Surface and Interface Energies

M. Ceriotti - MX304

EPFL

Outline

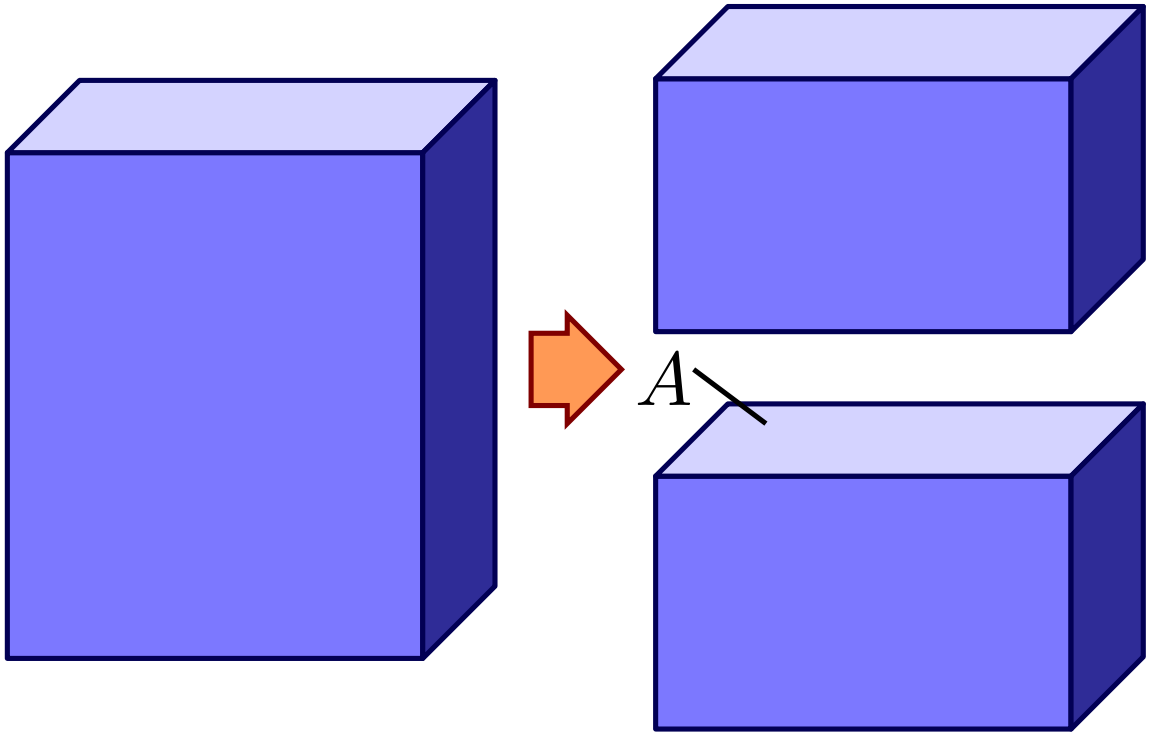
- Definition of surface energy as an excess of Gibbs free energy
- Surface energy and surface stress
- Estimating surface energy by bond counting
- Anisotropy of the surface energy - stereographic projections
- Wulff plots and Wulff construction - the equilibrium structure of a crystal
- Definition of interface free energy. Dupré equation

Definition of Surface Energy

- The surface energy $G_s = E_s - TS_s \equiv \gamma$ is the excess Gibbs free energy associated with the creation of a unit of surface

$$G = NG_a + G_s A = NG_a + \gamma A$$

- Can be understood as originating from all the broken bonds introduced by creating the surface



