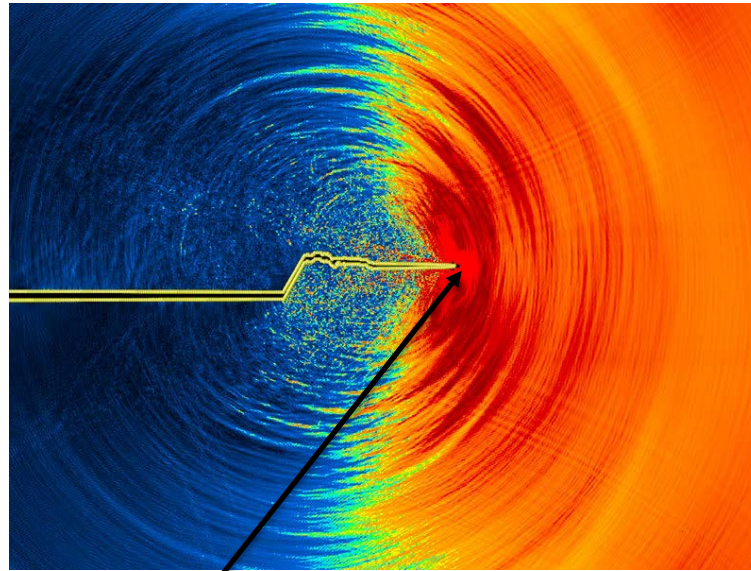


2.4 *Ab initio* Modeling of Brittle and Ductile Solids



In brittle solids, the imposition of external stress results in the extension of pre-existing cracks: **the stress concentration at the crack tip, leads to bond-breaking and cleavage.**

In a ductile substance, **the large stress at the crack tip is absorbed by generation and motion of dislocations** which blunts the crack; the net effect is plastic deformation of the material but no breaking.

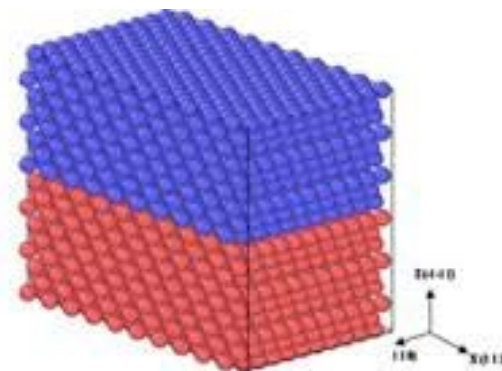
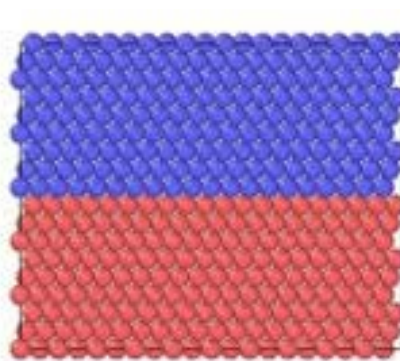
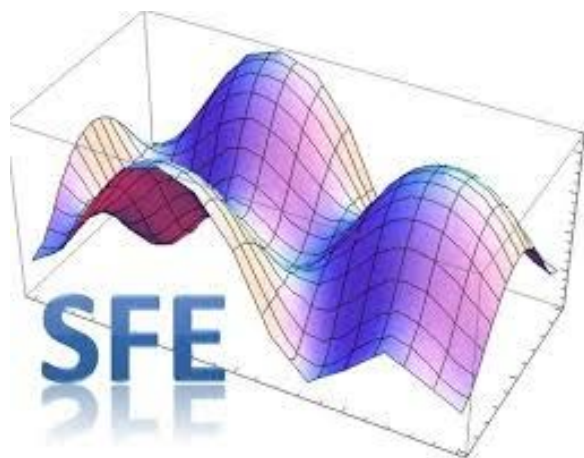
Capture the atomistic processes responsible for bond breaking/cleavage (for a brittle solid) or dislocation nucleation/motion (for a ductile solid)

- ◆ Successful modeling of physical phenomena that involve atomistic processes and their implications for macroscopic behavior relies on a combination of methodologies at different length scales.
- ◆ A simpler approach is to couple phenomenological macroscopic theories with first-principles calculations, which determine the values of any physical parameters of the phenomenological description.

