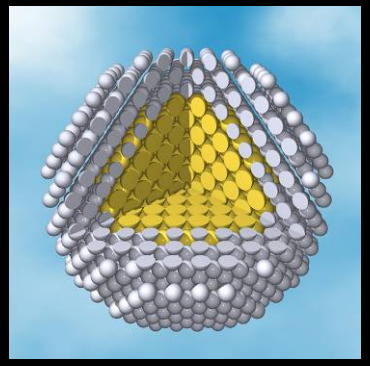
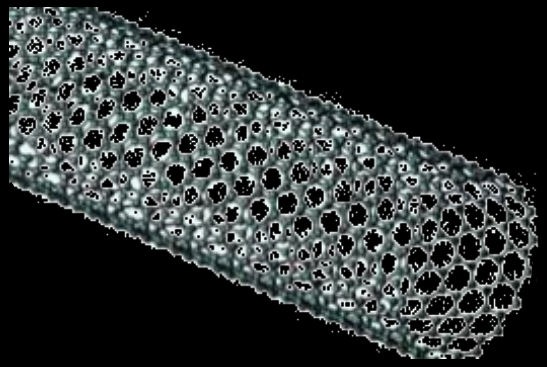
The Thermodynamics of Crystalline Interfaces: Thermodynamics at the Nanoscale

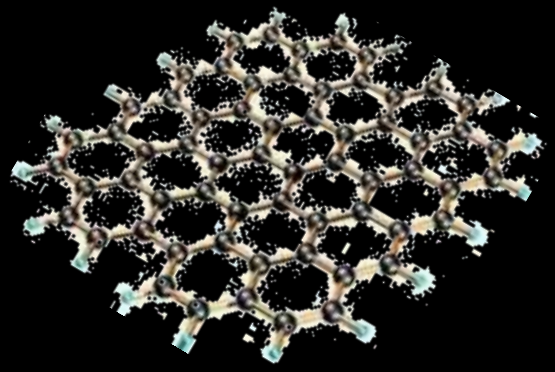
Low-Dimensional Materials

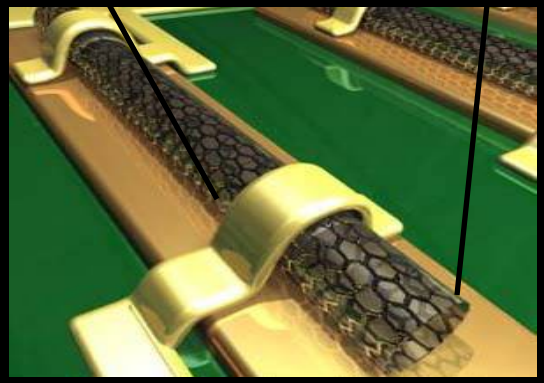
Low-dimensional materials enable new science and technology

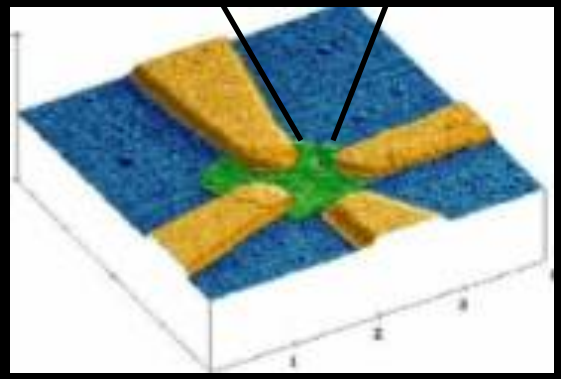
O-D **1-D** **2-D**





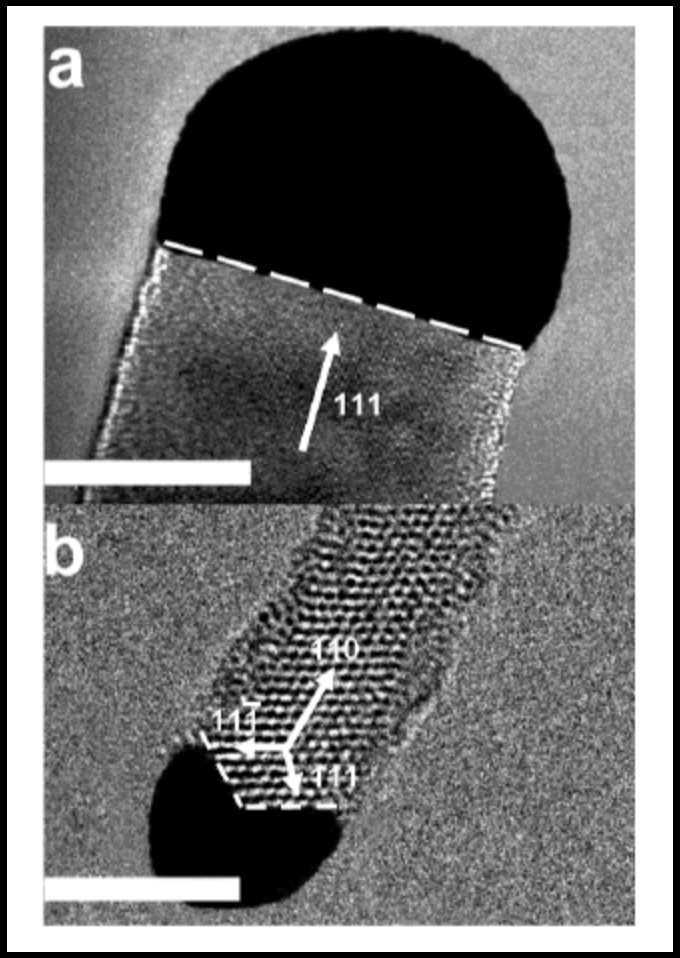






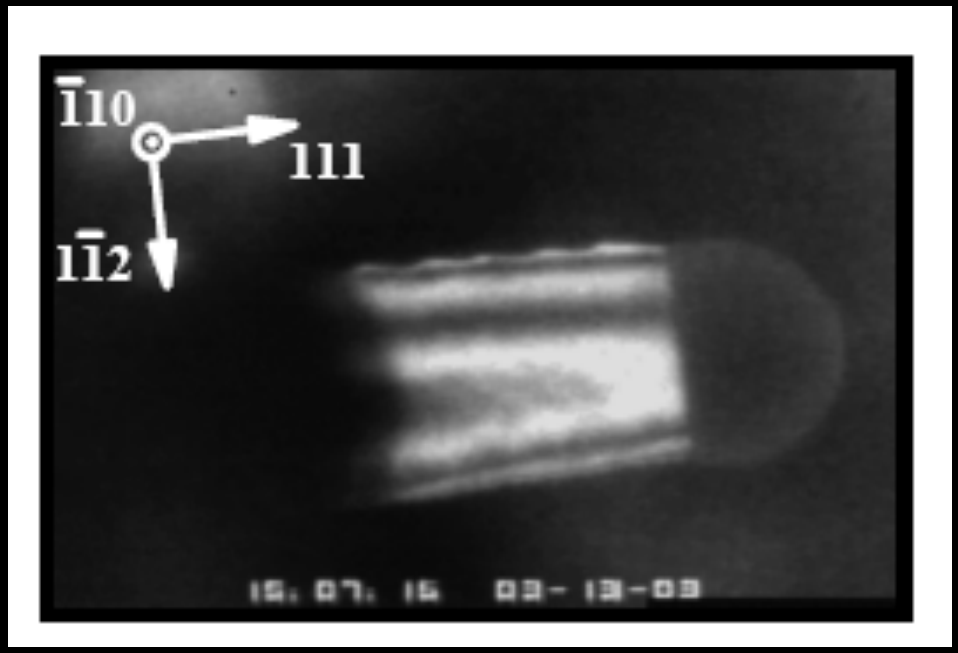
Philips C. Dekker, Delft P. Kim, Columbia

