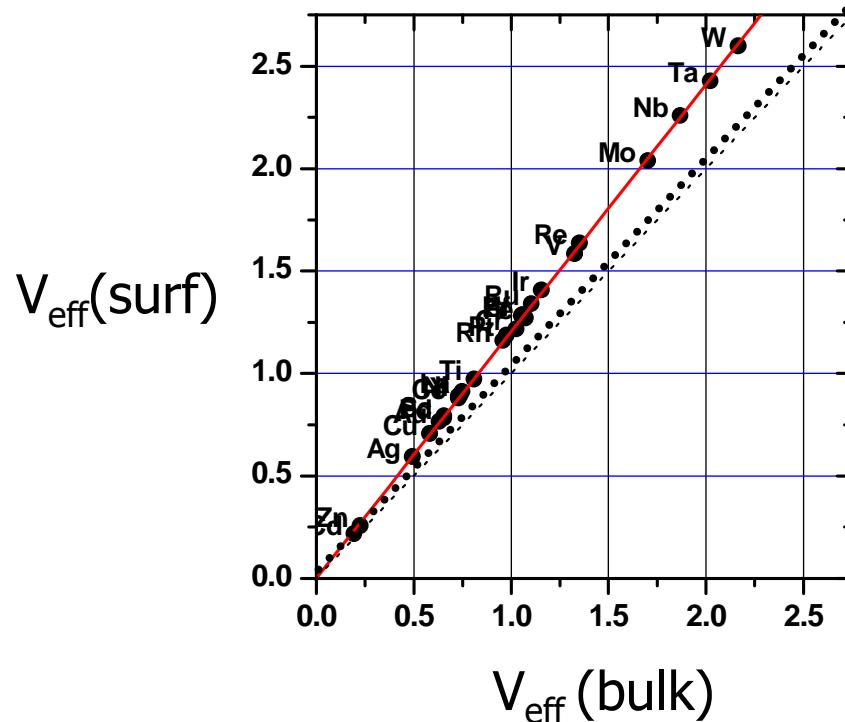
$$\gamma_{surf} = \frac{1}{2N\Delta x} (E_{slab} - E_{vol}) = \frac{1}{\Delta x} \left[\frac{k_s}{2} (\Delta x - a_s)^2 - \frac{k}{2} (\Delta x - a)^2 \right]$$

$$s_{surf} = \frac{M\Delta x}{2} (\sigma_{slab} - \sigma_{vol}) = \boxed{k_s(\Delta x - a_s)} - k(\Delta x - a).$$

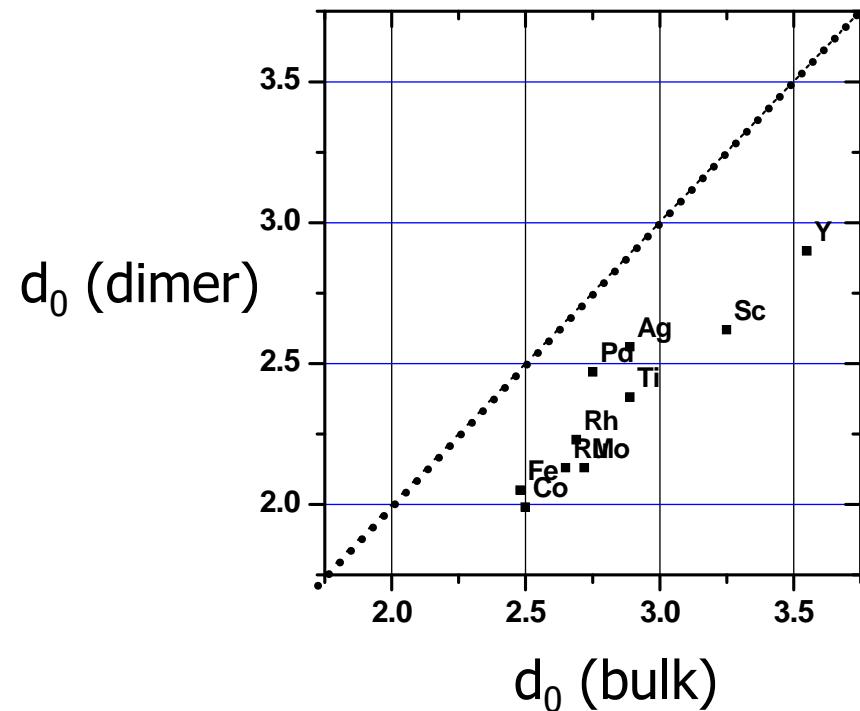
Surface stress : physical origin

The **bond strength increases** when the **coordination number decreases**

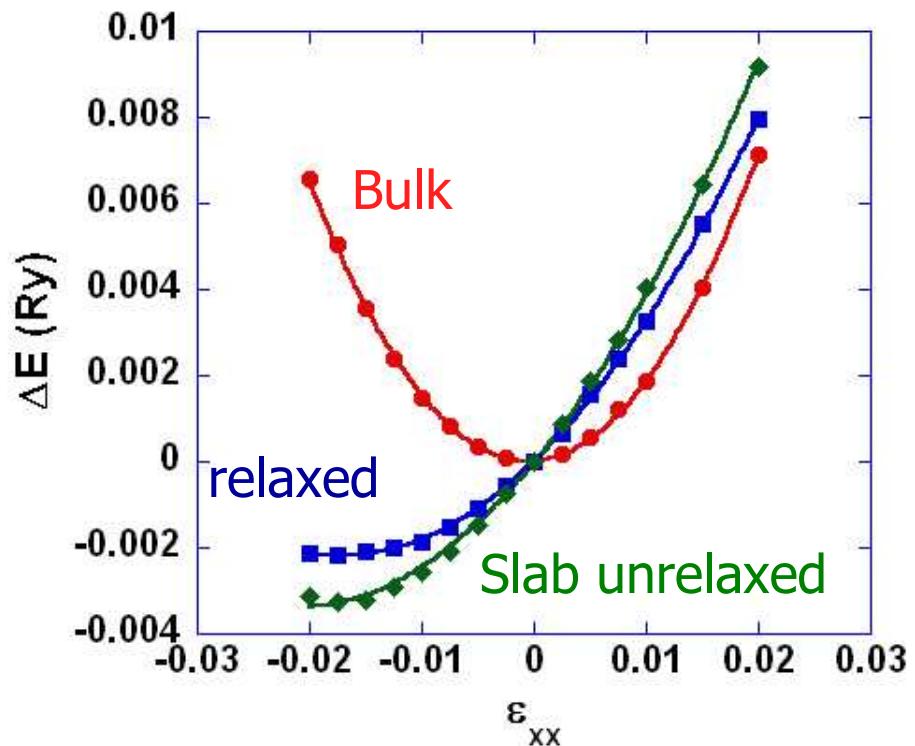
- The effective pair interaction V_{eff} increases



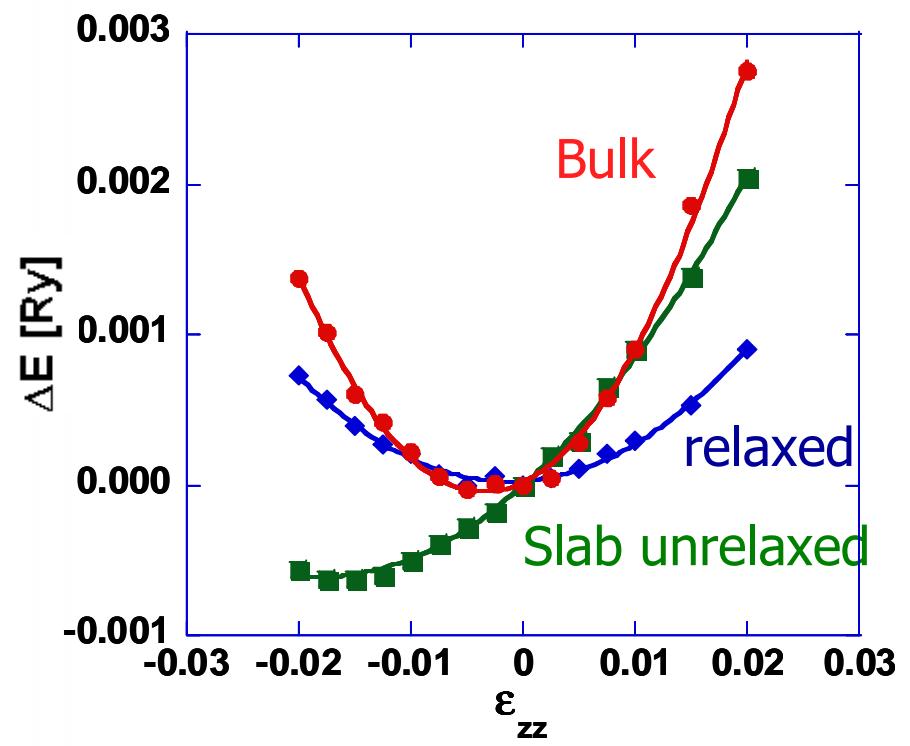
- The inter-atomic distance d_0 decreases