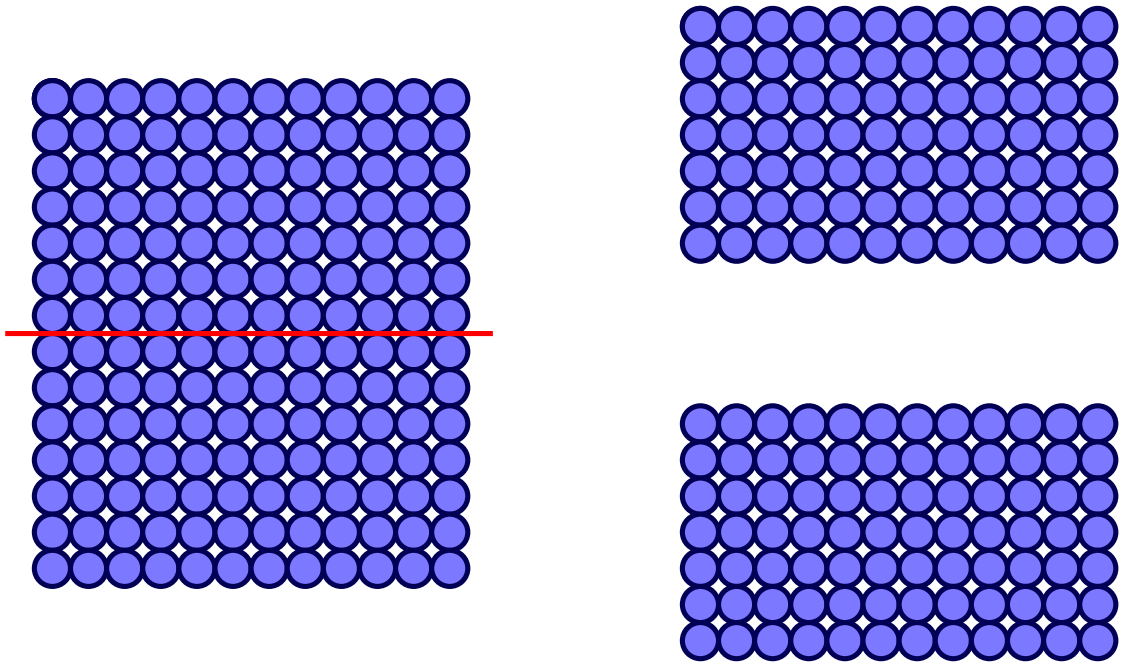
$$\Delta G = 2\gamma A$$

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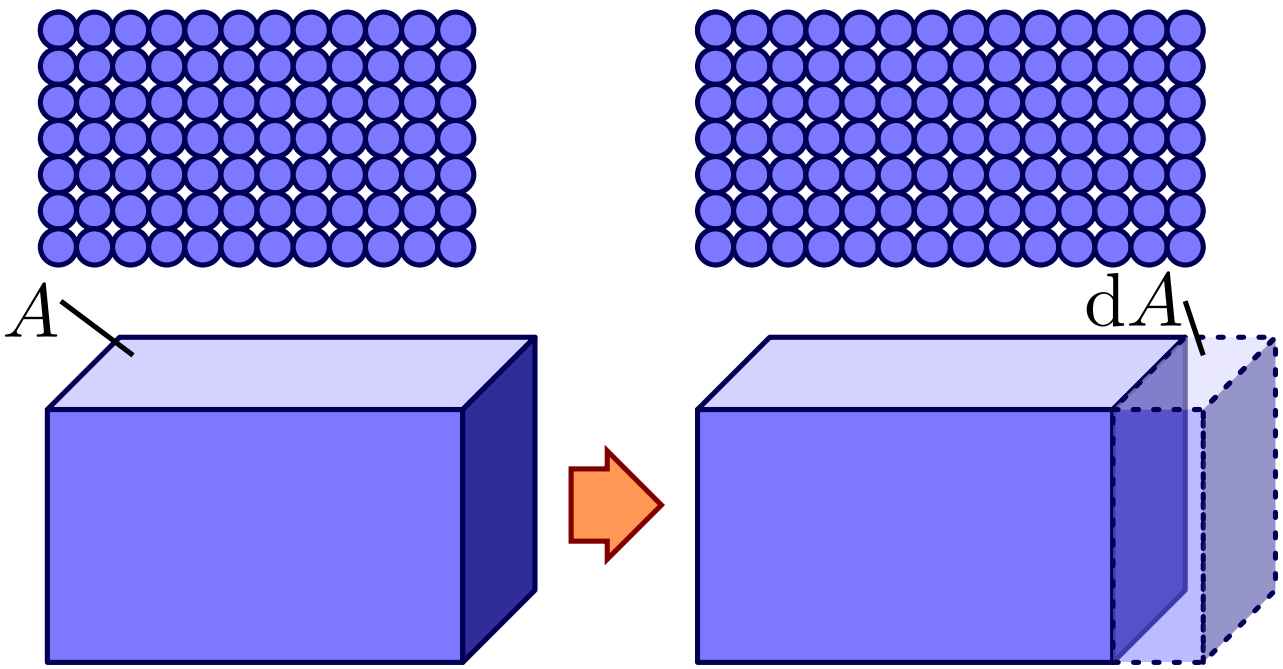
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Surface Energy and Surface Stress/1

- What is the reversible work associated with changing the extent of a surface? Depends!
- You can consider creating more surface atoms (constant γ)
- Or you can strain the existing surface without increasing the number of surface atoms (excess elastic energy, only possible for a solid!)

$$\mathrm{d}W = \gamma \mathrm{d}A$$

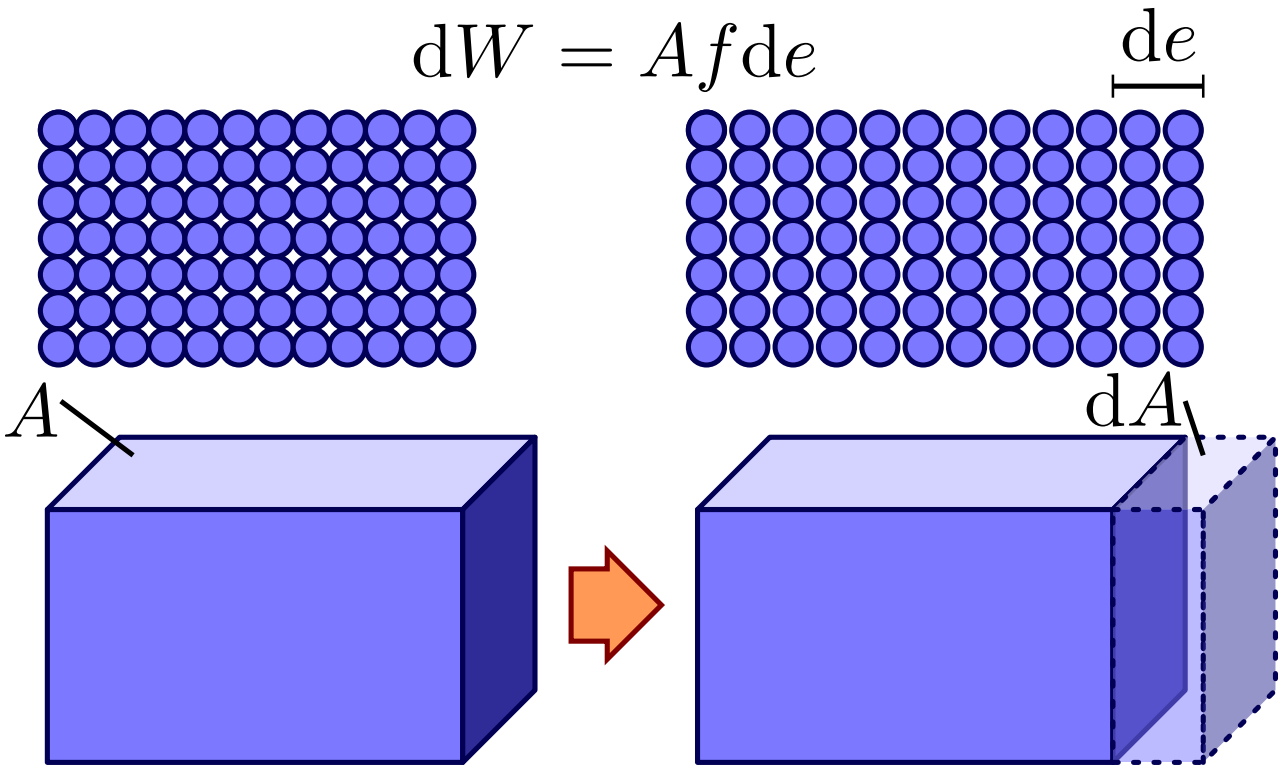


$$\mathrm{d}W = \mathrm{d}(\gamma A)$$

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$$\mathrm{d}W = Af\mathrm{d}e$$