Si Nanowires



5 nm

Wu et al, Nanoletters, 2004



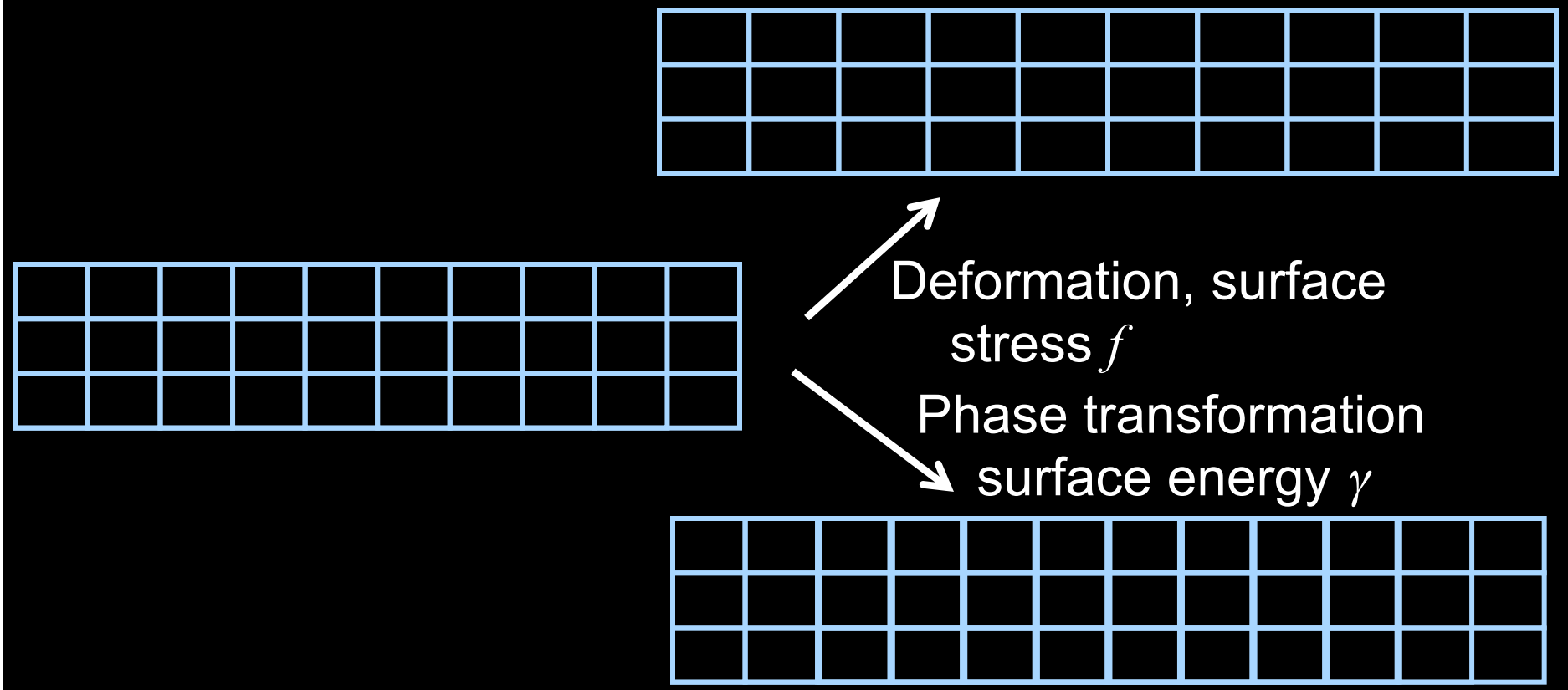
Ross and Hannon

Nanoscale Thermodynamics

- Surface to volume ratio is very large
- Implies that surface/interfacial energies are very important
- Surface forces can be important
- How can we include these in a thermodynamic description for these two-phase systems?
- What is an interfacial energy?
- Is there a difference between surface tension and surface energy?
- What is responsible for motion by mean curvature and the Gibbs-Thompson equation?

Surface Stress and Surface Energy

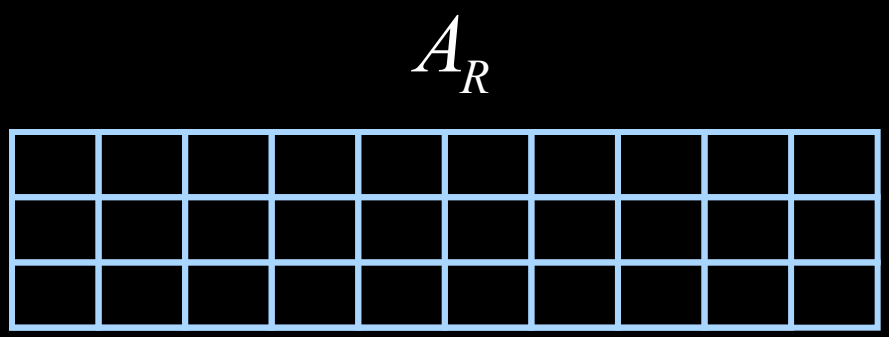
- The presence of a crystalline lattice allows us to differentiate between variations that involve deformation and those that involve phase transformations



Surface Stress and Surface Energy

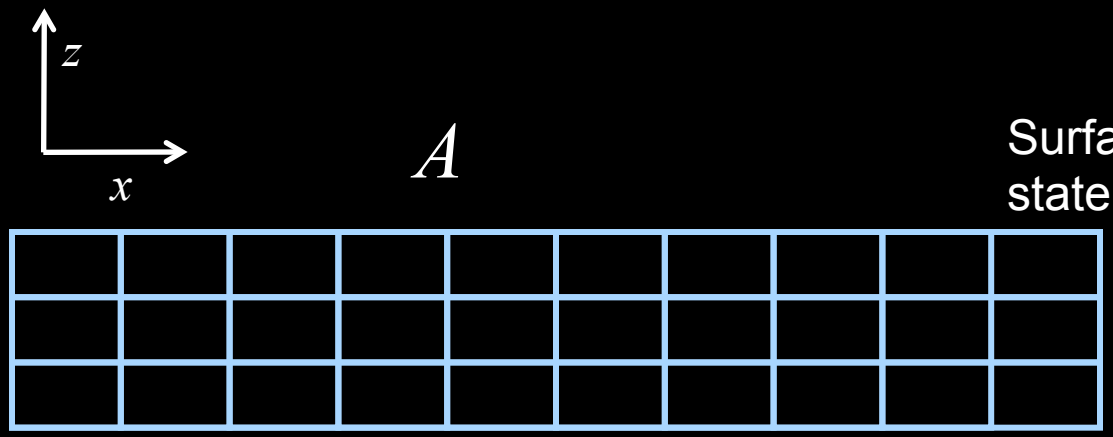
- For a fluid as soon as the block is deformed, atoms move from the bulk to the surface, thus $f = \gamma$
- Surface stress can be either positive or negative!
- Surface energy must be positive for stability. This prevents surfaces from spontaneously creating interfacial area
- Is there a relationship between surface stress and surface energy?

Surface Stress and Surface Energy



Surface energy per area in the reference state:

$$\gamma_R = \gamma_R(T, \mu_i, e_{ii})$$



Surface energy per area in the physical state:

$$\gamma = \gamma(T, \mu_i, e_{ii})$$

$$A = A_R\left(1 + e_{ii}\right) \qquad e_{ii} = e_{xx} + e_{yy}$$

Surface Stress and Surface Energy

$$f_{ij} = \frac{\partial \gamma_R}{\partial e_{ij}}$$

Energy must be independent of reference state:

$$\gamma A = \gamma_R A_R$$

Using the expression for the area change: $A = A_R \left(1 + e_{ii}\right)$

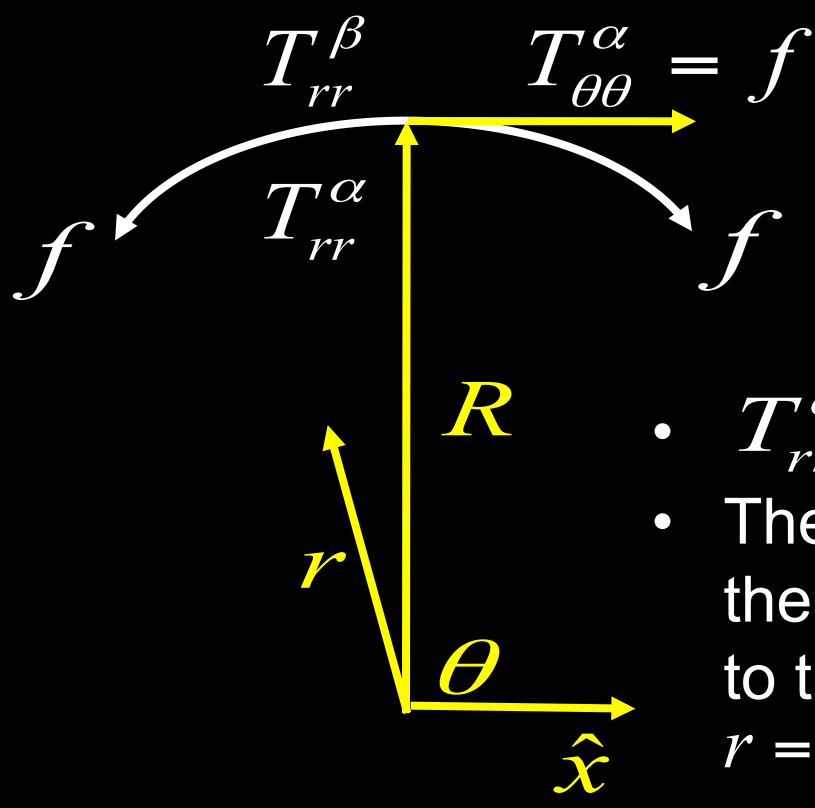
$$\gamma \left(1 + e_{ii}\right) = \gamma_R$$

Using this in the above:

$$f_{ij} = \frac{\partial \gamma}{\partial e_{ij}} + \gamma \delta_{ij} + O(e_{ij}^2)$$