Parallel to the surface



Perpendicular to the surface



$$\begin{pmatrix} s_{11} & s_{12} & s_{13} \\ s_{21} & s_{22} & s_{23} \\ s_{31} & s_{32} & s_{33} \end{pmatrix} \xrightarrow{\text{relaxation}} \begin{pmatrix} s_{11} & s_{12} & 0 \\ s_{21} & s_{22} & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

Contrainte de surface : en pratique, comment la calculer

$$\gamma = \frac{1}{2A} \left\{ E \left(\overbrace{\hspace{10em}}^{\text{top face}} \right) - E \left(\overbrace{\hspace{10em}}^{\text{bottom face}} \right) \right\}$$

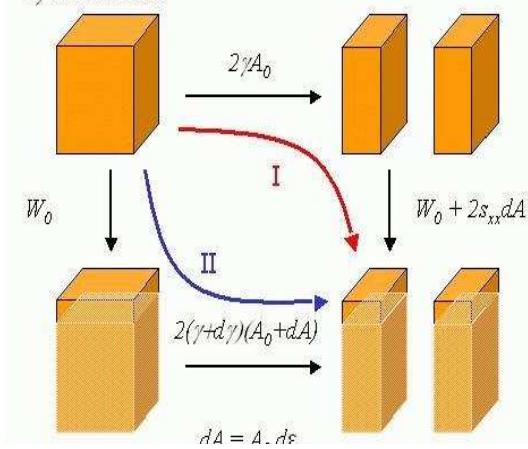
Energie totale d'un slab totalement relaxé

Energie totale d'un volume du même nombre d'atomes

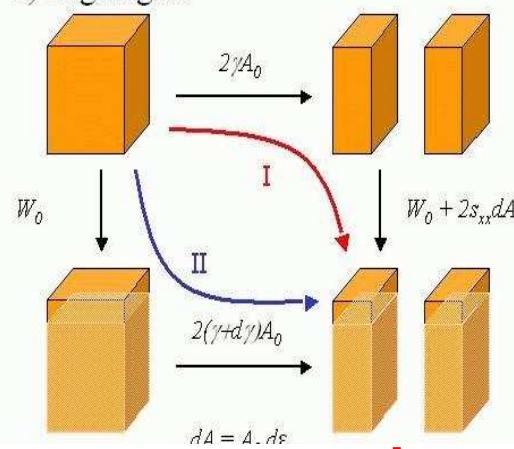
$$\sigma_{ij} = \frac{1}{A} \left. \frac{\partial A\gamma}{\partial \epsilon_{ij}} \right|_{\sigma_{iz}=0} = \frac{1}{2A} \left\{ \left. \frac{\partial E_{\text{slab}}}{\partial \epsilon_{ij}} \right|_{\sigma_{iz}=0} - \left. \frac{\partial E_{\text{bulk}}}{\partial \epsilon_{ij}} \right|_{\sigma_{iz}=0} \right\}$$

Lien énergie de surface-constraints de surface

a) Eulerian



b) Lagrangian



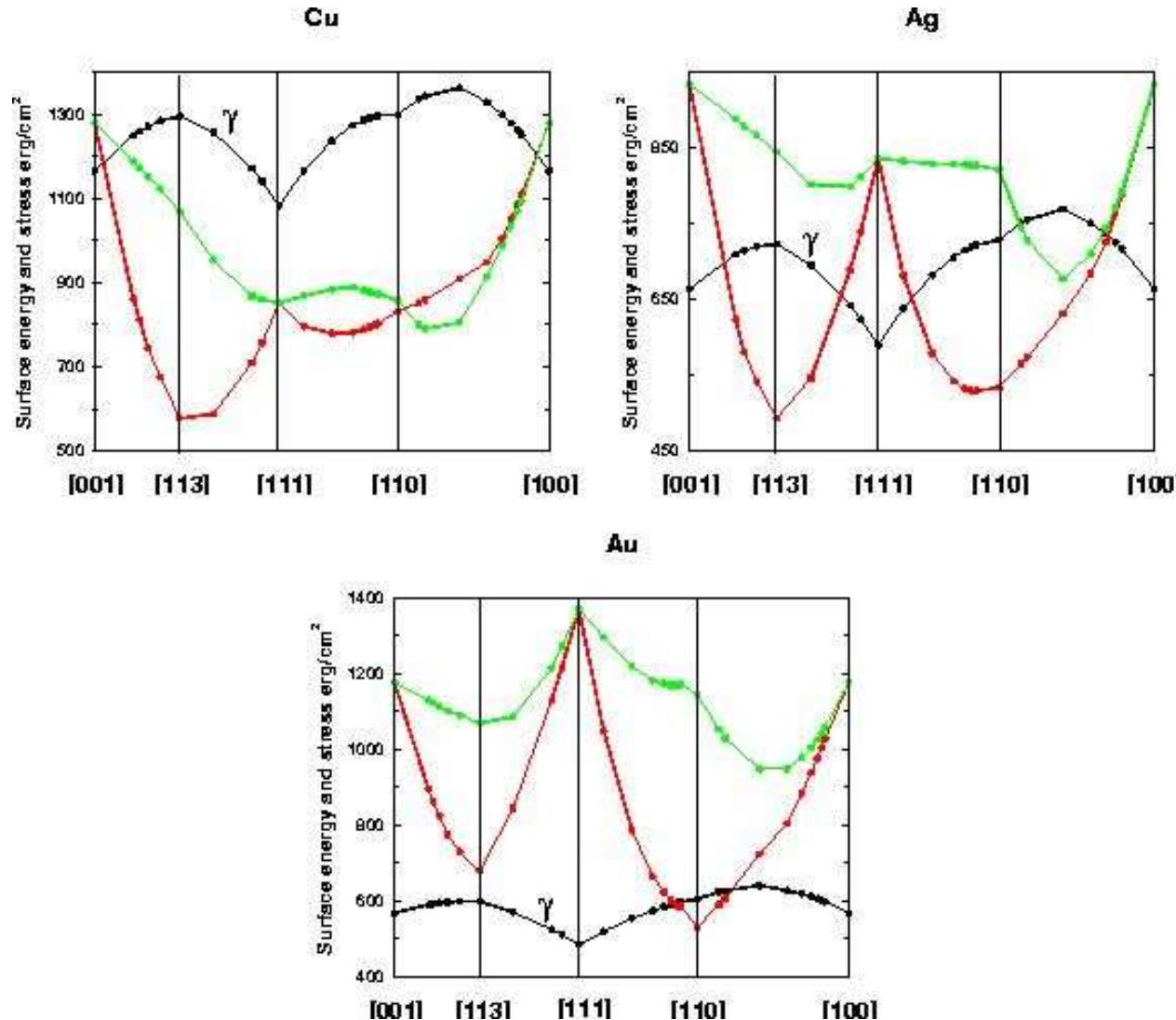
$$s^E = \gamma^E + \frac{\partial \gamma^E}{\partial \epsilon} \Bigg|_{\epsilon=0}$$

$$s^L = \frac{\partial \gamma^L}{\partial \epsilon} \Bigg|_{\epsilon=0}$$

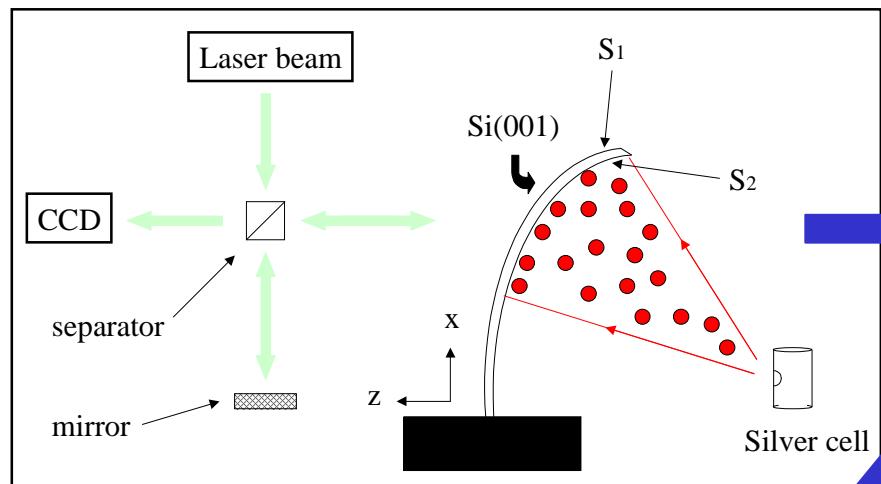
R.Schuttleworth, Proc. Roy. Soc. London 163 (1950) 644

