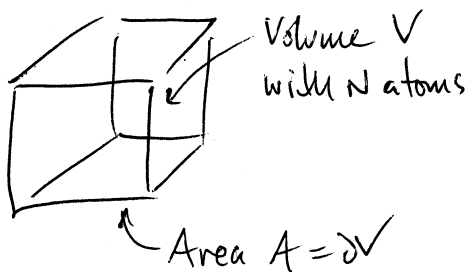


* LEED reveals structure of periodic surfaces

→ but most crystals have interesting deviations from periodicity (e.g. steps)

→ important to have the ability to image the surface directly (either with AFM or STM)

* For a finite system, the free energy includes correction terms proportional to the area of the boundary



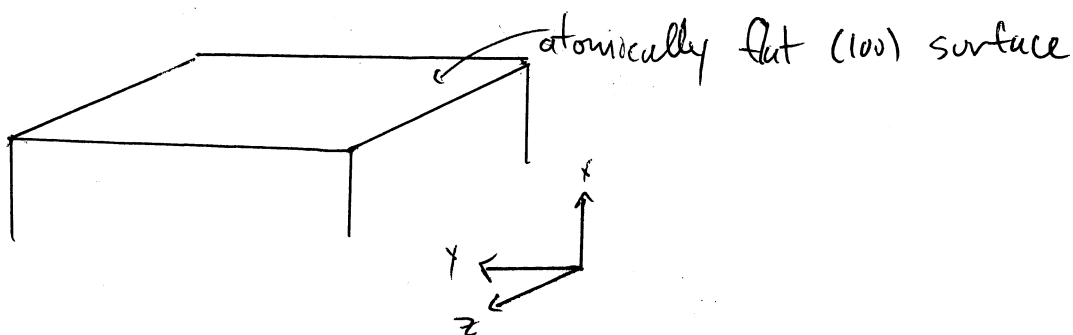
→ surface always raises the energy wrt the infinite crystal because of dangling bonds

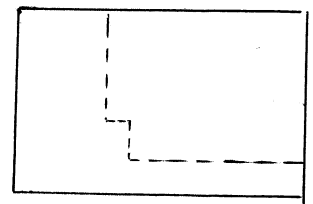
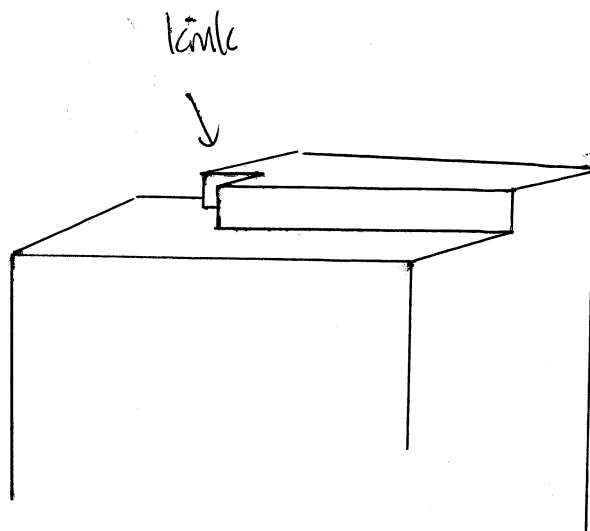
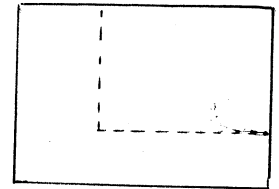
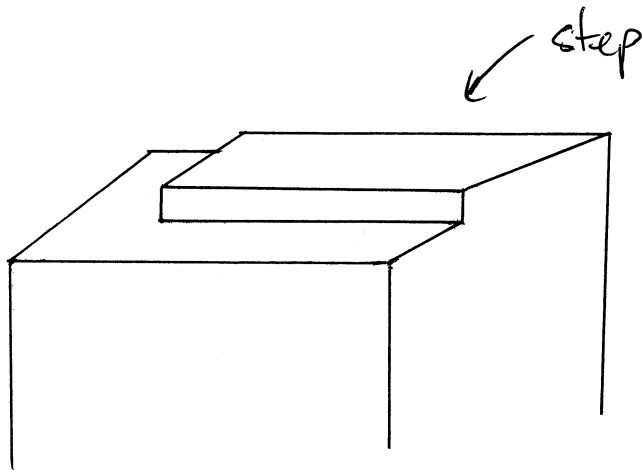
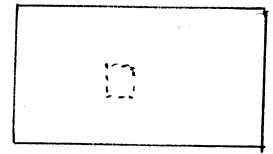
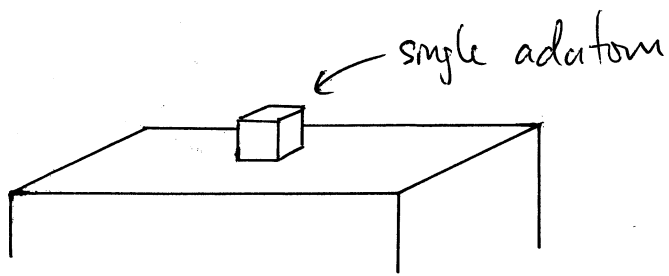
→ coarse-grained free energy of the form $G = \mu N + \gamma A$