Surface Stress Enters the Force Balance

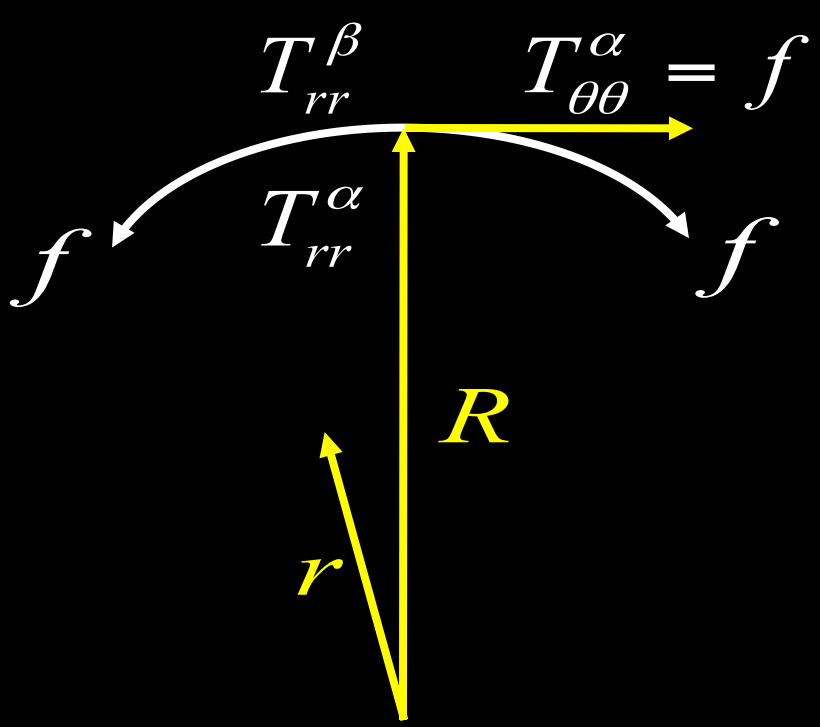
- Surface stress is a force per unit length along the surface
- Consider a cylindrical surface a portion of which is:



- $T_{rr}^{\alpha} \neq T_{rr}^{\beta}$
- There is a jump in the force tangential to the interface at $r = R$

Surface Stress Enters the Force Balance

- Can determine the equilibrium conditions by using geometry and resolving the forces along the radial direction (r) and the tangential (θ) direction



- An easier approach is to write the conditions for mechanical equilibrium in cylindrical coordinates
- Since there is no angular dependence of the stress in the two bulk phases the equilibrium condition:

$$\nabla \cdot \mathbf{T} = \mathbf{0}$$

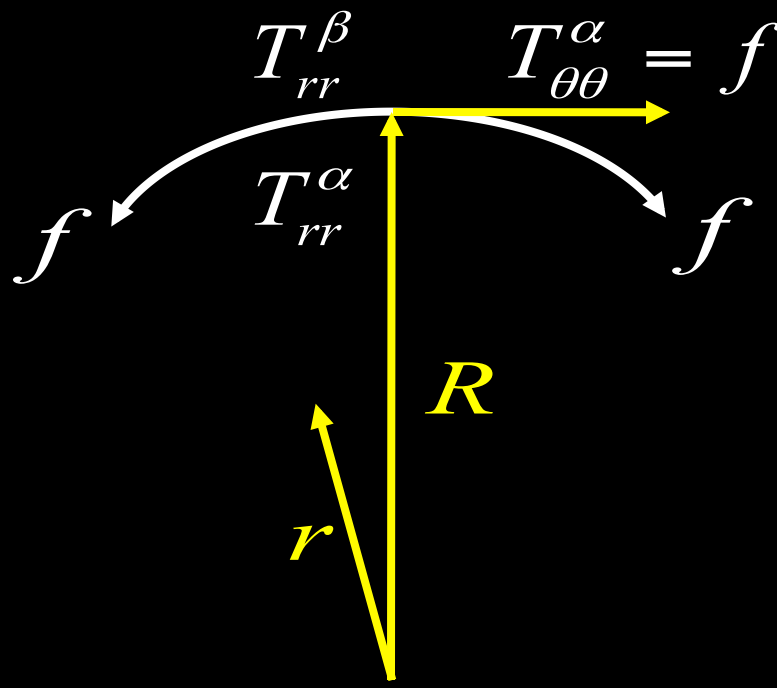
Surface Stress Enters the Force Balance

- Becomes

$$\frac{\partial\left(rT_{rr}\right)}{\partial r} - T_{\theta\theta} = 0$$

- $T_{\theta\theta}$ has a jump at r = R which we can represent as

$$-f\,\delta\left(r-R\right)$$



- The pressures jump as one crosses the surface too
- Thus the radial stress has jumps at the surface
- Concentrating only on the effect of surface stress

Surface Stress Enters the Force Balance

- Elastically isotropic thus

$$\frac{\partial\left(rT_{rr}\right)}{\partial r}+f\,\delta(r-R)=0$$

- Integrate this from the center of the particle to infinity,

$$\int_0^{\infty}\frac{\partial\left(rT_{rr}\right)}{\partial r}dr=rT_{rr}\,|_0^R+rT_{rr}\,|_R^{\infty}=RT_{rr}^{\alpha}(R)-RT_{rr}^{\beta}(R)$$

$$\int_0^{\infty}f\,\delta(r-R)dr=f$$

and thus,

$$T_{rr}^{\alpha}(R)-T_{rr}^{\beta}(R)=-\frac{f}{R}$$

Surface Stress Enters the Force Balance

- The force balance at the surface is:

$$T_{rr}^{\alpha}(R) - T_{rr}^{\beta}(R) = -\frac{f}{R}$$

- So the stress inside the particle is larger than the stress outside for a compressive (negative) surface stress
- If the cylinder is hydrostatically stressed,

and thus $$T_{rr} = -P$$

$$P^{\alpha}(R) - P^{\beta}(R) = \frac{f}{R}$$

and we obtain the well known Laplace-Young result

Surface Stress

- In most cases the magnitude of the surface stress is on the order of the surface energy
- Using the equations for the jump in the stress, the stress generated by a typical surface stress with a 100 nm diameter wire is 10^8 Pa, (equal to putting the entire weight of a SUV on your fingernail)
- Using a Lagrangian representation of the area,
- $$f_{ij} = \frac{\partial \gamma}{\partial \hat{e}_{ij}}$$ ($\hat{e}_{ij}$ is the surface strain)
- Letting $f_{ij} = f\,\delta_{ij}$ (true for any surface with inversion symmetry) and integrating (to first order in strain)