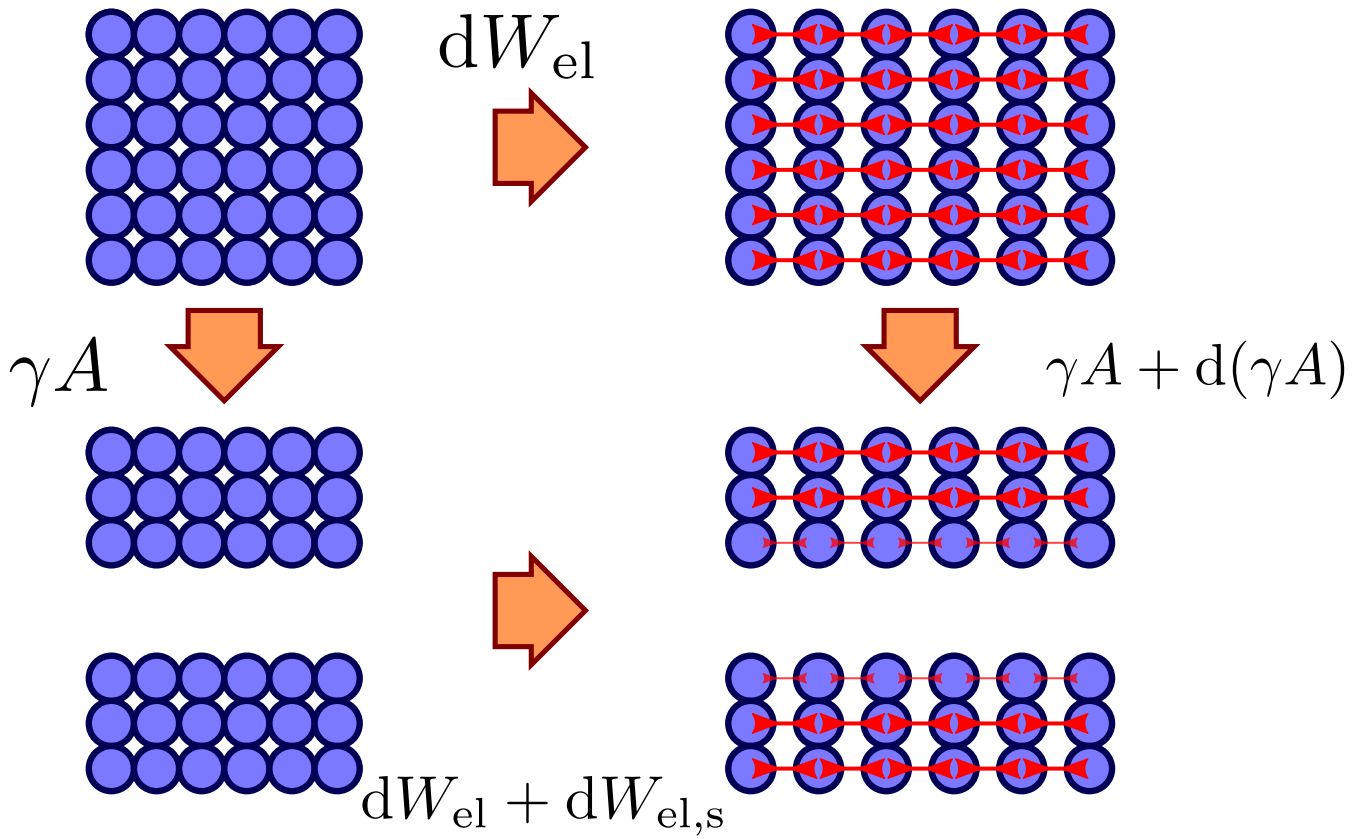


$$\mathrm{d}W = \mathrm{d}(\gamma A)$$

Surface Energy and Surface Stress/2

- The excess of elastic energy depends on the fact that atoms at the surface are held in place by the underlying bulk. It can be expressed in terms of a surface stress tensor f_{ij}
- For high-symmetry surfaces $f_{ij} = \delta_{ij} f$, and $f = \gamma + \partial\gamma/\partial e$

$$\mathrm{d}W = A \sum_{ij} f_{ij} \mathrm{d}e_{ij}, \qquad \mathrm{d}A = A \sum_{i} \mathrm{d}e_{ii}$$

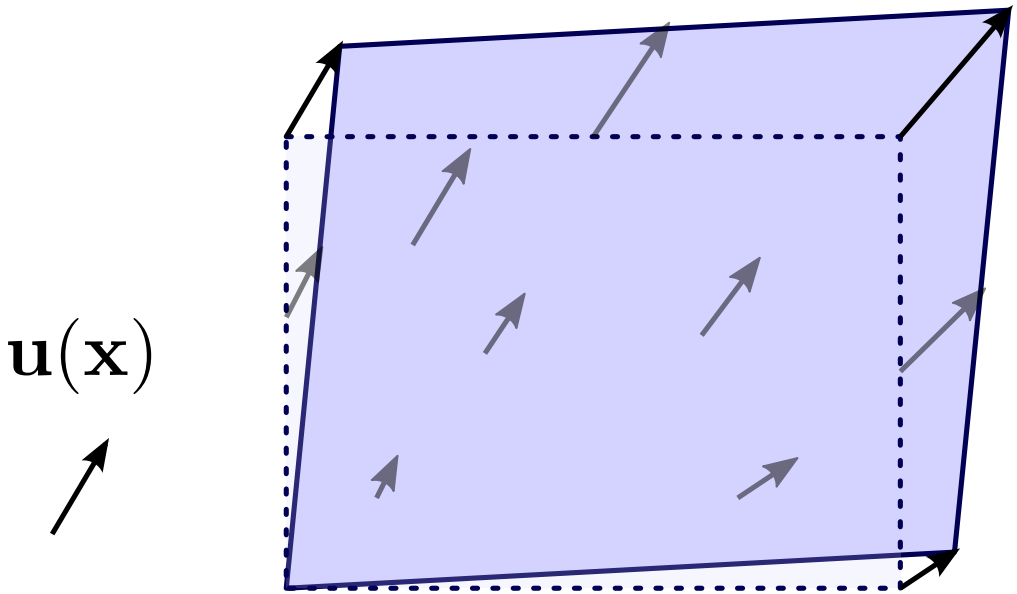


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$$\mathrm{d}e_{ij} = \partial u_i / \partial x_j$$