bulk
chemical
potential

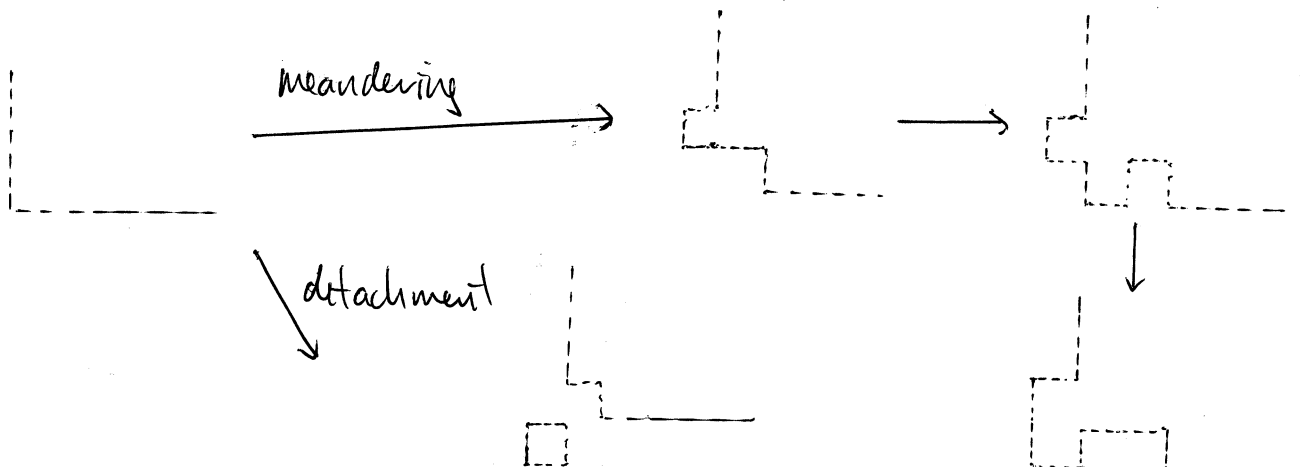
surface tension
 $\gamma > 0$

* Simple model: cubic crystal with nearest-neighbour interactions only

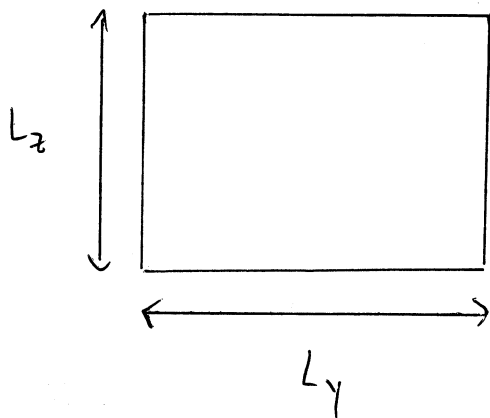




→ step edge has dynamics (thermally driven)

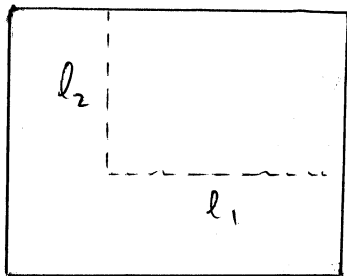


→ assume that each atom gains a bonding energy ϵ_b for each of its six neighbours (unit cell of length $a=1$)