$$\gamma = \gamma_o + f\,\delta_{ij}\hat{e}_{ij}$$

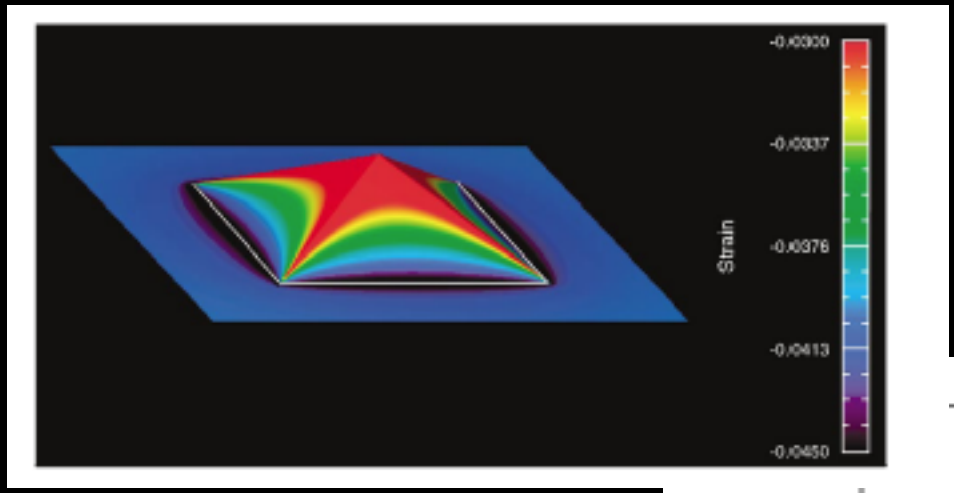
Surface Stress

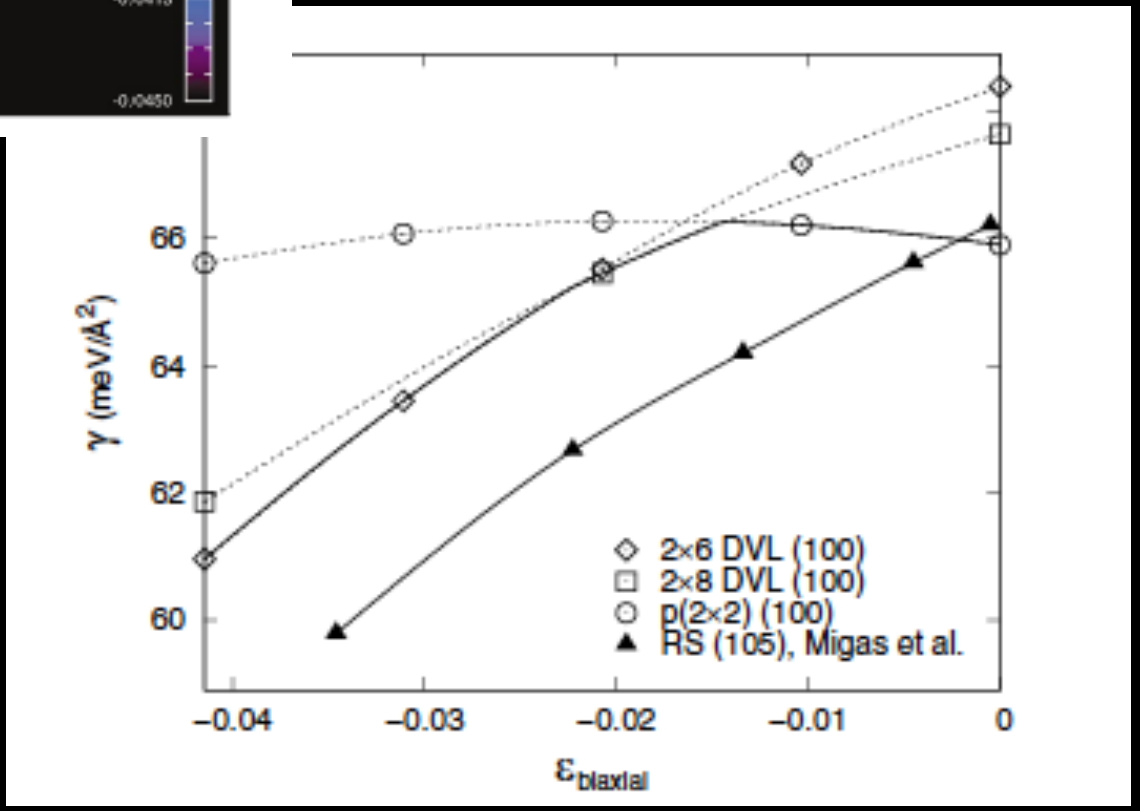
- Thus the surface energy depends on the surface stress as

$$\gamma = \gamma_o + f\hat{e}_{ii}$$

- So as the surface strain changes the surface energy changes. It can increase or decrease depending on the sign of f
- This can be important in many semiconductor surfaces, e.g. Ge (001)

Surface Stress: Ge





Shklyaev et al., PRL 2005

Surface Energy

- Surface energy measures the change in energy with a change in the area due to the addition of lattice points, or, at constant strain.
- Assume the solid is hydrostatically stressed
- The first and second laws implies that the reversible variation (δ) of the energy must be an extremum,

$$\delta E\big|_{S,V,n_i} = 0$$

where S is the entropy and n_i is the number of moles of component i. these are constraints

- Assume that we can divide the system into two bulk phases and excess quantities associated with the interface. This is possible for systems with planar interfaces, but there are subtleties associated with nonplanar interfaces
- Thus,

$$E = E^{\alpha} + E^{\beta} + E^{\Sigma}$$

where

$$E^{\alpha} = \int_{V^{\alpha}} E_V^{\alpha}(S^{\alpha}, \rho_i^{\alpha}) dV$$

$$E^{\beta} = \int_{V^{\beta}} E_V^{\beta}(S^{\beta}, \rho_i^{\beta}) dV$$

$$E^{\Sigma} = \int_{A} E^{\Sigma}(\hat{S}, \hat{n}_i) dA$$

The energy of the surface is not a function of volume since the interface is infinitesimally thin. The quantities with hats are quantities associated with the interface, per area. Assume isotropy

- The constraints are

$$S = \int_\alpha S_V^\alpha dV + \int_\beta S_V^\beta dV + \int_A S^\Sigma dA$$

$$n_i = \int_\alpha \rho_i^\alpha dV + \int_\beta \rho_i^\beta dV + \int_A n_i^\Sigma dA$$

- The first variation in the energy is

$$\delta E = \delta E^\alpha + \delta E^\beta + \delta E^\Sigma = 0$$

- Considering just the variations where the interface does not move.
- The first variation in the energy is:

$$\delta E = \delta \int E_V(S_V, \rho_i) dV = \int \delta E_V(S_V, \rho_i) dV = \int \left(\frac{\partial E_V}{\partial S_V} \delta S_V + \sum_{i=1}^{N} \frac{\partial E_V}{\partial \rho_i} \delta \rho_i \right) dV$$

$$\delta E = \int \left(T \delta S_V + \sum_{i=1}^{N} \mu_i \delta \rho_i \right) dV$$

$$\int_{V^\alpha}\left(T^\alpha \delta S_V^\alpha + \sum_{i=1}^{N} \mu_i^\alpha \delta\rho_i^\alpha\right) dV + \int_\beta \left(T^\beta \delta S_V^\beta + \sum_{i=1}^{N} \mu_i^\beta \delta\rho_i^\beta\right) dV$$

$$+\int_A \left(\hat{T}\delta\hat{S} + \sum_{i=1}^{N} \mu_i^\Sigma \delta\hat{n}_i\right) dA = 0$$

The variation of the constraints are

$$\delta S = 0 = \int_\alpha \delta S_V^\alpha dV + \int_\beta \delta S_V^\beta dV + \int_A \delta\hat{S} dA$$

$$\delta\rho_i = 0 = \int_\alpha \delta\rho_i^\alpha dV + \int_\beta \delta\rho_i^\beta dV + \int_A \delta\hat{n}_i dA$$

Multiplying by Lagrange multipliers for the entropy, λ, and number of moles, λ_i and subtracting from the above,

$$\int_\alpha \left(\left(T^\alpha - \lambda\right)\delta S_V^\alpha + \sum_{i=1}^{N}\left(\mu_i^\alpha - \lambda_i\right)\delta\rho_i^\alpha\right) dV + \int_\beta \left(\left(T^\beta - \lambda\right)\delta S_V^\beta + \sum_{i=1}^{N}\left(\mu_i^\beta - \lambda_i\right)\rho_i^\beta\right) dV$$

$$+\int_A \left(\left(\hat{T} - \lambda\right)\delta\hat{S} + \sum_{i=1}^{N}\left(\mu_i^\Sigma - \lambda_i\right)\delta\hat{n}_i\right) dA = 0$$

Since the variations are arbitrary the only way to satisfy the above is,

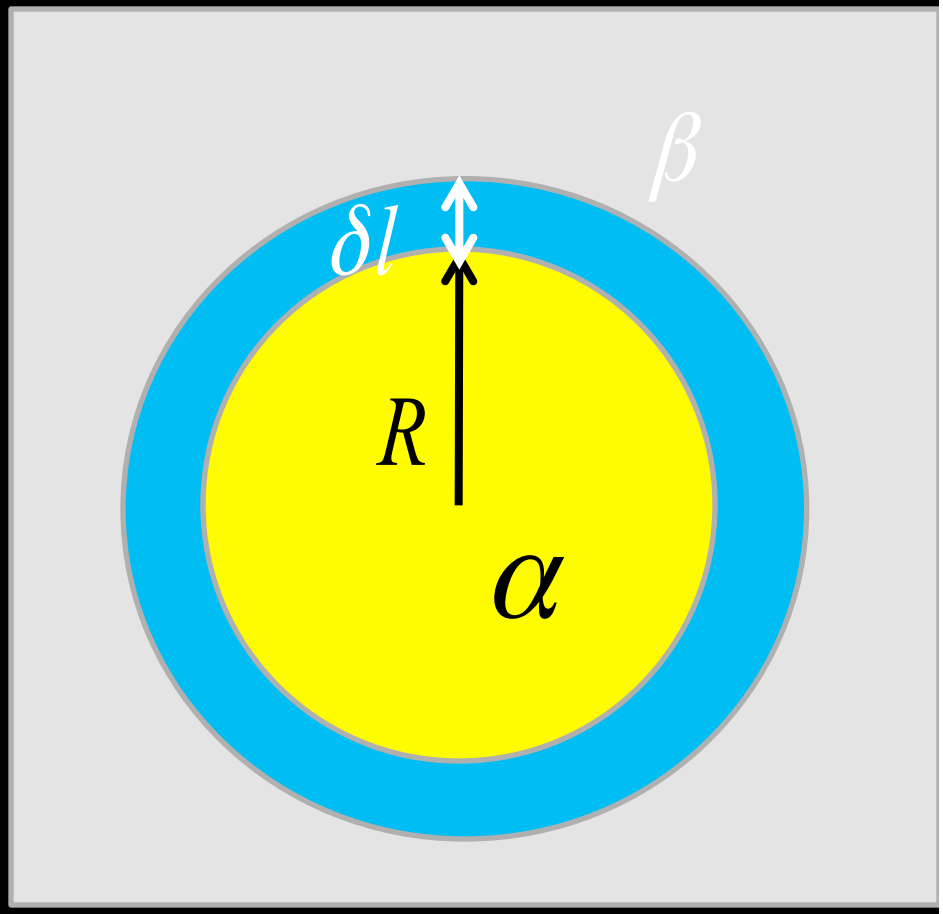
$$\lambda = T^{\alpha} = T^{\beta} = \hat{T}$$

$$\lambda_i = \mu_i^{\alpha} = \mu_i^{\beta} = \hat{\mu}_i$$

Thus the temperature and chemical potential are constant. The Lagrange multipliers are the temperature and chemical potentials!