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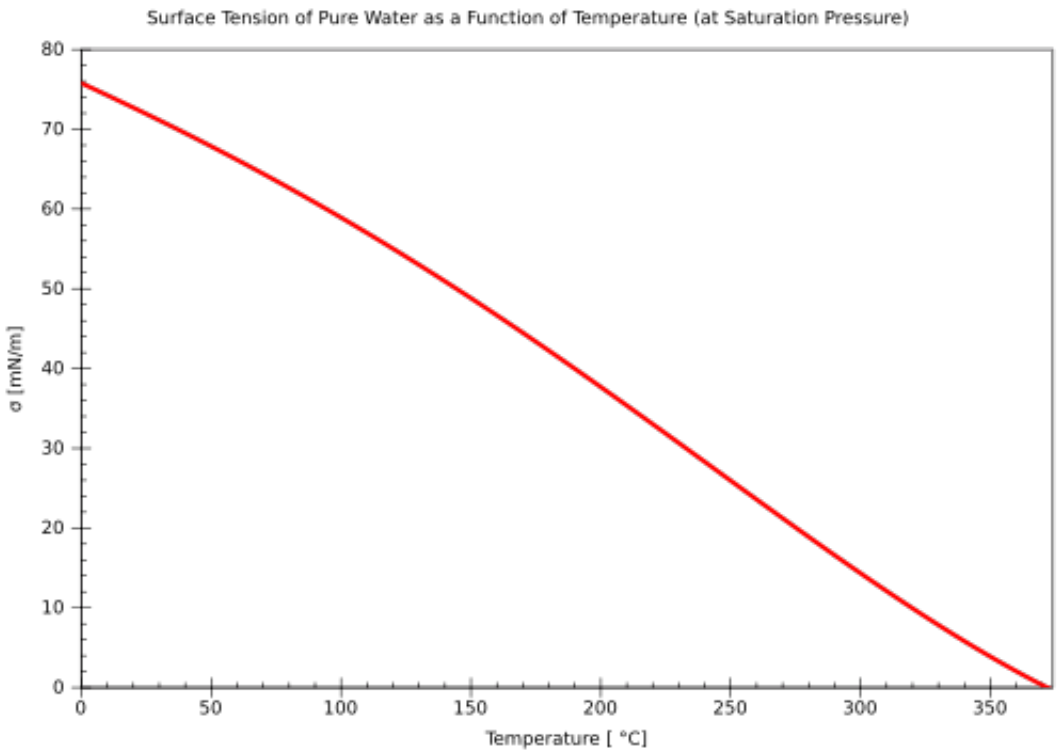
$$\mathrm{d}W = \mathrm{d}\left(\gamma A\right) = \gamma \mathrm{d}A + A \mathrm{d}\gamma$$

$$A \sum_{ij} f_{ij} \mathrm{d}e_{ij} = \gamma A \sum_{i} \mathrm{d}e_{ii} + A \sum_{ij} \frac{\partial \gamma}{\partial e_{ij}} \mathrm{d}e_{ij}$$

$$\boxed{f_{ij} = \gamma \delta_{ij} + \frac{\partial \gamma}{\partial e_{ij}}}$$

Temperature Dependence of Surface Energy

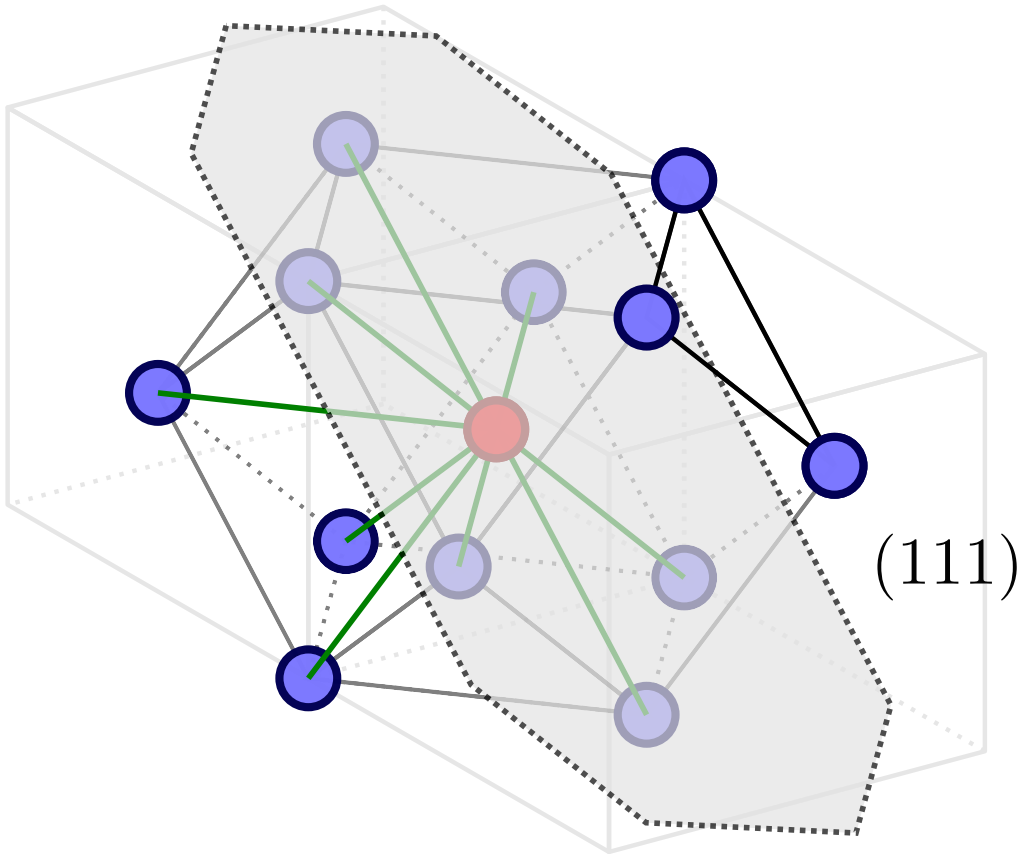
- Based on the definition $G_s = E_s - TS_s$, $(\partial\gamma/\partial T)_P = -S_s/A$.
- Typically the excess surface entropy is positive - atoms at the surface have more space to vibrate, and more ways to create defects
- γ is a decreasing function of temperature: at the critical temperature the liquid and the vapor become indistinguishable, and therefore $\gamma\,(T_c)$ must be zero.