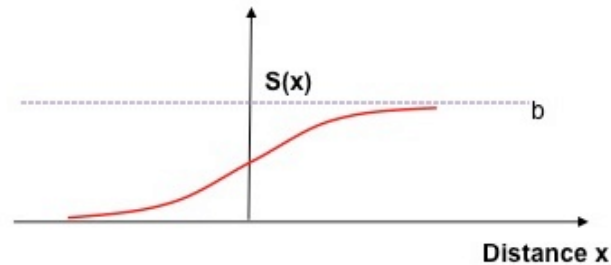
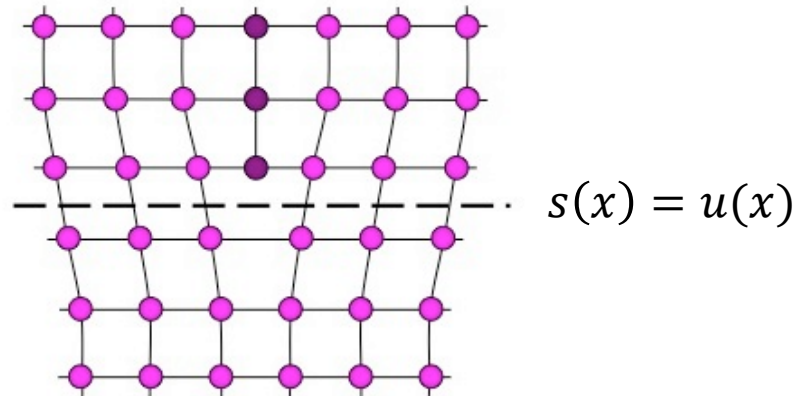
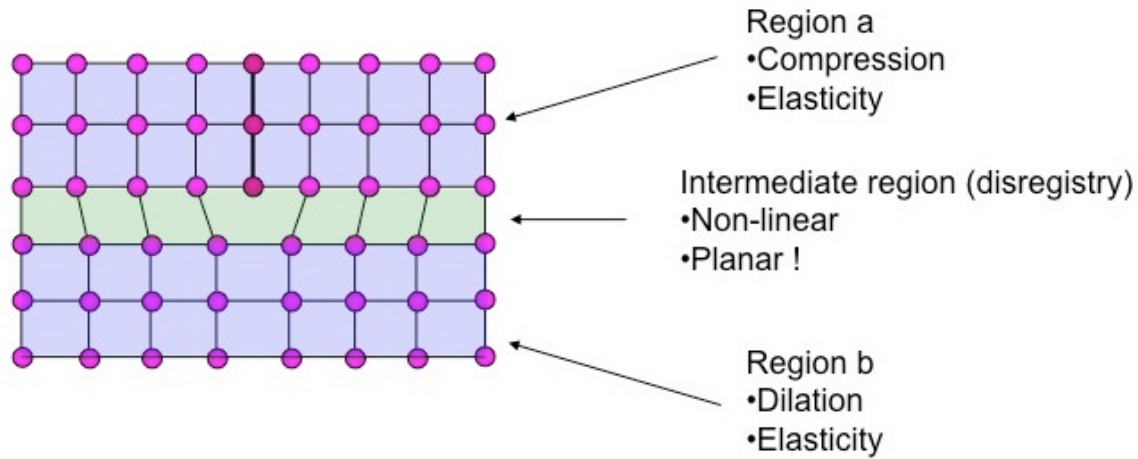
Macroscopic Theory of Brittle versus Ductile Behavior of a Solid

Consider a crystal cut into two halves parallel to the (hkl) crystallographic plane and suppose that one half is displaced relative to the other by a vector ν .

- **γ -surface (the generalized stacking fault energy surface):**
The change in energy per unit area of the crystal as a function of ν .
- The γ -surface is a fundamental material property which can be obtained from ab initio calculations.