- Next: variations in the location of the interface
- This is done using infinitesimal virtual displacements of the interface in the direction normal to the interface.

Here is a simple illustration with a spherical particle and a virtual displacement δl



The volume of α increases by:

$$\delta V = 4\pi R^2 \delta l$$

The volume of β decreases by:

$$\delta V = 4\pi R^2 \delta l$$

The surface area increases by:

$$\delta A = 4\pi \left(R + \delta l \right)^2 - 4\pi R^2 = 8\pi R \delta l + O(\delta l)^2$$

The ratio between the change in area and volume is

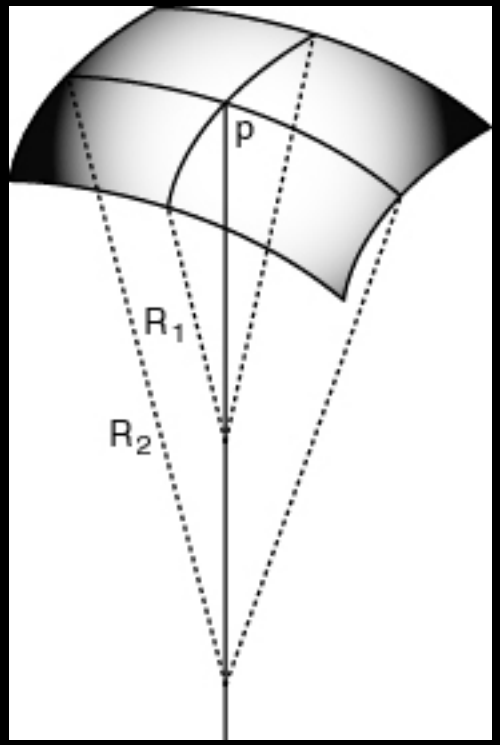
$$\frac{\delta A}{\delta V} = \frac{2}{R} = 2H$$

(H is the mean curvature)

- The general result for arbitrarily curved surfaces is,

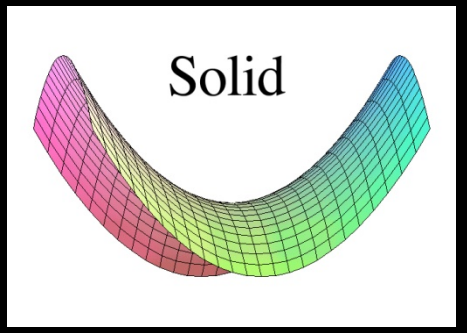
$$\frac{\delta A}{\delta V} = 2H = \frac{1}{R_1} + \frac{1}{R_2}$$

where R_1 and R_2 are the principal radii of curvature of the surface:



$R_1 > 0$

$R_2 < 0$

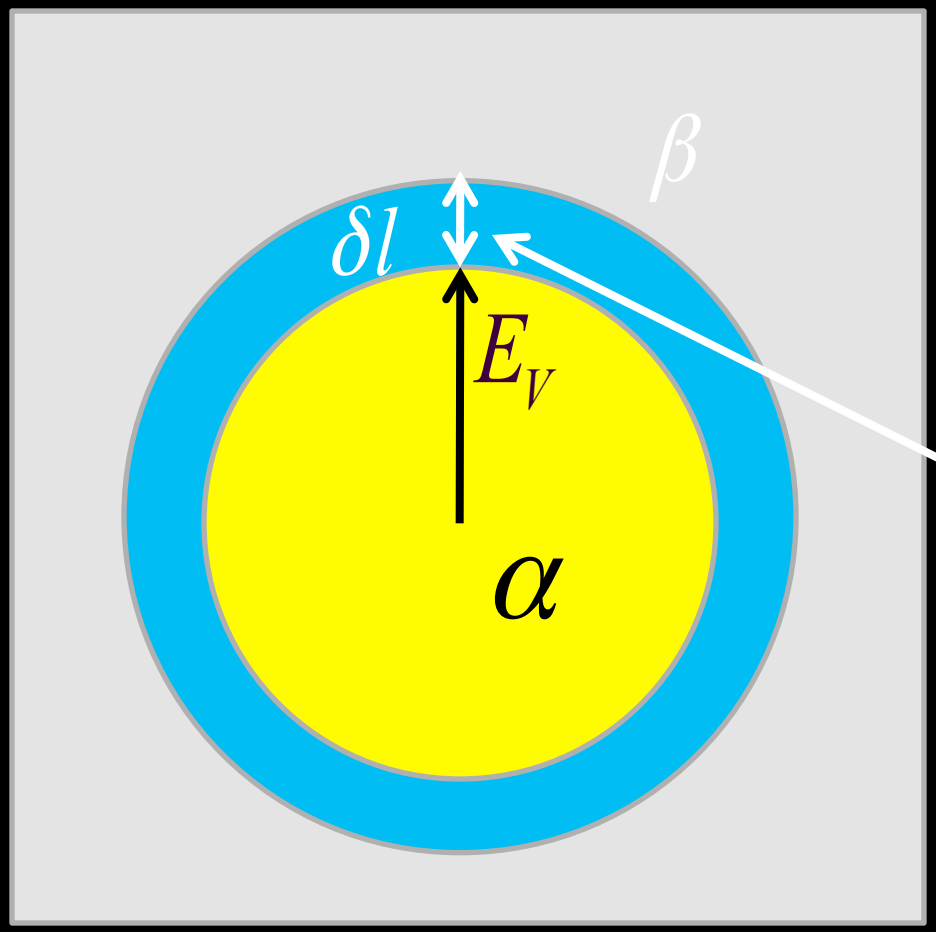


$R_1 > 0$

$R_2 = 0$

- If we allow for interface motion then

$$\delta E = \delta \int_V E_V(S_V, \rho_i) dV = \int_V \delta E_V(S_V, \rho_i) dV + \int_A E_V \delta l dA$$



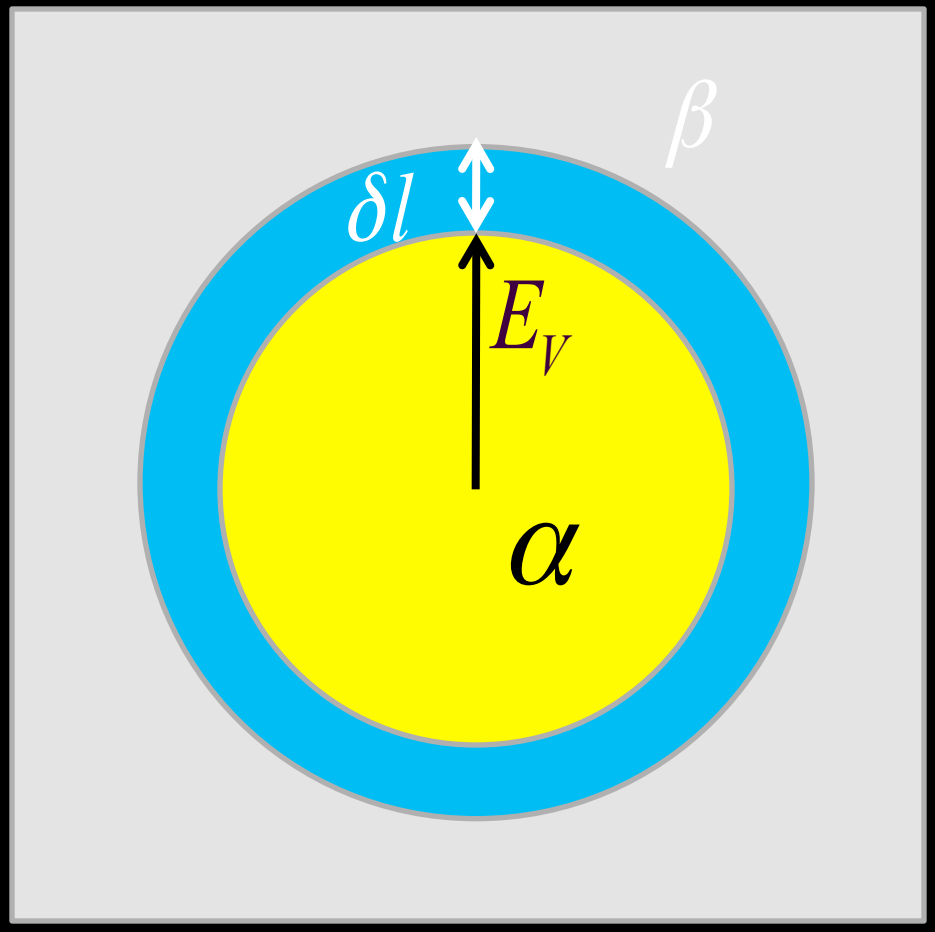
+ for α

– for β

$E_V 4\pi R^2 \delta l$

- If we allow for interface motion then

$$\delta E^{\Sigma} = \delta \int_A E^{\Sigma}(\hat{S}, \hat{n}_i) dA = \int_A \delta E^{\Sigma}(\hat{S}, \hat{n}_i) dA + \int_A E^{\Sigma} 2H \delta l dA$$