	Excès de contrainte	Excès d'énergie
Solides	Contrainte $s = \gamma + \delta\gamma/\delta\epsilon$	Energie γ
Liquides	Tension $s = \gamma$	Tension γ

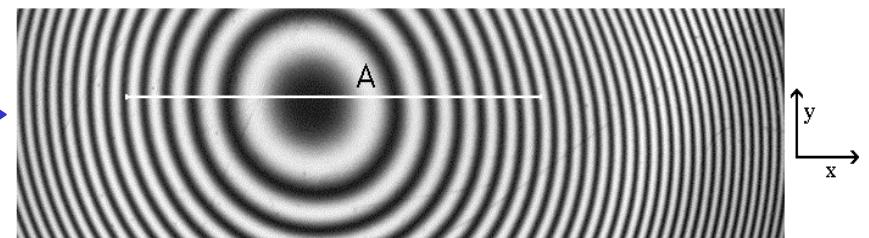
Exemples d'anisotropie de contraintes et d'énergie de surface



Adsorption et courbure spontanée

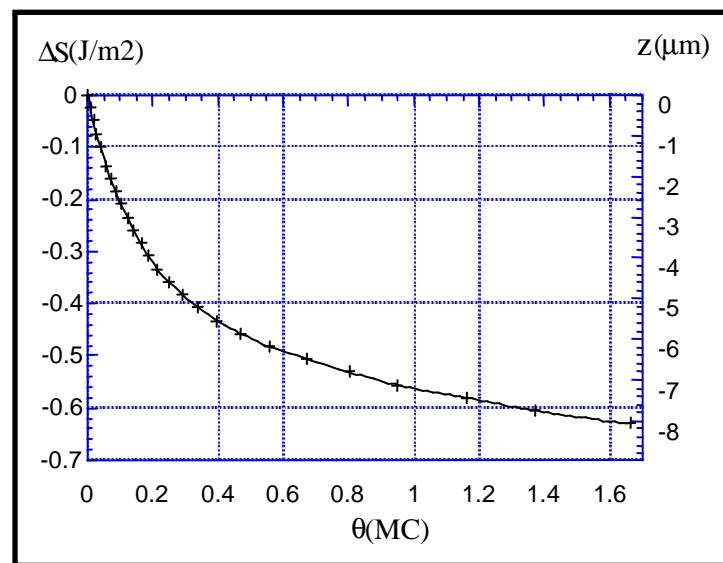


interférogramme

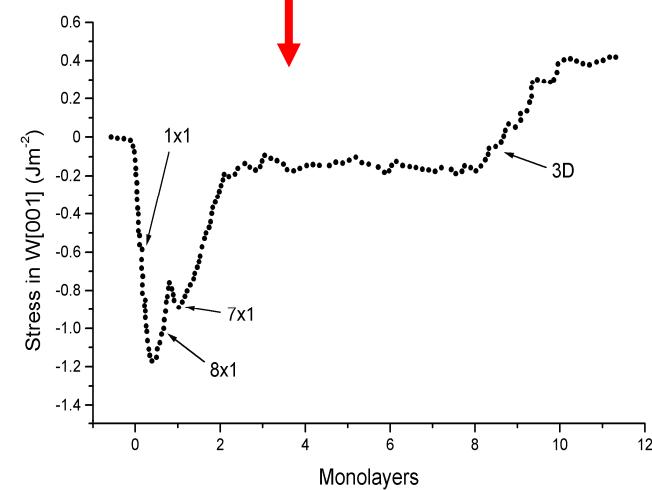


G.Degand, P.Müller, R.Kern, Surf. Rev. Lett. 4 (1997) 1047

Variations de contraintes de surface



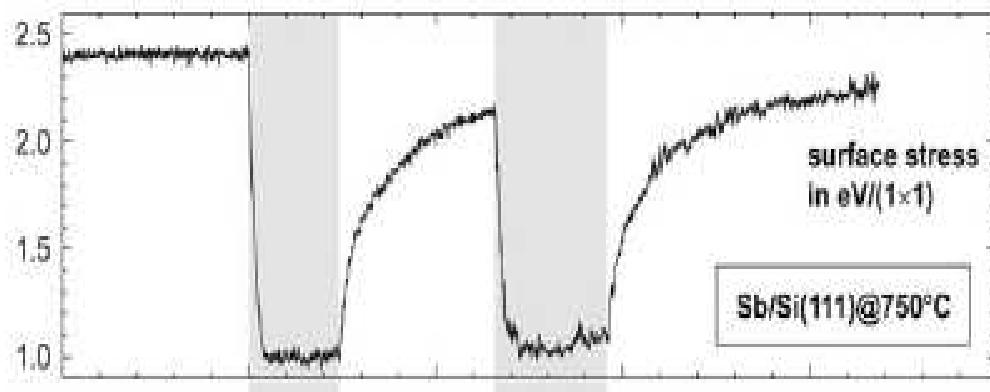
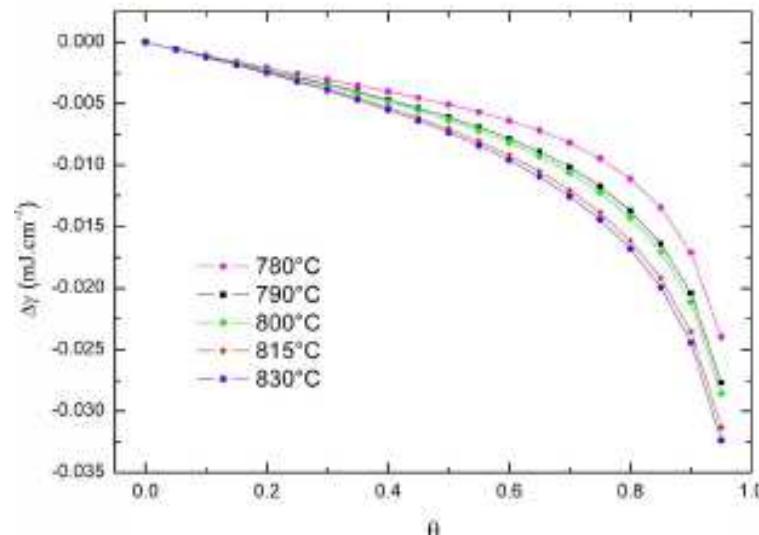
Cas du Ni/W110)



D.Sander, PRB 57, 1998, 1406

Exemple d'application: Sb/Si(111)

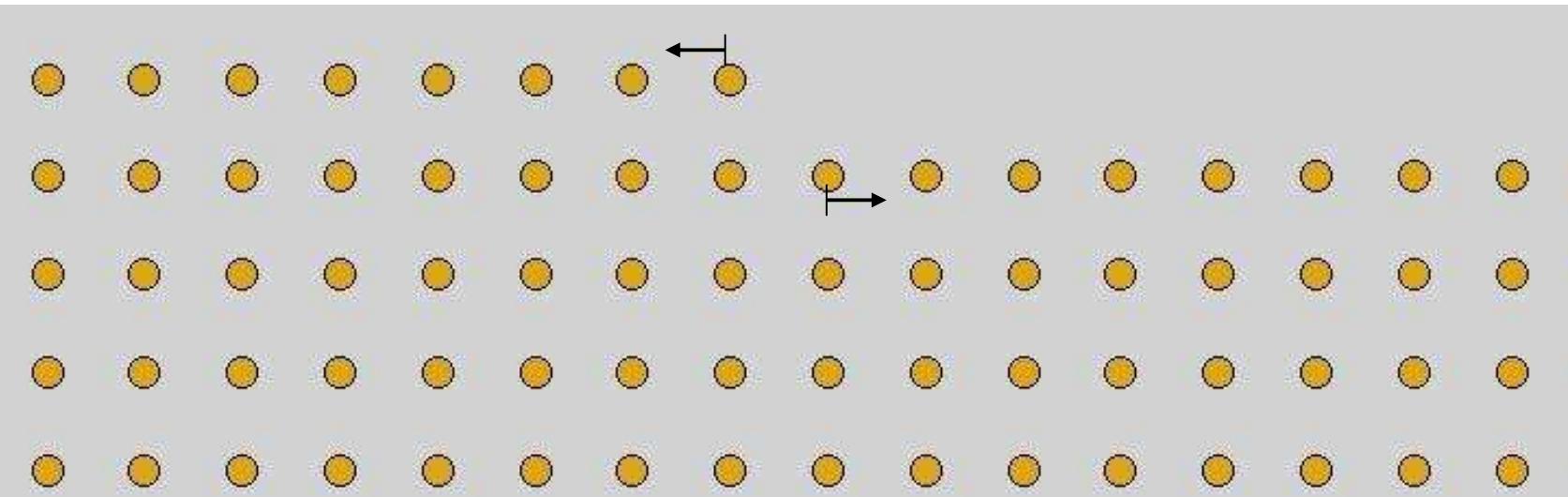
Si surface energy change versus
Sb coverage obtained from
adsorption/desorption isotherms
For 1ML $\Delta\gamma=-0.2\text{Jm}^{-2}$