Surface tension of water from the triple to the critical point [Stan J. Klimas at Wikipedia]

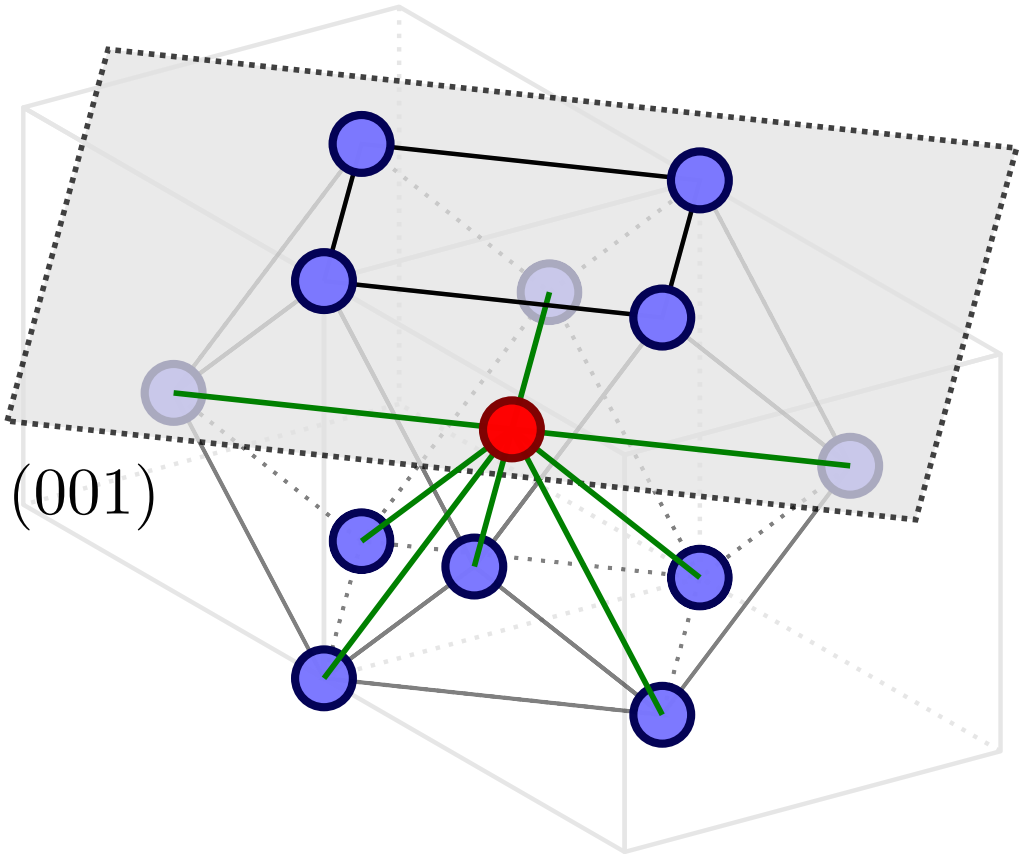
Surface Energy and Bond-Counting

- In a fcc structure, each atom has 12 neighbors. The energy per bond is $\epsilon_b \approx \Delta H_s / 6N_A$ (ΔH_s : molar heat of sublimation)
- Creating a (111) surface breaks 3 (half) bonds per atom, so $E_s = 3\epsilon_b/2 = \Delta H_s / 4N_A$. How about (100)?
- γ also contains the surface atom density: $\gamma_{100} = 2\epsilon_b / d^2$



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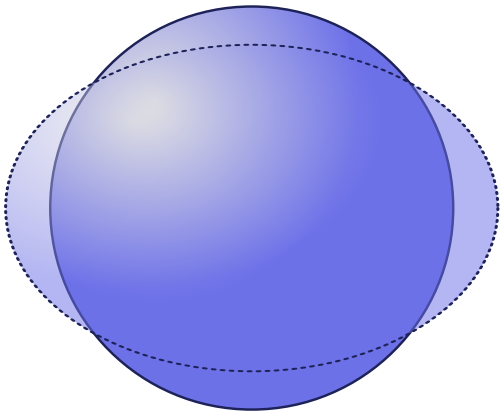
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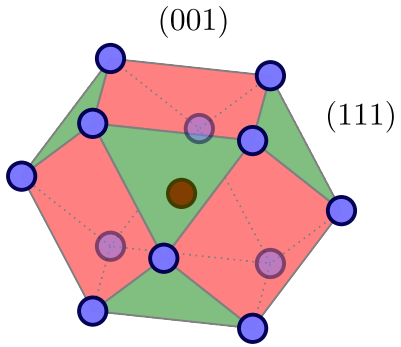


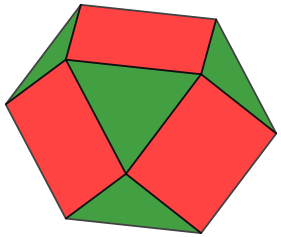
Equilibrium Shape of a Crystal

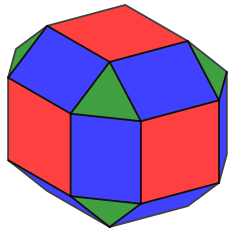
- In a liquid, γ is constant, so the system just want to minimize area at fixed volume $\longrightarrow$ spherical droplets
- In a solid, the surface energy γ is orientation-dependent. Minimize total surface energy at constant volume

$$\min \int \gamma\left(\hat{\mathbf{n}}\right) dA$$





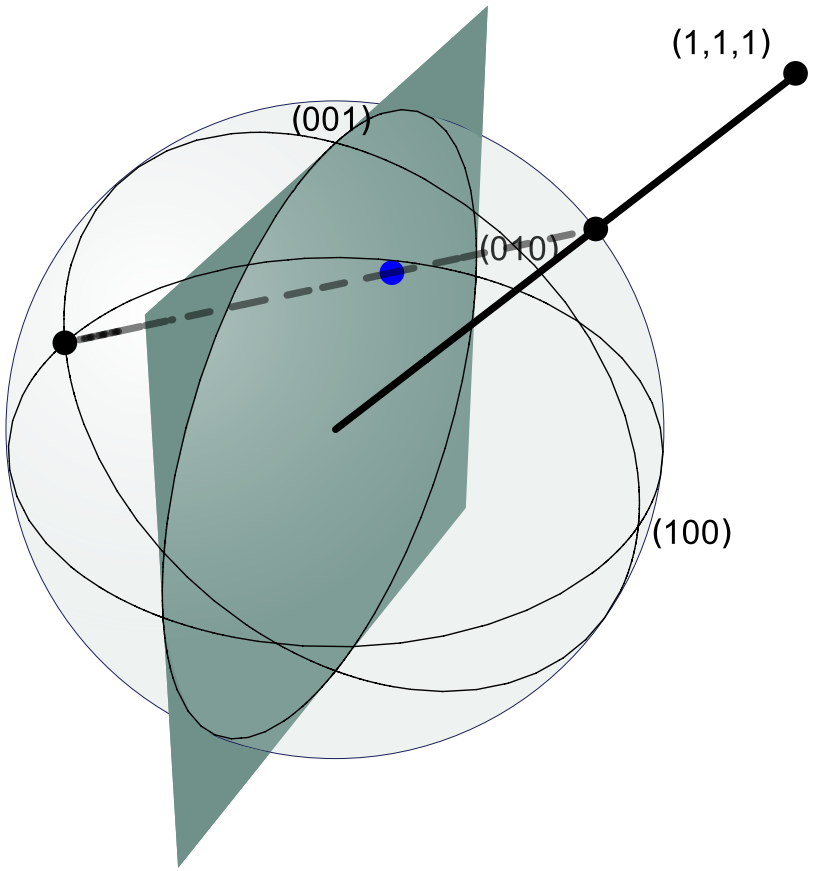




Stereographic Projections and γ Plots

- Stereographic projections: a concise 2D representation of crystal directions
- Can be used to represent the dependence of γ on the orientation:

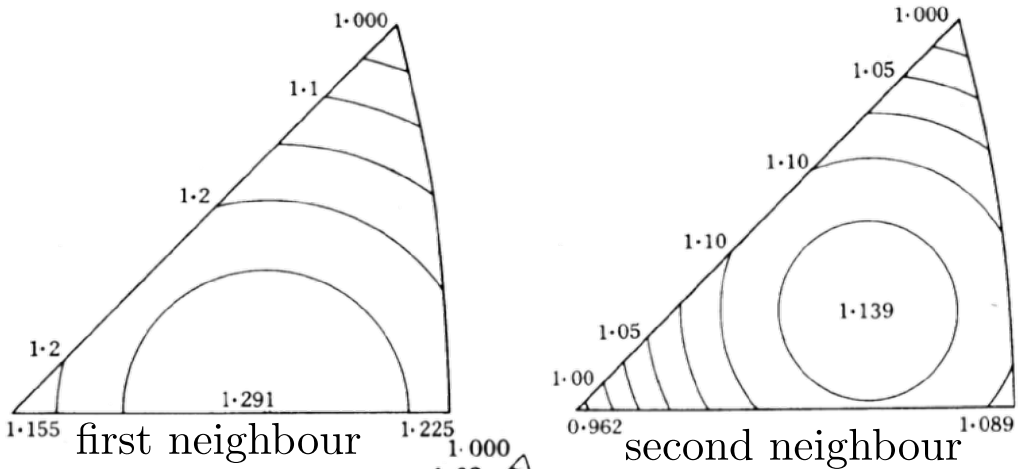
$$\gamma_{hkl} \approx -\frac{\epsilon_b}{2}\frac{d_{hkl}}{V_0}\sum_i \mathbf{u}_b^{(i)} \cdot \hat{\mathbf{n}}_{hkl}$$



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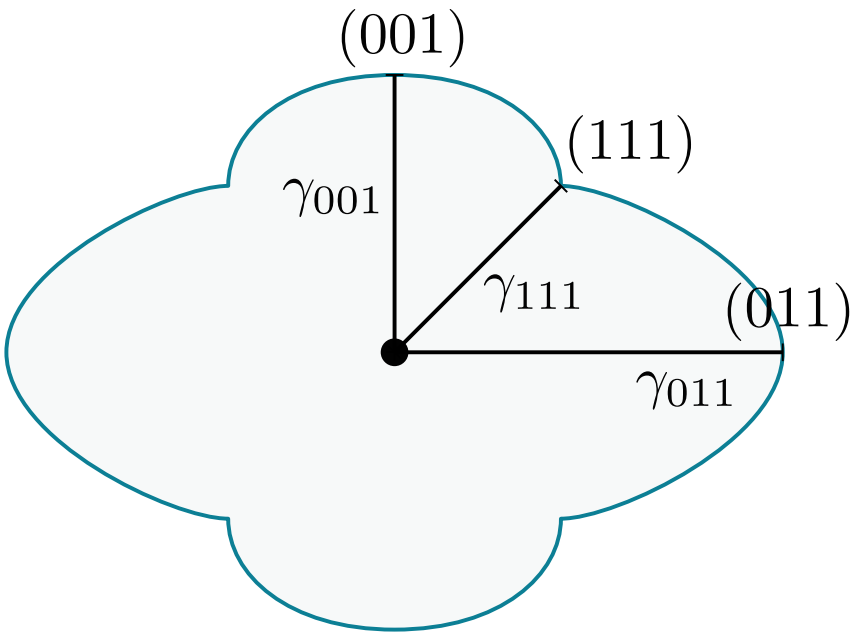
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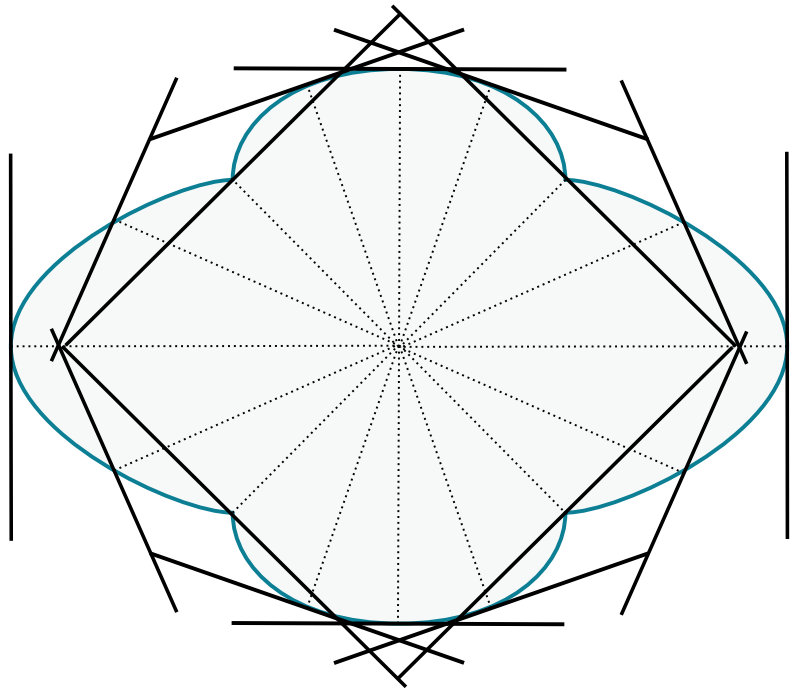
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Wulff Construction and Crystal shape