$$\delta A = 8\pi R \delta l$$

$$= 4\pi R^2 \left(2 / R\right) \delta l$$

$$= \int_A 2H \delta l dA$$

$$\delta E = \delta E^{\alpha} + \delta E^{\beta} + \delta E^{\Sigma}$$

$$\delta E = \int_V \delta E_V(S_V, \rho_i) dV + \int_A E_V \delta l dA$$

$$\delta E^{\Sigma} = \int_A \delta E^{\Sigma}(\hat{S}, \hat{n}_i) dA + \int_A E^{\Sigma} 2H \delta l dA$$

- We already examined the variations in white, just the variations in interface location yield:

$$\delta E = \int_A E_V^{\alpha} \delta l dA - \int_A E_V^{\beta} \delta l dA + \int_A E^{\Sigma} 2H \delta l dA = 0$$

- The constraints are:

$$\delta S = \int_A S_V^{\alpha} \delta l dA - \int_A S_V^{\beta} \delta l dA + \int_A S^{\Sigma} 2H \delta l dA = 0$$

$$\delta \rho_i = \int_A \rho_i^{\alpha} \delta l dA - \int_A \rho_i^{\beta} \delta l dA + \int_A \hat{n}_i 2H \delta l dA = 0$$

- Multiplying the constraints by Lagrange multipliers as before:

$$\lambda\left[\int_A S_V^\alpha \delta l dA - \int_A S_V^\beta \delta l dA + \int_A S^\Sigma 2H\delta l dA\right] = 0$$

$$\lambda_i\left[\int_A \rho_i^\alpha \delta l dA - \int_A \rho_i^\beta \delta l dA + \int_A \hat{n}_i 2H\delta l dA\right] = 0$$

And subtracting, since we did this previously,

$$\delta E = \int_A \left(E_V^\alpha - \lambda S_V^\alpha - \sum_{i=1}^N \lambda_i \rho_i^\alpha \right)\delta l dA - \int_A \left(E_V^\beta - \lambda S_V^\beta - \sum_{i=1}^N \lambda_i \rho_i^\beta \right)\delta l dA$$

$$+\int_A \left(E^\Sigma - \lambda \hat{S} - \sum_{i=1}^N \lambda_i \hat{n}_i \right) 2H\delta l dA = 0$$

Since the domains of integration are the same,

$$\delta E = \int_A \left[E_V^\alpha - \lambda S_V^\alpha - \sum_{i=1}^N \lambda_i \rho_i^\alpha - \left(E_V^\beta - \lambda S_V^\beta - \sum_{i=1}^N \lambda_i \rho_i^\beta \right) + \left(E^\Sigma - \lambda \hat{S} - \sum_{i=1}^N \lambda_i \hat{n}_i \right) 2H \right] \delta l dA$$

$$= 0$$

since δl is arbitrary,

$$E_V^\alpha - \lambda S_V^\alpha - \sum_{i=1}^N \lambda_i \rho_i^\alpha - \left(E_V^\beta - \lambda S_V^\beta - \sum_{i=1}^N \lambda_i \rho_i^\beta \right) + \left(E^\Sigma - \lambda \hat{S} - \sum_{i=1}^N \lambda_i \hat{n}_i \right) 2H = 0$$

from our earlier calculation,

using in the above, $\lambda = T, \lambda_i = \mu_i$

$$E_V^\alpha - TS_V^\alpha - \sum_{i=1}^N \mu_i \rho_i^\alpha - \left(E_V^\beta - TS_V^\beta - \sum_{i=1}^N \mu_i \rho_i^\beta \right) + \left(E^\Sigma - T\hat{S} - \sum_{i=1}^N \mu_i \hat{n}_i \right) 2H = 0$$

$$E_V^{\alpha} - TS_V^{\alpha} - \sum_{i=1}^{N} \mu_i \rho_i^{\alpha} - \left(E_V^{\beta} - TS_V^{\beta} - \sum_{i=1}^{N} \mu_i \rho_i^{\beta} \right) + \left(E^{\Sigma} - T\hat{S} - \sum_{i=1}^{N} \mu_i \hat{n}_i \right) 2H = 0$$

Remember the definitions of energy functions:

$$F = E - TS$$

$$H = E + PV$$

$$G = E - TS + PV$$

It is clear that none of these energies are given in the above.
The energies are Grand Canonical Free energies,

$$\Omega = E - TS - \sum_{i=1}^{N} n_i \mu_i$$

So,

$$\Omega_V^{\alpha} - \Omega_v^{\beta} = -2\Omega^{\Sigma} H$$

$$\Omega_V^{\alpha} - \Omega_V^{\beta} = -2\Omega^{\Sigma} H$$

In most other texts and papers,

$$\Omega^{\Sigma} = \gamma$$

So the interfacial energy is the Grand Canonical free energy of the surface:

$$\Omega_V^{\alpha} - \Omega_V^{\beta} = -2\gamma H$$

This is the equilibrium condition at a curved interface.

From before we have the force balance for a cylindrical particle,

$$T_{rr}^{\alpha}(R) - T_{rr}^{\beta}(R) = -\frac{f}{R}$$

Or for a generally curved interface with an isotropic surface stress,

$$T_{ij}^{\alpha} n_j - T_{ij}^{\beta} n_j = -2fHn_j$$

Where n_j is the normal to the interface.

So we have for chemical equilibrium,

$$\Omega_V^{\alpha} - \Omega_V^{\beta} = -2\gamma H$$

For mechanical equilibrium,

$$T_{ij}^{\alpha} n_j - T_{ij}^{\beta} n_j = -2 f H n_j$$

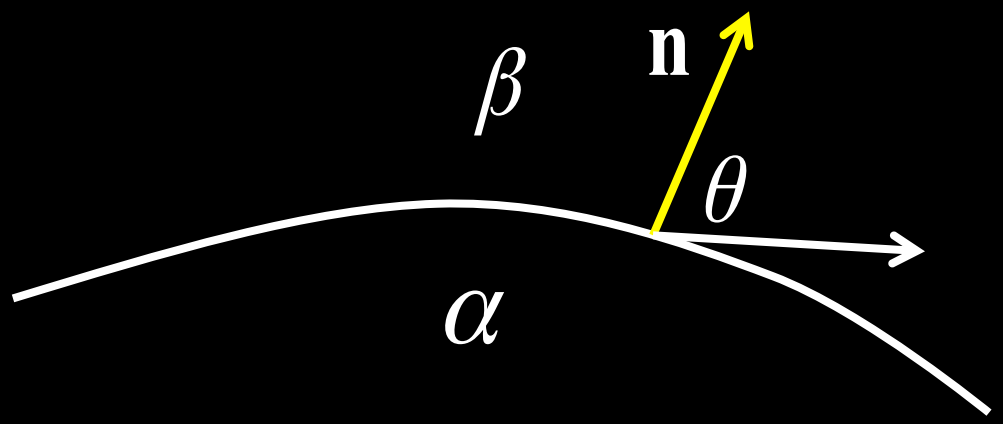
So the surface stress appears in the force balance but the surface energy appears in the chemical equilibrium condition.

The surface energy must be positive but the surface stress can be of either sign.