The Peierls and Nabarro Equation



The Peierls and Nabarro Equation

- Peierls stress is the force needed to move a dislocation within a plane of atoms. The magnitude varies periodically as the dislocation moves within the plane.
- The balance between the stress on the lattice at a position x due to the infinitesimal dislocation distribution $u(x)$ at that point and the force exerted by the lattice due to its distortion, which is given by the gradient of the γ -surface:

$$K \int_{-\infty}^{+\infty} dx' \frac{d\vec{u}(x')}{dx'} \frac{1}{|x - x'|} = -\nabla_x \gamma [\vec{u}(x)]$$

$$\text{with } \int_{-\infty}^{+\infty} dx' \frac{d\vec{u}(x')}{dx'} = \vec{u}(\infty) - \vec{u}(-\infty) = \vec{b}$$

- When this distribution of lattice disregistry $db(x) = |du(x)/dx| dx$ is moved by a distance ν , compute the energy change.
- The *Peierls stress* is given directly by the maximum gradient of the γ -surface along an extremal path.

[reference](#)

Ductility versus Brittleness

- The competing processes which lead to brittle or ductile behavior are the extension of the crack by creation of fresh surfaces (brittle response) or the generation of dislocations that exert a back stress which reduces the stresses by blunting the crack tip (ductile response).
- In brittle failure, the energy required for an incremental advance of the crack front is given by the Griffith criterion: $G = 2\gamma_s$, where G is the energy release rate and γ_s is the surface energy.
- Kelly Postulates: A material would be ductile if the crack tip stress exceeded the theoretical shear stress before the theoretical tensile stress was reached.
- RT Model: The onset of ductile behavior occurs when spontaneous emission of dislocations at the crack tip became feasible.
- Modern RT Model: The unstable stacking fault energy (γ_{us} , a measure of the nucleation energy for a dislocation) is the maximum energy barrier encountered along the extremal path. The criterion for dislocation nucleation at the crack tip (ductility) is reached when $G = \alpha\gamma_{us}$ with $\alpha \sim 1$.

Ductility versus Brittleness

- Brittle behavior is the consequence of the condition $G = 2\gamma_s$ being satisfied before the condition of $G = \alpha \gamma_{us}$. The converse is true for ductile materials.
- Define a disembrittlement parameter as : $D = \gamma_s / \gamma_{us}$, where γ_s and γ_{us} have to be established from accurate microscopic calculations.
- The critical value of the disembrittlement parameter D has been estimated to be between 1 (more brittle) and 10 (more ductile).
- Changes in D due to changes in the microscopic structure or chemical composition of a solid will correlate with changes in the solid's tendency to behave as a brittle or a ductile substance.

First-Principles Methods

- To calculate γ_s and γ_{us} , we can use slab configurations with multiples of the unit cell along the slab direction.
- Surface energies γ_s can be obtained from the difference between the total energy E_{tot} of a crystal cleaved across a given plane and of the bulk as

$$2\gamma_s = E_{tot}(supercell) - n E_{tot}(bulk)$$

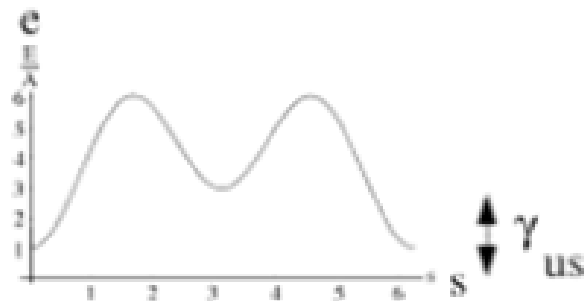
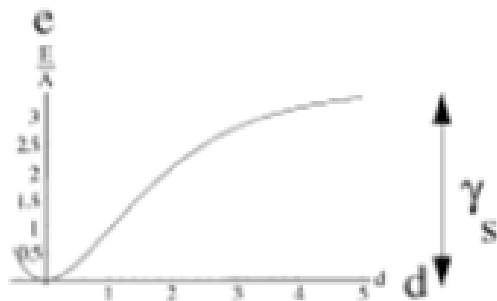
- Here $E_{tot}(bulk)$ is the total energy of bulk crystal per chemical unit, and $E_{tot}(supercell)$ the total energy of the given supercell, which contains n chemical units. The overall factor of two comes from the fact that each supercell has two surfaces.