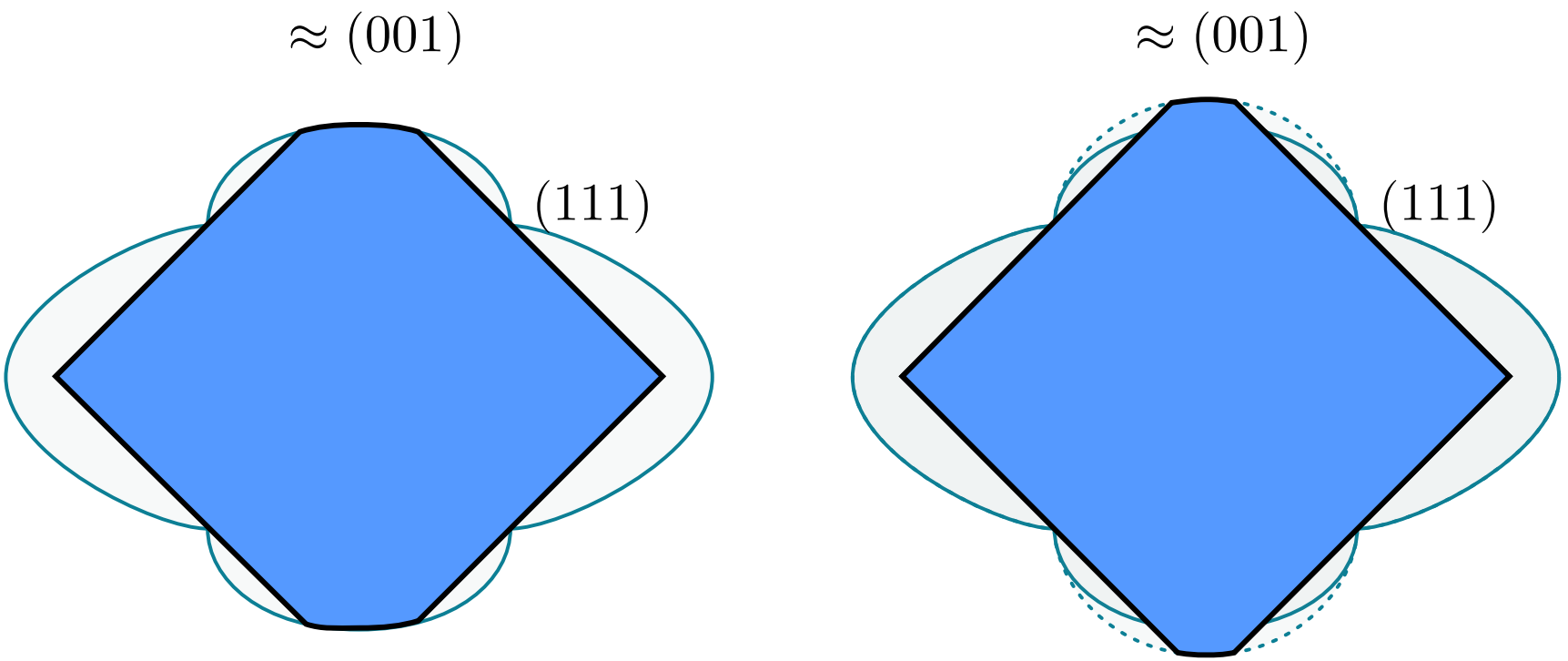
- Another way of representing γ_{hkl} is by a polar plot: for every surface orientation $\hat{\mathbf{u}}_{hkl}$ use γ_{hkl} as the radius: *Wulff plot*
- Wulff construction to determine the equilibrium crystal shape: envelope of the lines orthogonal to $\gamma_{hkl}\hat{\mathbf{u}}_{hkl}$





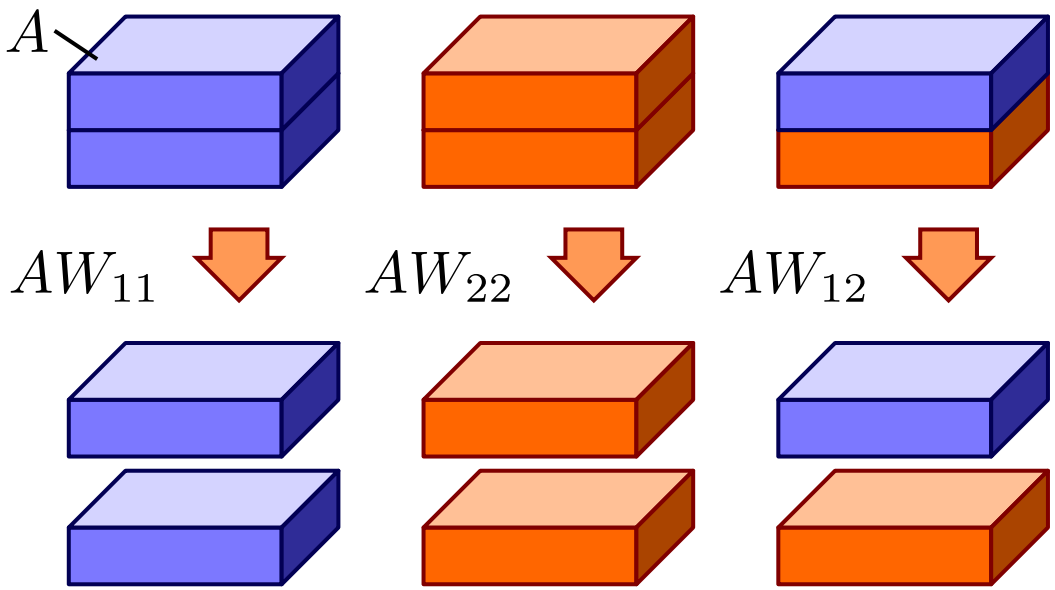
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Work of Adhesion & Interface Free Energy

- Work of cohesion (adhesion): for separating two parts of the same material, $W_{11} = 2\gamma_1$ or different materials W_{12}
- **Interface free energy** between two different materials:
- Can be generalized to multiple components