Surface energies of solids can also be anisotropic. In two dimensions this implies that the chemical equilibrium condition becomes.

$$\Omega_V^{\alpha} - \Omega_V^{\beta} = -2\left(\gamma + \frac{\partial^2 \gamma}{\partial \theta^2}\right) H$$

Where

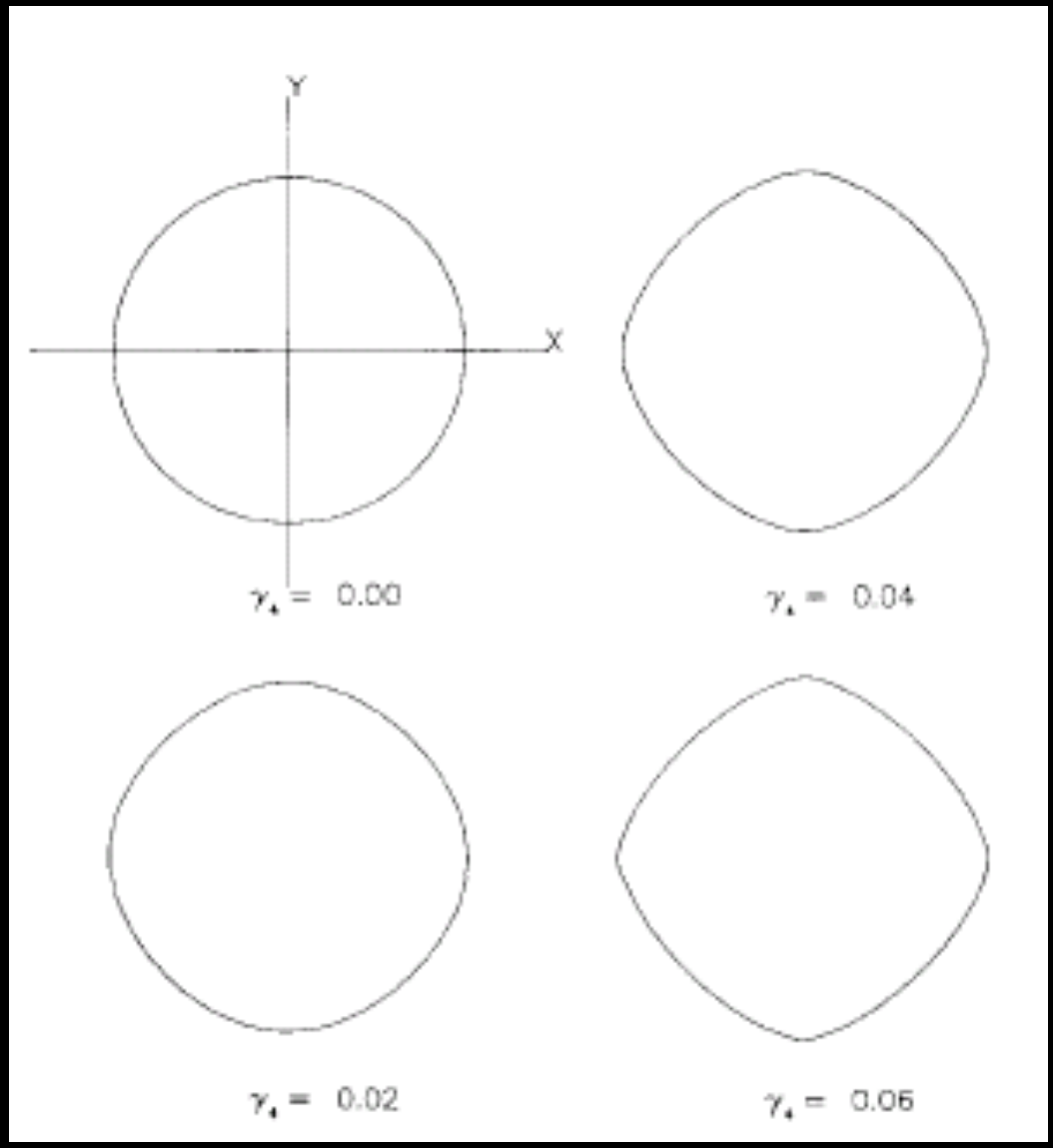


$$\Omega_V^{\alpha} - \Omega_V^{\beta} = -2\left(\gamma + \frac{\partial^2 \gamma}{\partial \theta^2}\right) H$$

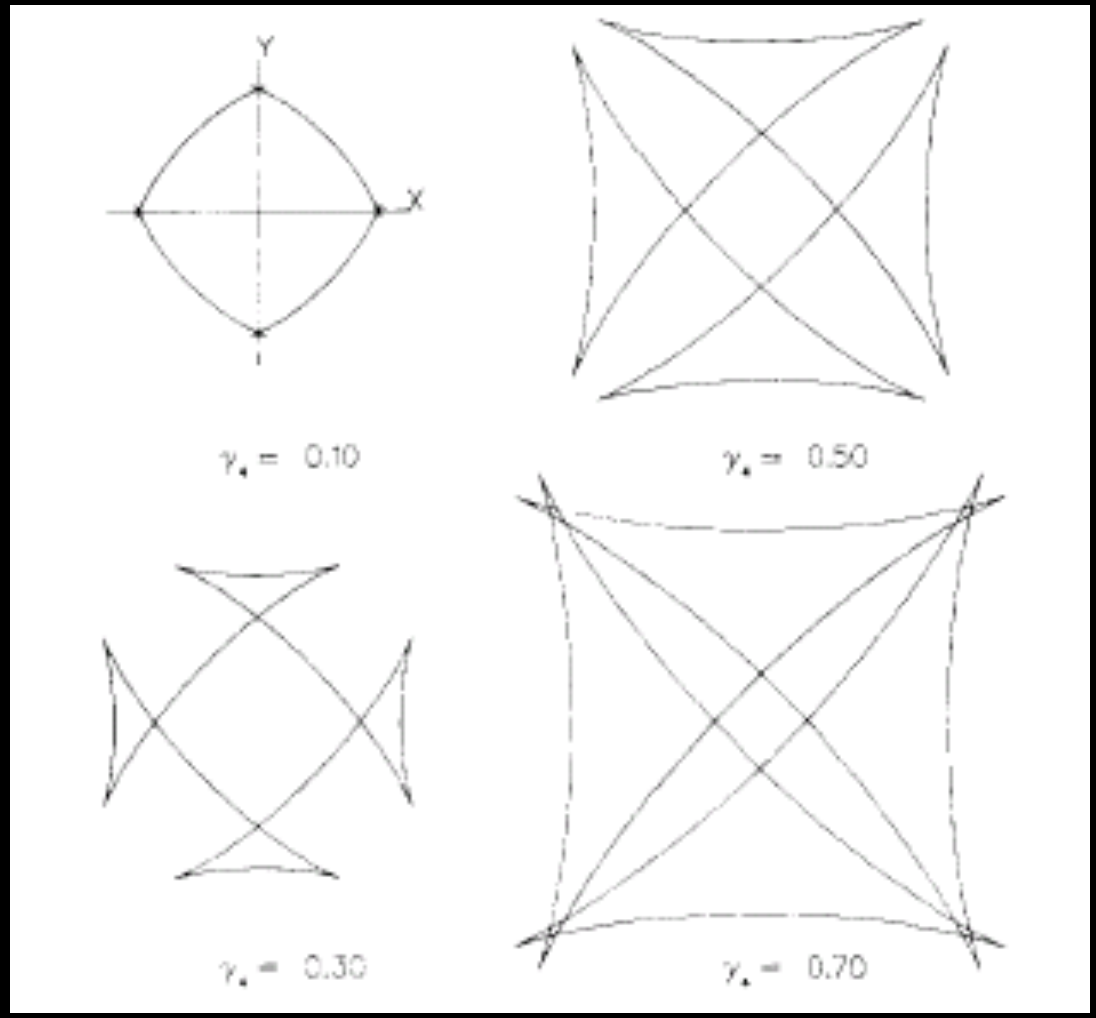
If the jump is constant we have equilibrium. This gives an equation for the equilibrium shape of a particle

If the surface energy is isotropic then the equilibrium shape is given by the condition that H = constant

If the surface energy is anisotropic then this is not the case and the shapes will be noncircular



$$\gamma = \gamma_o + \gamma_4 \cos(4\theta)$$



$$\gamma = \gamma_o + \gamma_4 \cos(4\theta)$$

$$\Omega_V^{\alpha} - \Omega_V^{\beta} = -2\left(\gamma_o - 15\gamma_4 \cos(4\theta)\right) H$$