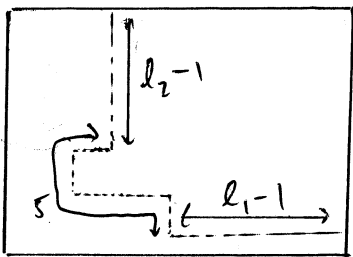
~~the~~ energy cost of the flat

$$\text{surface is } \epsilon_b L_y L_z = \epsilon_b A$$



additional cost to the step edge that goes linearly in its perimeter

$$\epsilon_b (L_y L_z + l_1 + l_2)$$

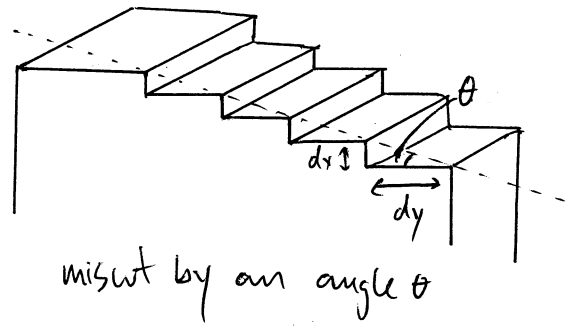
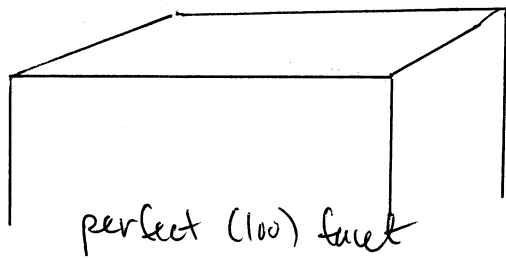


reticulated edges are necessarily expensive

$$\epsilon_b (L_y L_z + l_1 + l_2 + 3)$$

→ steps can wander and have entropy

→ a slightly miscut crystal



$$\gamma = \frac{\epsilon_b}{2} \frac{|dx| + |dy|}{\sqrt{dx^2 + dy^2}} = \gamma_{100} + \left(\frac{\epsilon_b}{2}\right) |\theta|$$

→ large atomically flat facets are preferred

* Must account for the entropy terms in the free energy

→ goes as $k_B \log(\# \text{ configurations})$

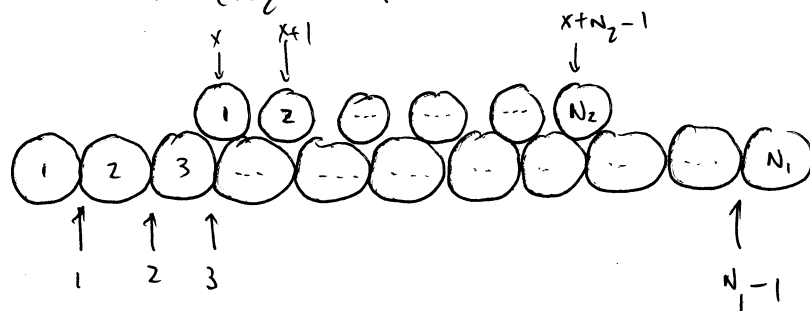
→ enters as $F = E - TS$ so large $\#$ configurations can reduce the free energy

→ possible to have entropy contribution large enough that it overwhelms the energy cost of creating a step

→ proliferation of steps in equilibrium is called a roughening transition

→ Example of a "one dimensional surface": consider a bilayer of N_2 circles close packed onto N_1

(1) suppose that the second layer consists of a single small island ($N_2 \ll N_1$)

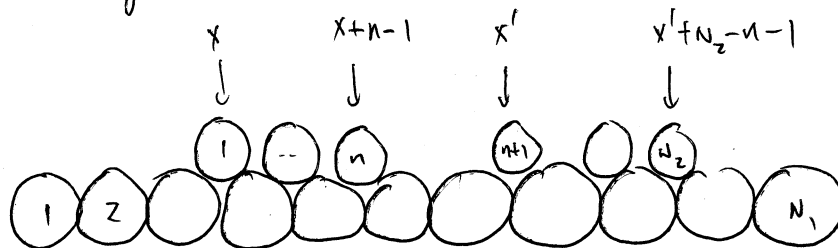


$$1 \leq x \leq N_1 - N_2$$

number of possible positions is $N_1 - N_2$

hence $S = k_B \log (N_1 - N_2) \sim k_B \log N_1$

(2) second layer forms two small islands



number of possible positions (ignoring overlap) is

$$\sim \sum_{n=2}^{N_1 - N_2 - 1} (N_1 - n) (N_1 - (N_2 - n)) = \frac{2N_1^3}{3} + O(N_1^2)$$

The ~~difference~~ difference in free energy $F = E - TS$ is

$$\Delta F = \varepsilon_b - k_B T \log \frac{2N_1^3}{3} + k_B T \log N_1 = \varepsilon_b - k_B T \log \frac{2}{3} - k_B T \log N_1$$

$$< 0 \quad \text{if } N_1 \rightarrow \infty$$

→ free energy to make a new island is negative (favorable)
so the surface will be rough for any $T \neq 0$.