First-Principles Methods

- We consider a periodic supercell containing several units of the ideal crystal cell and calculate the total energy as a function of d , the distance between two atomic layers separated by the desired cleavage plane in the supercell. These energies are fit to a universal energy function

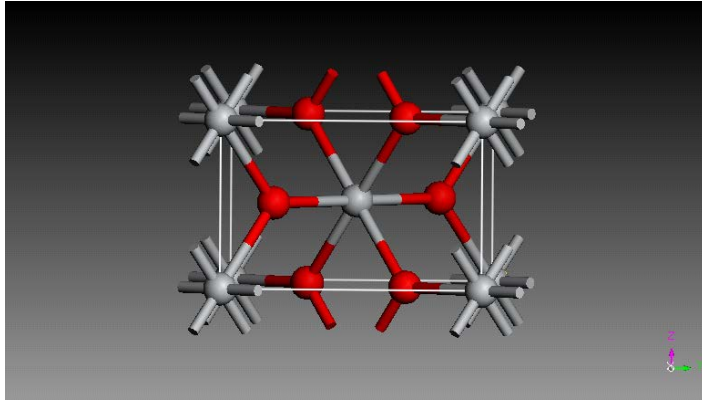
$$e(d) = E_{tot}(d)/A = e_{\infty} - 2\gamma_s(1 + f)e^{-f}$$

- Here $f = (d - d_0)/\lambda$, e_{∞} is the energy per unit area (A) of the cleaved crystal, d_0 is the inter-planar separation in the ideal bulk crystal and λ is a fitting parameter.
- The unstable stacking fault energy γ_{us} can be obtained from the total energy of a supercell containing the fault plane with the two halves of the cell displaced in the direction of the fault vector \vec{v} with respect to each other.



Case Study of Surface Energy on TiO₂(111)

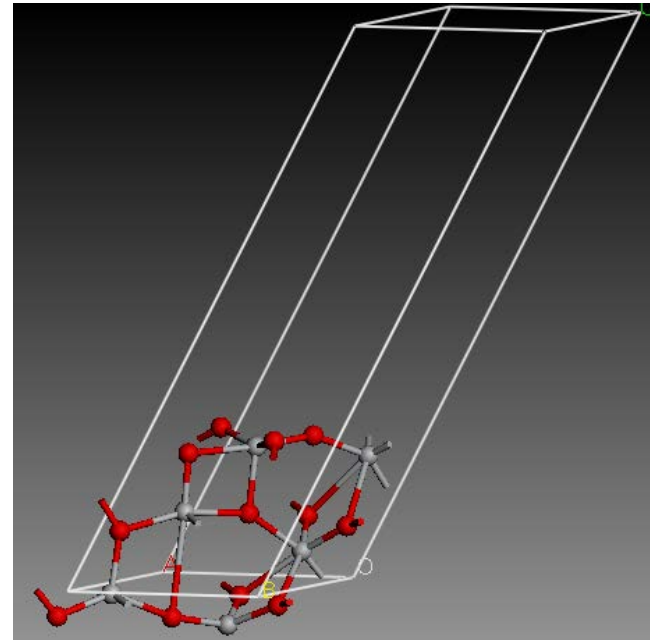
1. Create a project
2. Optimize bulk TiO₂
3. Build the TiO₂(111) surface and Optimize the surface Structure



Unit Cell of TiO₂ (rutile)

Results:

1. $E_{tot}(bulk, 2TiO_2 \text{ units}) = -4.962782 \times 10^3 \text{ eV};$
2. $V(\text{unit cell volume}) = 64.554 \text{ \AA}^3$



Supercell of TiO₂ (111)

Results:

1. $E_{tot}(\text{supercell}, 6TiO_2 \text{ units}) = -1.4883 \times 10^4 \text{ eV}$
2. $\text{Area}(\text{supercell}) = ab \sin(\alpha) = 5.528^2 \sin(113.2) = 28.12 \text{ \AA}^2$

$$2\gamma_s = [E_{tot}(\text{supercell}) - n E_{tot}(\text{bulk})] \times 1/\text{Area}$$

$$=[-14883.485 + 4962.782 \times 6/2] \times 1/\text{Area}$$

$$= 4.861 \times 1/28.1 \text{ eV/\AA}^2 = 0.298 \text{ eV/\AA}^2 = 173 \text{ meV/\AA}^2$$

$$\gamma_s(111) = 87 \text{ meV/\AA}^2$$

The equilibrium shape of a macroscopic crystal of TiO_2 using the Wulff construction