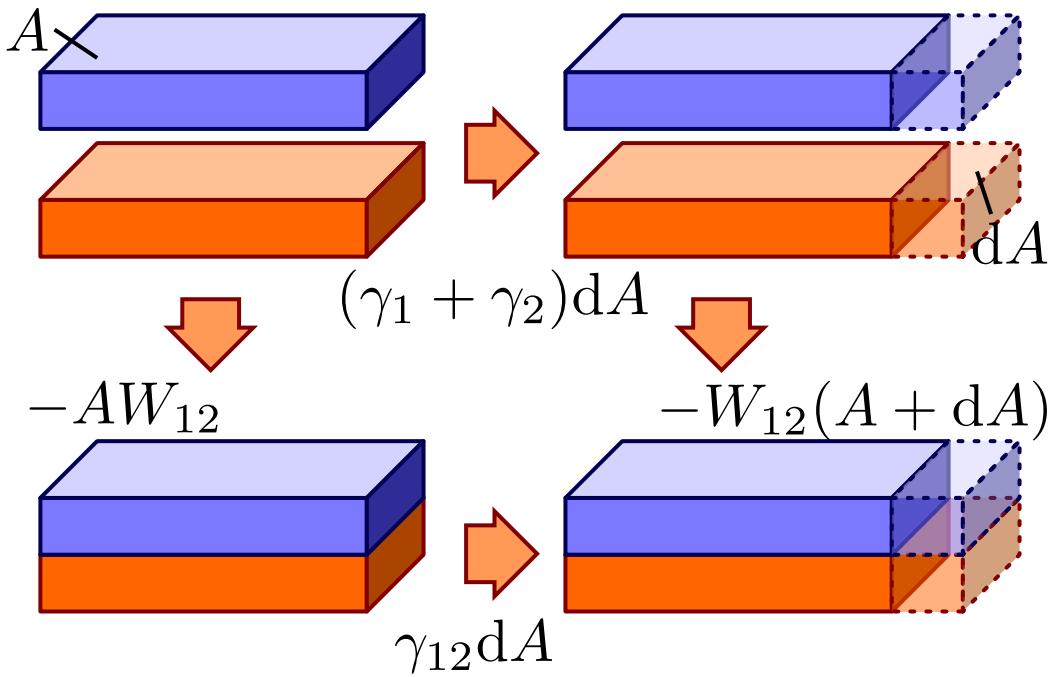


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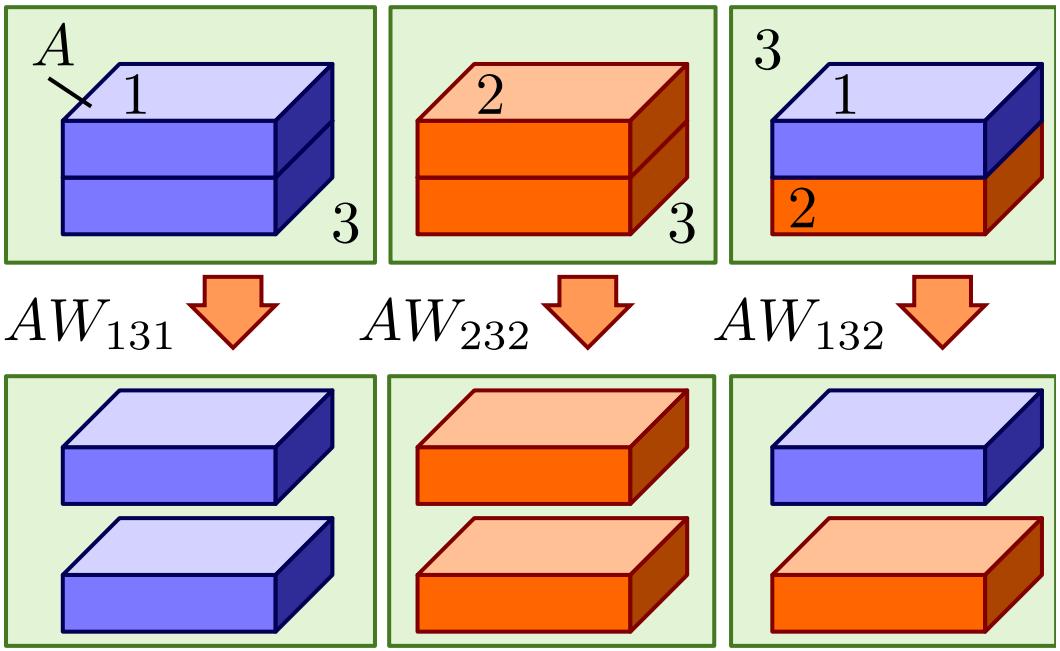
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$$W_{132} = W_{33} + W_{12} - W_{13} - W_{23}$$



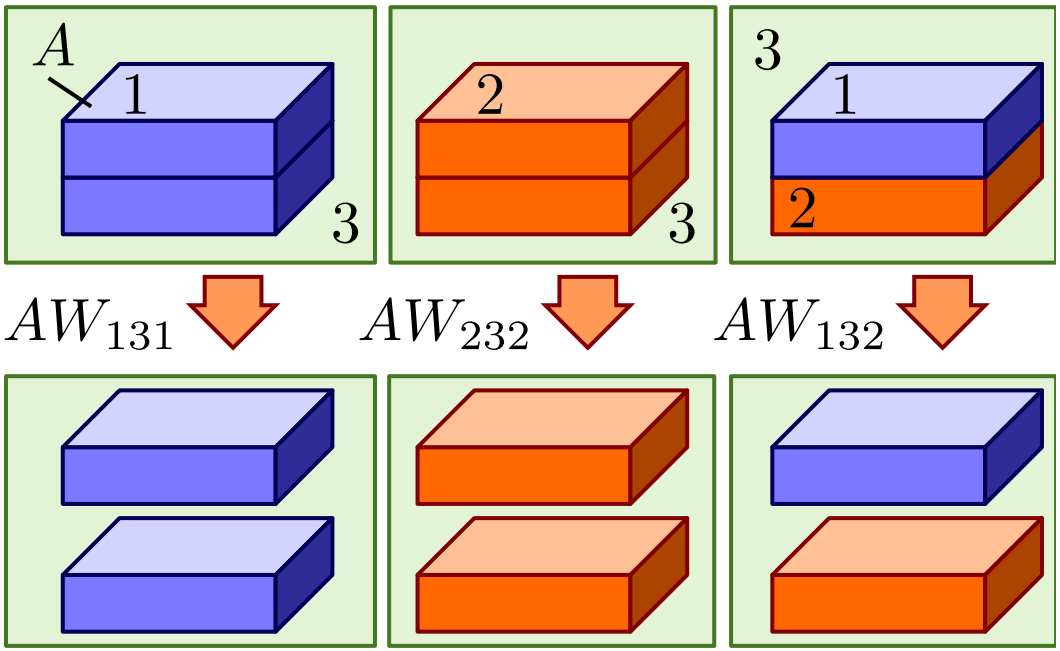
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$$W_{132} = 2\gamma_3 + (\gamma_1 + \gamma_2 - \gamma_{12}) - (\gamma_1 + \gamma_3 - \gamma_{13}) - (\gamma_2 + \gamma_3 - \gamma_{23})$$



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