→ artifact of the low dimensionality (in 1D, the boundary to any region is two points, not a perimeter)

* How does the same argument proceed for a 2D surface?

→ suppose an island exists that occupies a finite fraction of the N surface sites

→ its length is on the order of $N^{1/2}$

→ break the island into two of comparable size with edge length l

→ energy cost $\sim \epsilon_b l$

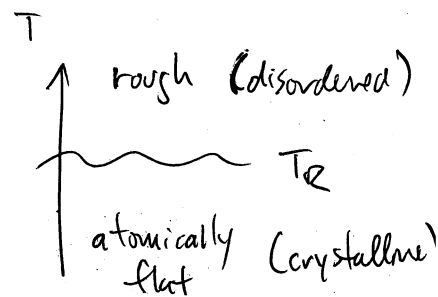
→ estimate entropy by a random walk of $z(z-1)^{l-1}$ links steps ($z=4$ in cubic symmetry)

$$k_B \log(N z(z-1)^{l-1}) \simeq k_B l \left(\log(z-1) + \frac{1}{l} \log N \right)$$

$$\sim k_B N^{1/2} \left(\log(z-1) + \frac{\log N}{N^{1/2}} \right) \xrightarrow{0 \text{ as } N \rightarrow \infty}$$

→ free energy per unit length is

$$\frac{F}{l} = \varepsilon_b - k_B T \log(z-1)$$



which changes sign at $T_R \approx \frac{\log(z-1)}{k_B \varepsilon_b}$

* Crystalline defects in the bulk come in two forms

→ vacancies and interstitials (we've already shown that these are always present in thermal equilibrium!)

→ dislocations, which are line defects

* The dynamics of defects are crucial to understanding the properties of materials

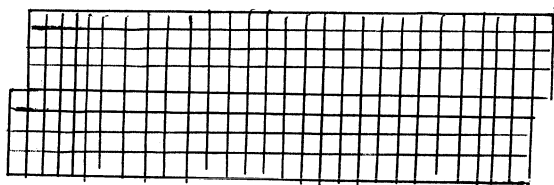
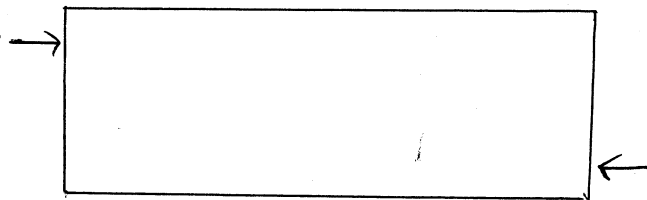
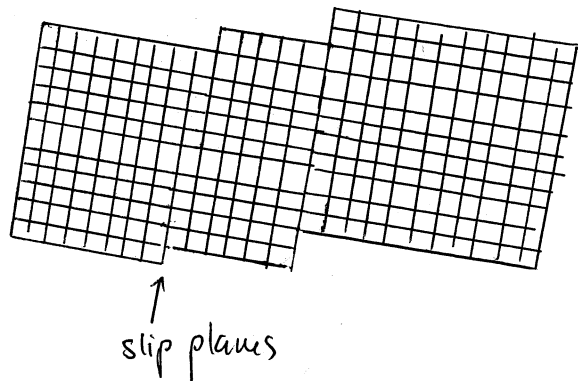
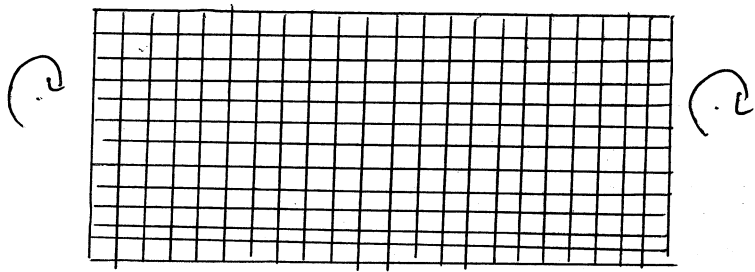
→ e.g. glass is brittle and shatters on impact;

metal is ductile and will bend but not break

→ the difference depends entirely on the mobility of dislocations

→ requires plastic deformation (i.e. permanent and irreversible)

* Crystals relieve stresses and strains by propagation of dislocations



→ slip in fcc occurs along the closepacked planes

→ bcc has no closepacked layers

→ slip can occur via edge or screw motion