Si surface stress change versus
Sb coverage obtained from
curvature method
For 1ML $\Delta s=-1.9 \text{ Nm}^{-1}$

Description élastique d'une surface non plane

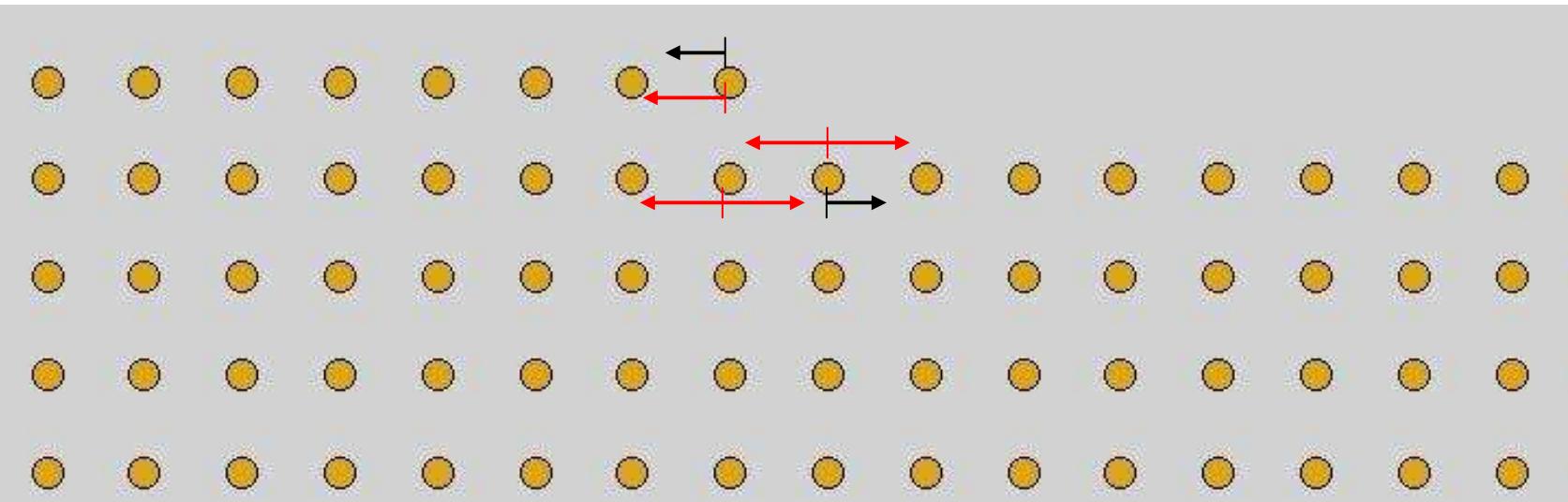
Description élastique de défauts de surface : marche



Quand on s'approche à la marche la discontinuité dans la contrainte de surface fait apparaître des forces non compensées.

- Il n'y a pas de force nette.
- Le premier ordre dans le développement est dipolaire...
- L'ordre de grandeur du moment dipolaire est donné par
contrainte de surface x hauteur de marche

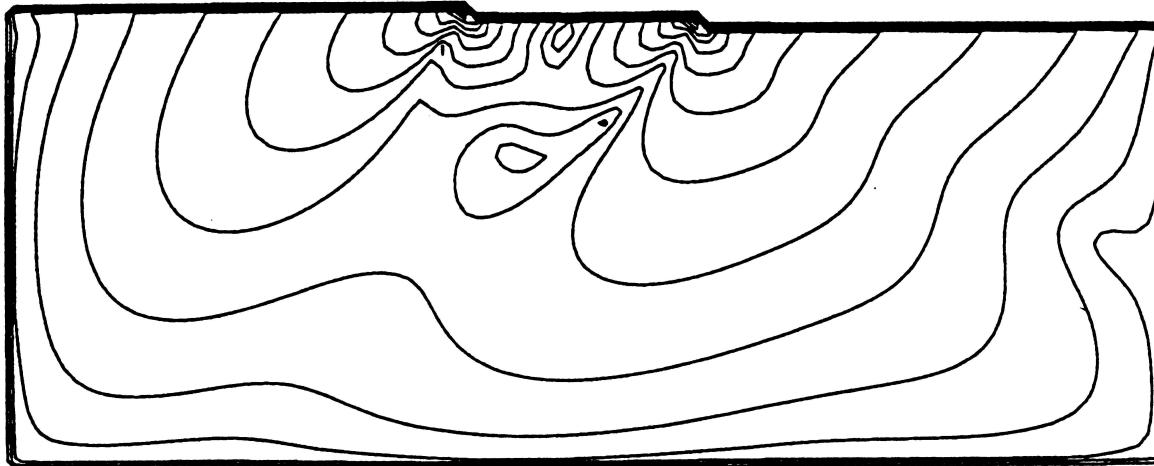
Description élastique de défauts de surface : marche



Quand on s'approche à la marche la discontinuité dans la contrainte de surface et de volume fait apparaître des forces non compensées.

- Il y a une force nette!!!
- Le premier ordre dans le développement est mono-polaire...
- L'ordre de grandeur de la force appliquée est donné par la
contrainte de volume x hauteur de marche

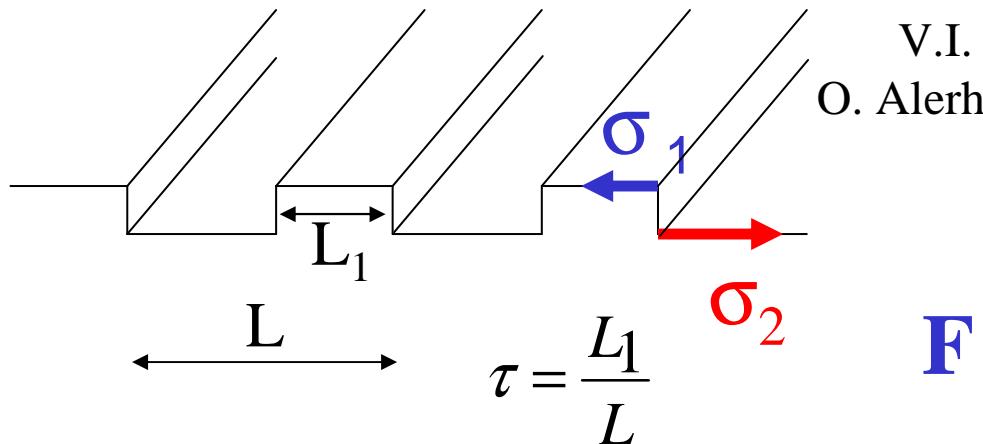
Calcul de l'énergie élastique via le tenseur de Green



$$W^{\text{el}} = -\frac{1}{2} \sum_{ij} \int \int F_i(\vec{x}) D_{ij}(\vec{x}, \vec{x}') F_j(\vec{x}') \, d^3x \, d^3x'.$$

Tenseur de Green connu
pour un milieu infini isotrope
pour un milieu semi infini

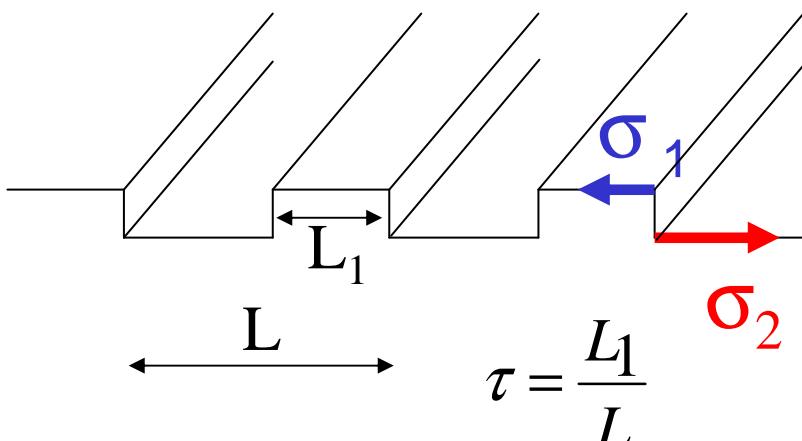
Elasticité et auto-organisation de surface



V.I. Marchenko, Sov. Phys. JETP 54, 605 (1981)
 O. Alerhand and D. Vanderbilt, PRL 61, 1973 (1988)



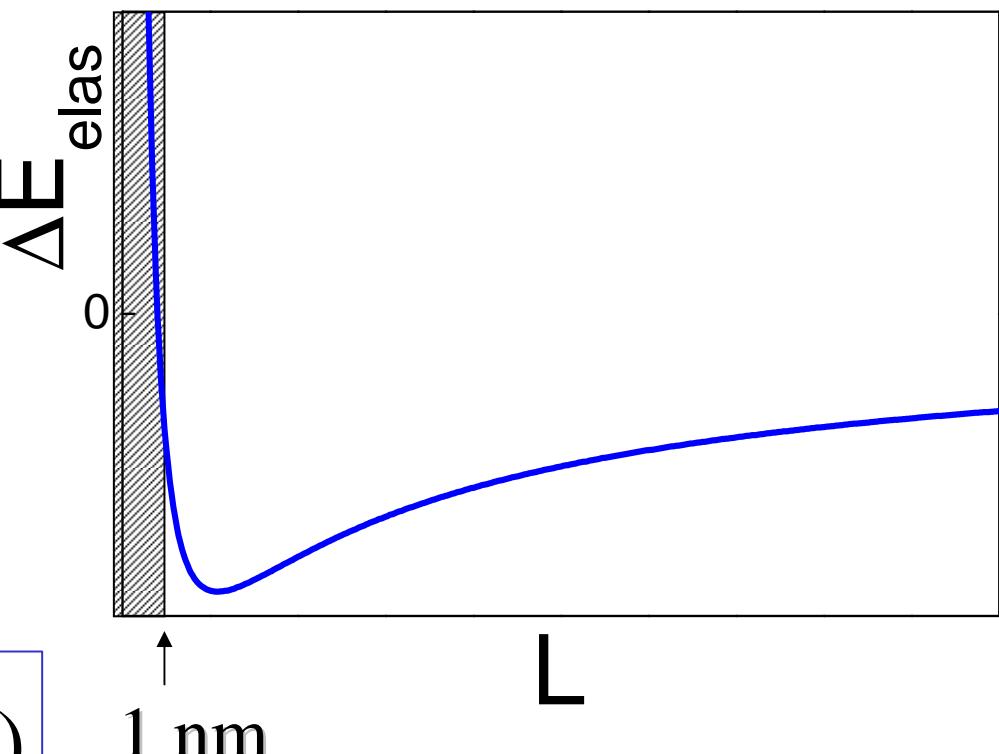
$$E_{elas} = -\frac{1}{2} \int_S \vec{F}_i \cdot \vec{u}_i \, dS$$



Periodic stripes ($\tau=0,5$) :

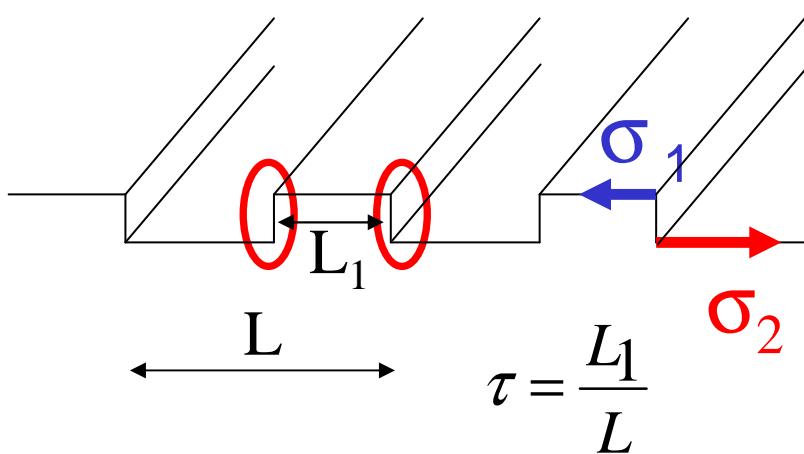
$$\Delta E_{\text{elas}} = -\frac{C_2}{L} \ln\left(\frac{L}{2\pi a}\right)$$

$$C_2 \approx \frac{(\sigma_2 - \sigma_1)^2}{Y}$$



a : atomic cutoff

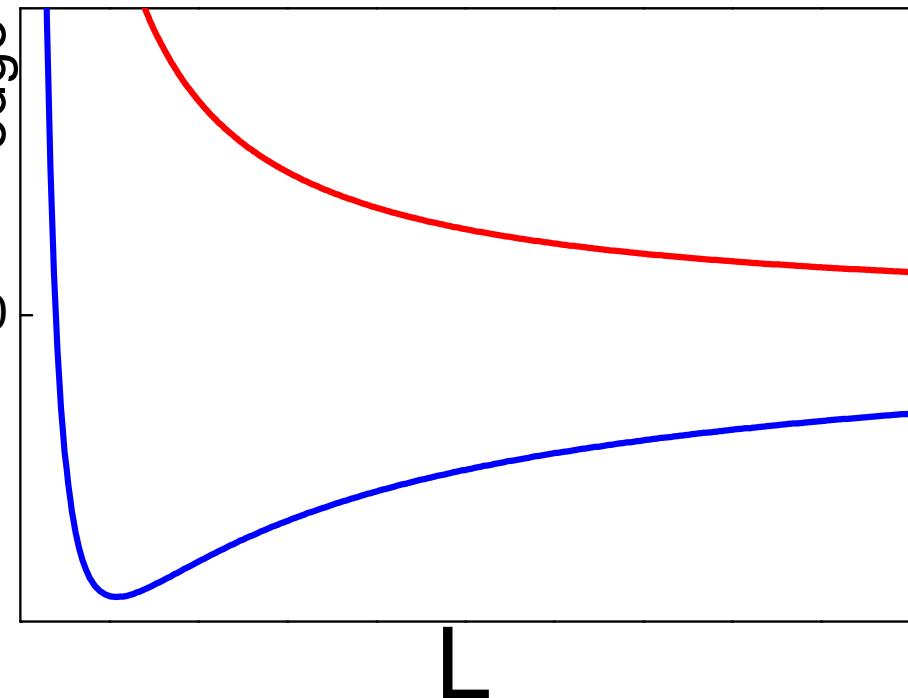
Repulsive interaction between stripes

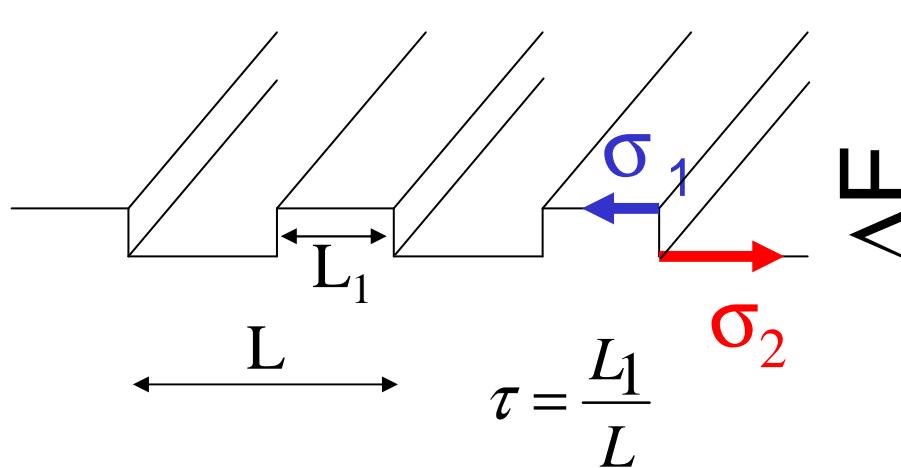


Periodic stripes ($\tau=0,5$) :

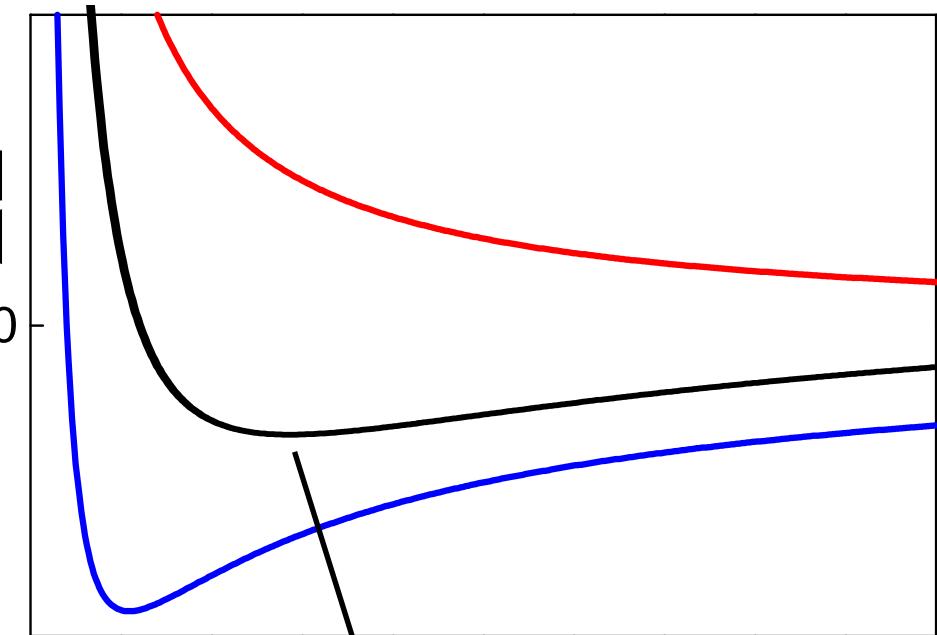
$$\Delta E_{\text{boundary}} = \frac{C_1}{L}$$

C_1 = boundary energy





Periodic stripes ($\tau=0,5$) :



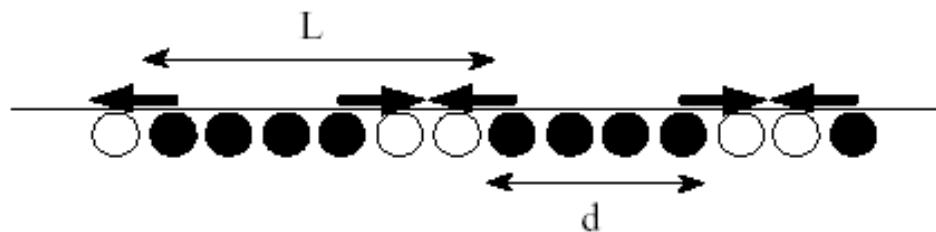
$$\Delta E_{\text{tot}} = \frac{C_1}{L} - \frac{C_2}{L} \ln\left(\frac{L}{2\pi a}\right)$$

$$C_2 \approx \frac{(\sigma_2 - \sigma_1)^2}{Y}$$

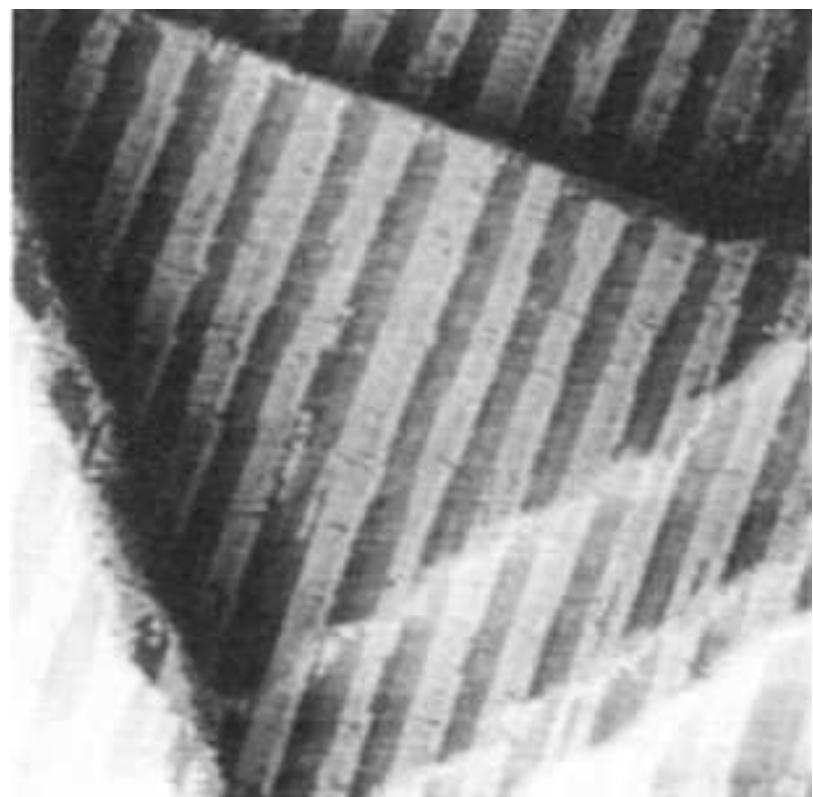
C_1 = boundary energy

$$L_{\text{opt}1/2} = 2\pi a \exp\left(1 + \frac{C_1}{C_2}\right)$$

Les contraintes de surface varient avec l'adsorption



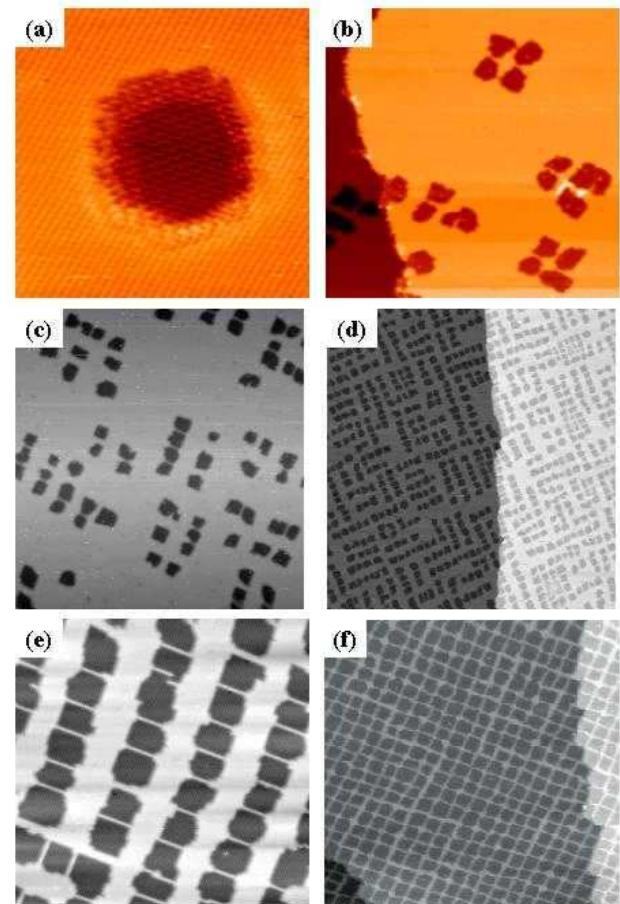
Cas O/Cu(110)



K. Kern et al PRL 67 (1991) 855

Existence de forces entre domaines d'adsorption $\rightarrow \lambda$

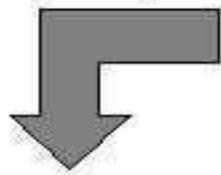
Cas de N/Cu



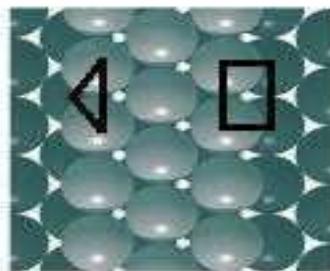
B.Croset et al. PRL 2002

Cas du facettage de l 'or

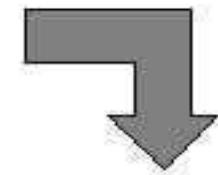
vicinals
with $\{111\}$ steps



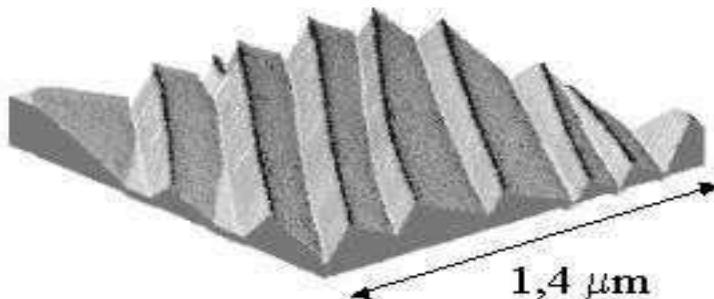
Au(4,5,5) :



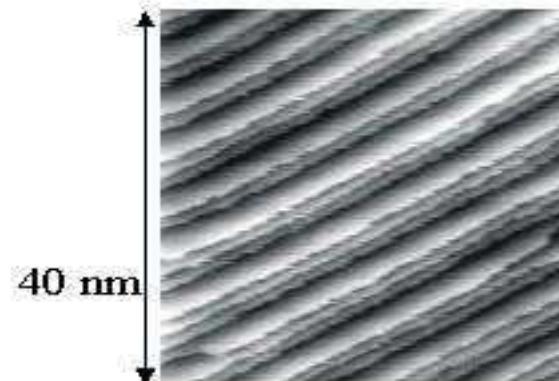
vicinals
with $\{100\}$ steps



Au(11,9,9) :



period ~ 200 nm

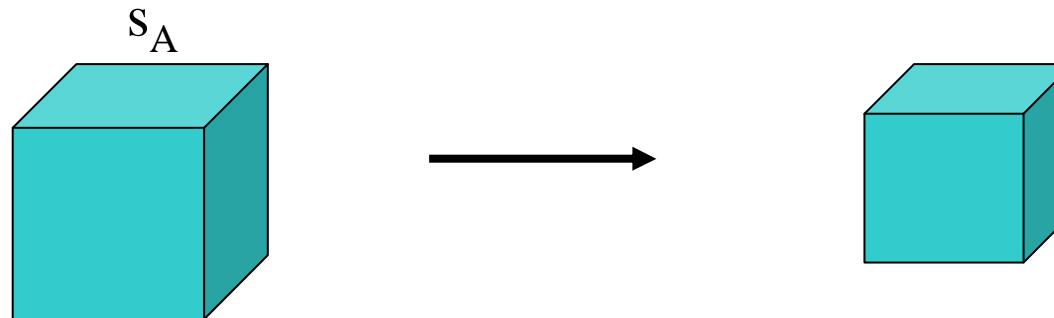


period ~ 6 nm

Mesures de contraintes de surface

Contrainte de surface : en pratique, comment la mesurer

Cristal soumis à son propre surface stress (isotrope)



$$W = f(C)\varepsilon^2 + g(s)\varepsilon$$

À l'équilibre $\longrightarrow \varepsilon_{xx}^* = -4 \frac{1-2\nu_A}{E_A} \frac{s_A}{\ell}$

Contraction du cristal soumis à ses propres contraintes de surface

Lattice contraction for small crystals

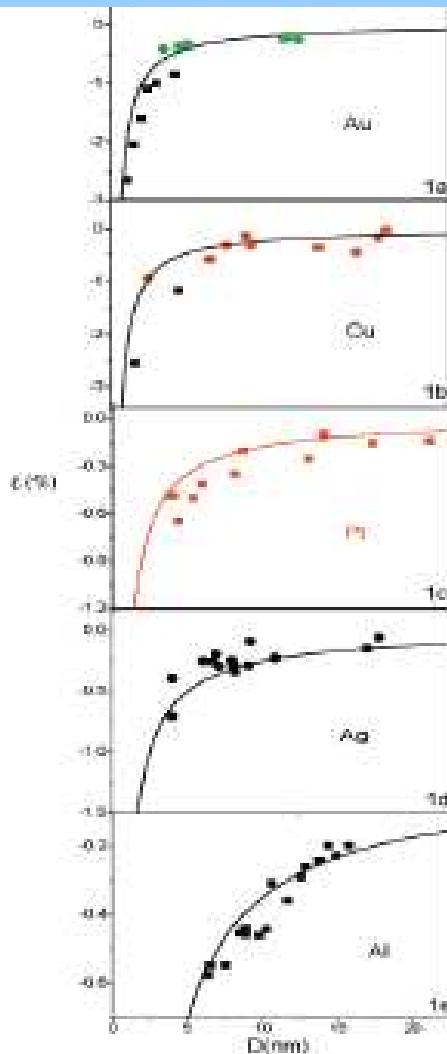
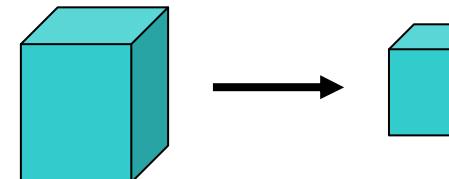


Figure 1. $s(D)$ functions of particles (solid lines) in terms eq 13 with parameters shown in Table 1 ($D_0 = 3R$). The symbols show the experimental data where \bullet^1 and \blacksquare^1 are the measured mass values of $\Delta a/a$ for Au in 1a; \bullet^2 and \blacksquare^2 are that of $\Delta a/a$ for Cu in 1b; \blacksquare^3 is the measured values of $\Delta a_{\text{exp}}/\Delta a_{\text{cal}}$ for Pt in 1c; \bullet^4 denotes that of $\Delta a_{\text{exp}}/\Delta a_{\text{cal}}$ for Ag in 1d and \blacksquare^5 shows that of $\Delta a/a$ for Al in 1e.

Mays et al. Surf. Sci. 12 (1968) 134

Wasserman et al. Surf. Sci. 22 (1970) 164; 32 (1972) 168



Isotropic assumption

$$f = -3rKe/2 = -1.5rK\Delta a/a$$

TABLE 1: Comparison of Surface Stresses among Different Model Estimations and Experimental Results*

	Au	Pt	Ag	Cu	Ni	Al	Pb	Ir
$K(\text{nm})^{12}$	0.2884	0.2775	0.2889	0.2556	0.2492	0.2863	0.3500	0.2174
$V_a (\text{cm}^3 \text{mol}^{-1})^{12}$	10.2	9.1	10.3	7.1	6.59	10	18.17	8.54
$H_a (\text{kJ mol}^{-1})^{12}$	12.55	19.6	11.3	13.05	17.47	10.79	4.799	26.1
$T_a (\text{K})^{12}$	1337.6	2045	1234	1357.6	1726	933.25	600.6	2716
$S_a (J \text{mol}^{-1} \text{K}^{-1})$	9.38	9.58	9.16	9.61	10.12	11.56	7.99	9.61
$K(10^{-12} \text{Pa}^{-1})$	5.848	3.623	9.653	7.257	5.640	13.30	21.83	2.695
$\gamma_s (\text{J m}^{-2})$	0.119	0.136	0.111	0.160	0.189	0.168	0.045	0.110
$f_1 (\text{J m}^{-2})$	2.097	2.795	1.578	2.051	2.502	1.648	0.737	2.577
$f_2 (\text{J m}^{-2})$	2.77	5.60					1.25	0.82
$f_3 (\text{J m}^{-2})^2$	1.714		1.041	1.106	0.817			
$f_4 (\text{J m}^{-2})^{12}$			1.94		1.67			
$f_5 (\text{J m}^{-2})^{-1}$		1.175 ± 0.2	2.574 ± 0.4	1.415 ± 0.3				

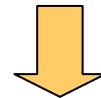
* See $\gamma_s S_a = H_a T_a$, and $\kappa = 1/B$ where B is the bulk modulus cited from reference 27. γ_s is calculated in terms of eq 10 at $T = 298$ K. The term f_5 is determined by eq 12 with $D_0 = 2h$ at $T = 298$ K. f_5 denotes the results of the first principles calculation and f_5 the computer simulation results, f_5 gives the results of the modified embedded atom method potentials, f_5 is the experimental results.

Generally, $\Delta a/a < 0$ so that
s>0 for pure materials

but s<0, dilatation for $\text{Si}_x\text{Ge}_{1-x}$ particles

Mesure directe des déformations par diffraction X

Diffraction → Résolution de structure



Structure périodiques de surface

Marches

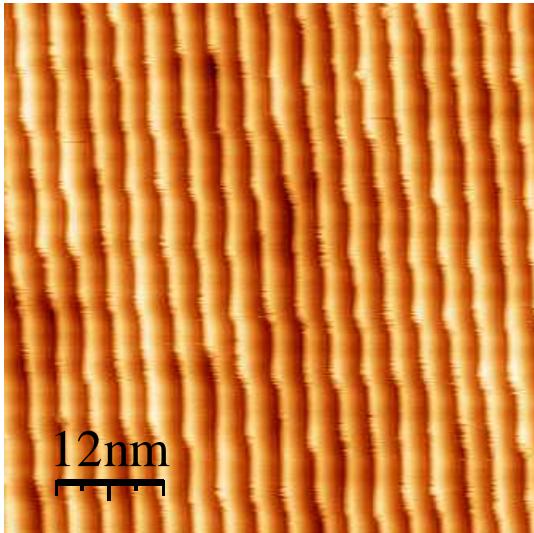


Image STM: surface vicinale
d'Au(677) (F. Leroy et al.
PRB (2008))

Adsorbats

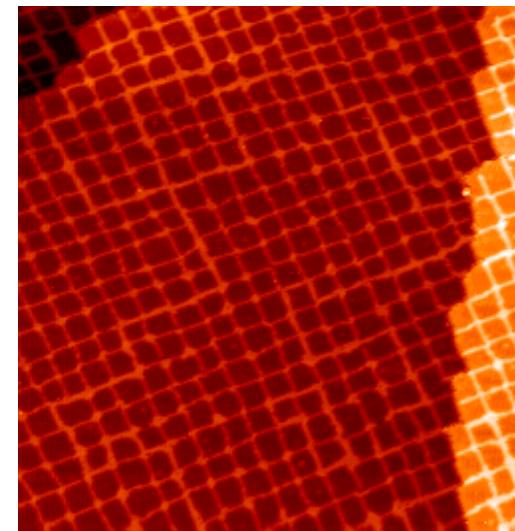
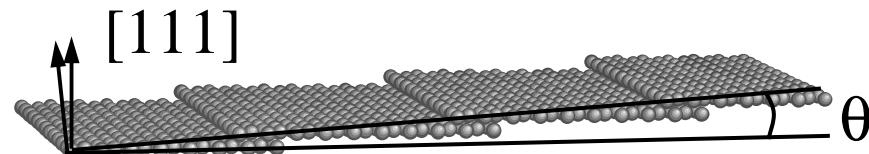


Image STM: adsorption
N/Cu(001) (Croset et al. PRL
2002)

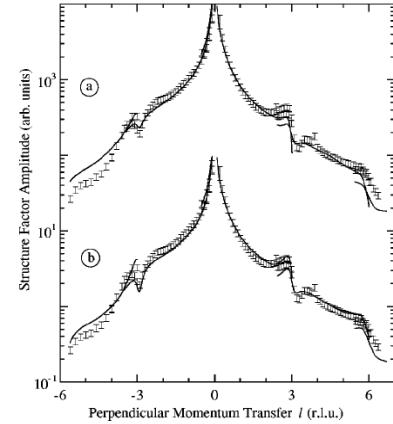
Diffraction X de surface (marche monoatomique)

Pt(977) surface vicinale de
Pt(111)



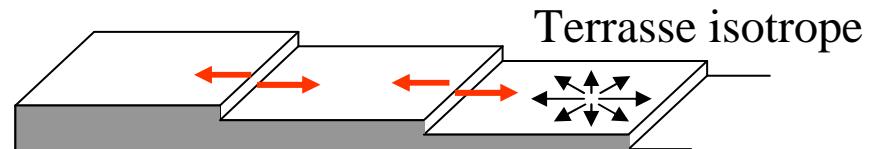
Espace réciproque

Tige de troncature
perpendiculaire à la surface

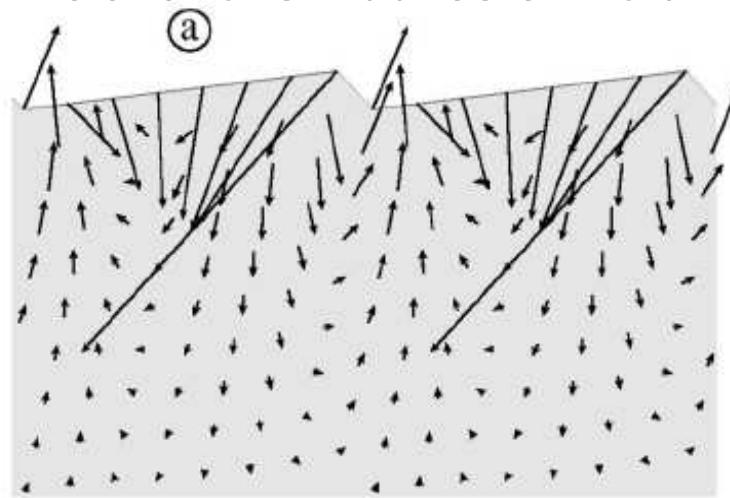


Modélisation

Equivalent élastique d'une marche
(ligne de dipôles de force élastique)



Relaxations induites en volume

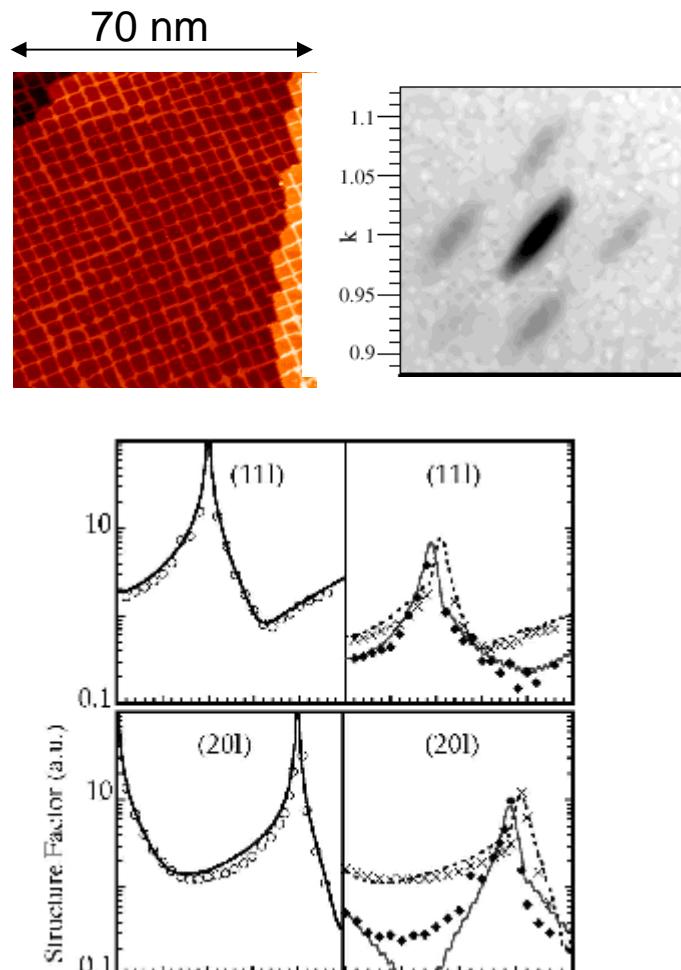


Prévot et al. PRB 67 (2003)

Moment dipolaire linéique $P = 10^{-9} \text{ N}$

Diffraction X de surface (adsorbat)

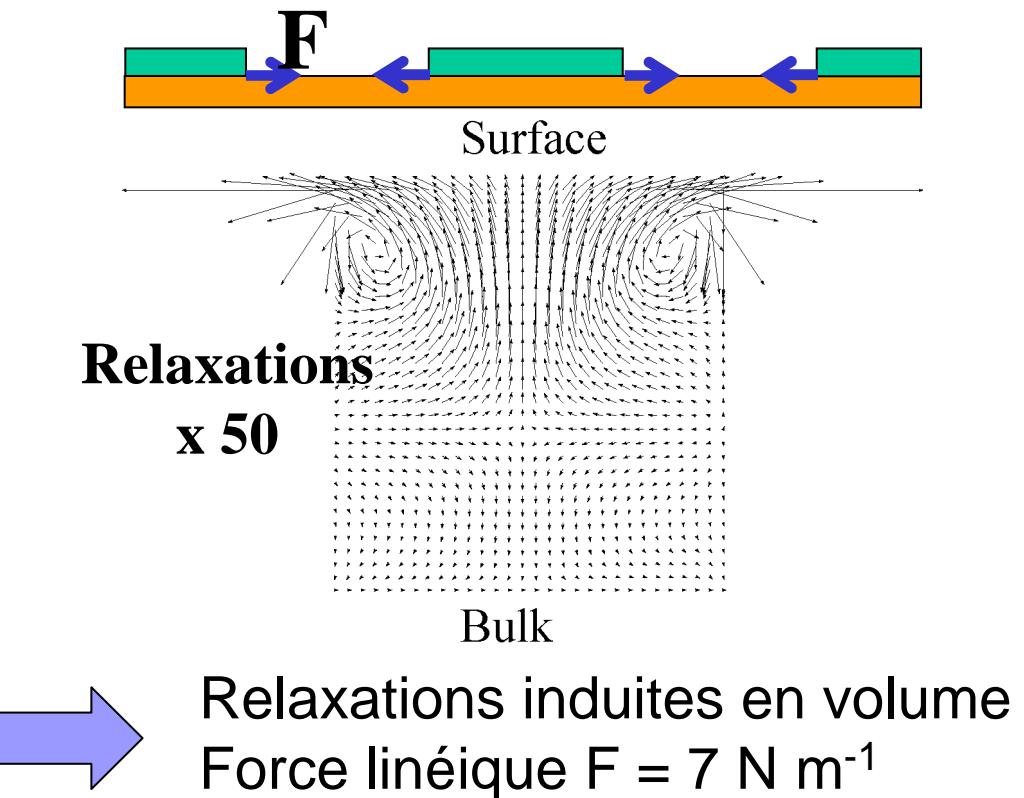
Cas N/Cu(001)



Pics satellites autour du Bragg

Modélisation

Equivalent élastique d'un adsorbat
(Monopole de force élastique)



Croset et al. Phys. Rev. Lett. 88 (2002)

Conclusion sur les contraintes de surface

- * Une grandeur fondamentale différente de l'énergie de surface
- * Une grandeur physique délicate à calculer

Pour un matériau pur (Ag)

Energie d'un atome isolé	: 144000 eV
Energie de cohésion	: 3 eV
Energie de surface	: 0.7 eV
Energie d'une déformation de $\varepsilon=0.01$: 0.015 eV

- * Une grandeur physique difficile à mesurer : pas de valeurs expérimentales absolues ... Possibilité de mesurer des différences : courbure d'une couche mince
- * A la base de processus spontanés de surface
- * Une grandeur qui joue chaque fois qu'il y a déformation d'une surface