For a hydrostatically stressed fluid under pressure, P

$$E = TS - PV + \sum_{i=1}^{N} \mu_i n_i$$

Thus,

$$E_v = TS_v - P + \sum_{i=1}^{N} \mu_i \rho_i$$

Or,

$$E_V - TS_V - \sum_{i=1}^{N} \mu_i \rho_i = -P$$

$$\Omega_V = -P$$

And thus for a hydrostatically stressed fluid,

$$\Omega_V^{\alpha} - \Omega_V^{\beta} = -2\gamma H$$

becomes

$$P^{\beta} - P^{\alpha} = -2\gamma H$$

As we saw before, for a spherical (instead of cylindrical) fluid under hydrostatic pressure

$$T_{ij} n_j = T_{rr} = -P$$

Thus,

$$T_{ij}^{\alpha} n_j - T_{ij}^{\beta} n_j = -2 f H n_j$$

Becomes,

$$P^{\beta} - P^{\alpha} = -2 f H$$

The force balance is,

$$P^{\alpha} - P^{\beta} = 2fH$$

The chemical equilibrium condition is,

$$P^{\alpha} - P^{\beta} = -2\gamma H$$

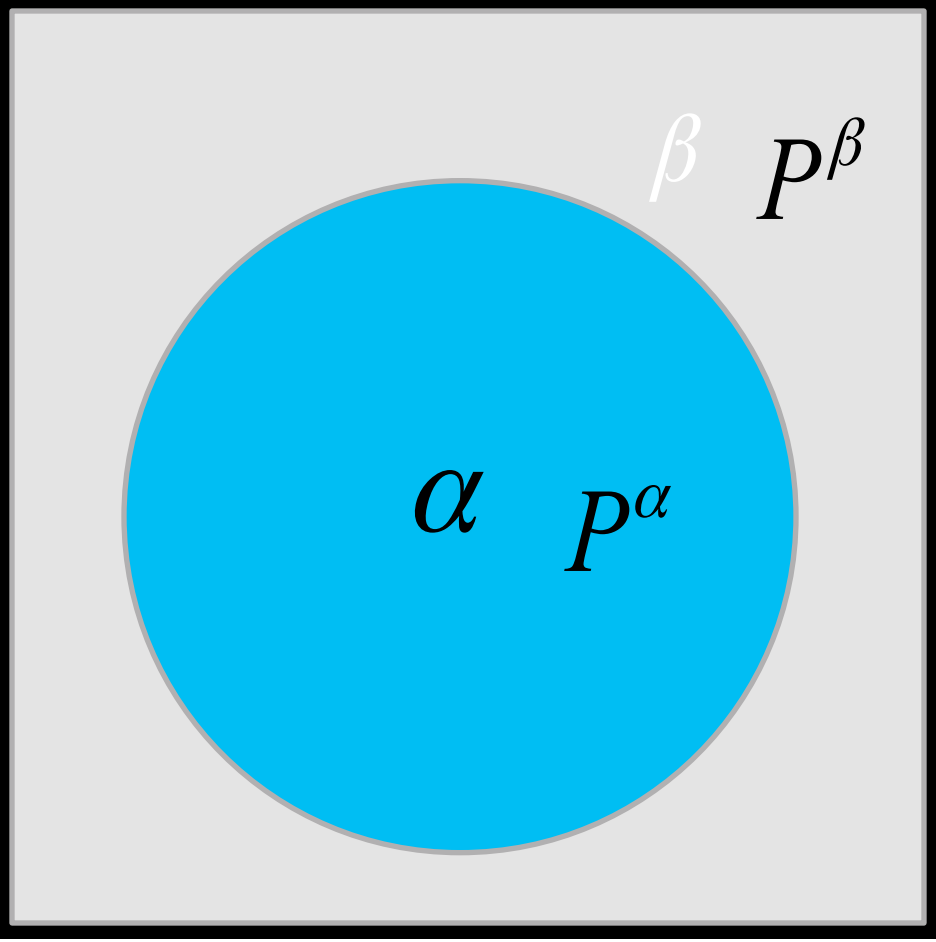
And thus for a fluid,

$$\gamma = f$$

And the pressure inside a droplet of α is greater than the matrix β. Hence the confusion of surface stress and surface energy. In a solid this is not necessarily true.

Applications: Equilibrium Concentration at a Curved Interface

- Assume a binary, isothermal solid under hydrostatic pressure, $f = \gamma$



Equilibrium:

$$\mu_1^{\alpha}(C^{\alpha}(R), P^{\alpha}) = \mu_1^{\beta}(C^{\beta}(R), P^{\beta})$$

$$\mu_2^{\alpha}(C^{\alpha}(R), P^{\alpha}) = \mu_2^{\beta}(C^{\beta}(R), P^{\beta})$$

where C is the mole fraction of component 1

$$P^{\beta} - P^{\alpha} = -2\gamma H$$

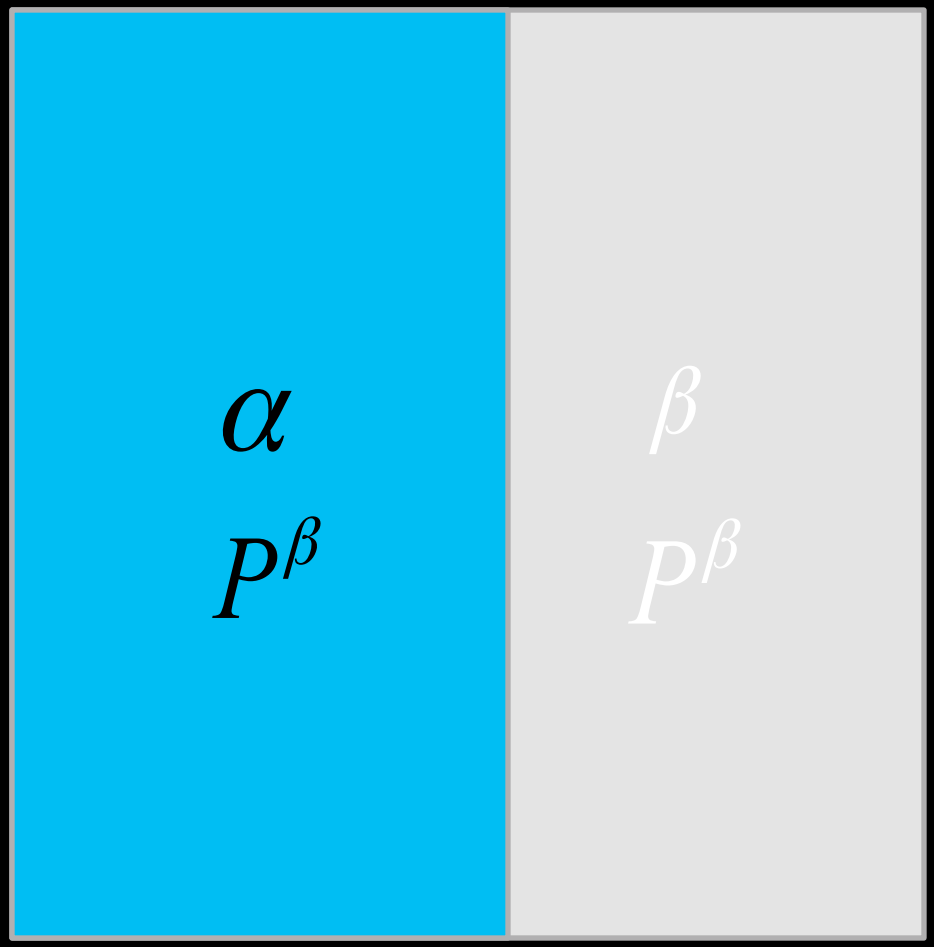
or

$$P^{\alpha} - P^{\beta} = 2\gamma / R$$

$$\mu_1^{\alpha}(C^{\alpha}(R), P^{\alpha}) = \mu_1^{\beta}(C^{\beta}(R), P^{\beta})$$
$$\mu_2^{\alpha}(C^{\alpha}(R), P^{\alpha}) = \mu_2^{\beta}(C^{\beta}(R), P^{\beta})$$

- These are two equations for the two unknown concentrations.
- The chemical potentials can be a nonlinear function of the composition
- Thus analytical solutions for any composition are not possible
- However, we can determine the shift in the composition from those given by the equilibrium phase diagram by assuming small changes in composition from those given by the phase diagram.

The phase diagram compositions are given by those when the two phases are in equilibrium at a flat interface,



Equilibrium:

$$\mu_1^{\alpha}(C_e^{\alpha}, P^{\beta}) = \mu_1^{\beta}(C_e^{\beta}, P^{\beta})$$

$$\mu_2^{\alpha}(C_e^{\alpha}, P^{\beta}) = \mu_2^{\beta}(C_e^{\beta}, P^{\beta})$$

$$P^{\alpha} = P^{\beta}$$

Thus they must be at the same pressure and the matrix, β is under the same hydrostatic pressure as in the system with the particle

- Employ Taylor's expansions for the compositions about the equilibrium state:

$$\mu_1(C,P) = \mu_1(C_e,P_o) + \left(\frac{\partial \mu_1}{\partial C}\right)_{C_e,P_o}(C - C_e) + \left(\frac{\partial \mu_1}{\partial P}\right)_{C_e,P_o}(P - P_o)$$

- We know that

$$\left(\frac{\partial \mu_1}{\partial C}\right)_{C_e,P_o} = (1 - C_e)\left(\frac{\partial^2 G_m}{\partial C^2}\right)_{C_e,P_o}$$

$$\left(\frac{\partial \mu_1}{\partial P}\right)_{C_e,P_o} = \bar{V}_1(C_e,P_o)$$

- Similarly for component 2

- Using the equilibrium conditions,

$$\mu_1^{\alpha}(C^{\alpha}(R), P^{\alpha}) = \mu_1^{\beta}(C^{\beta}(R), P^{\beta})$$

$$\mu_2^{\alpha}(C^{\alpha}(R), P^{\alpha}) = \mu_2^{\beta}(C^{\beta}(R), P^{\beta})$$

$$P^{\alpha} - P^{\beta} = 2\gamma / R$$

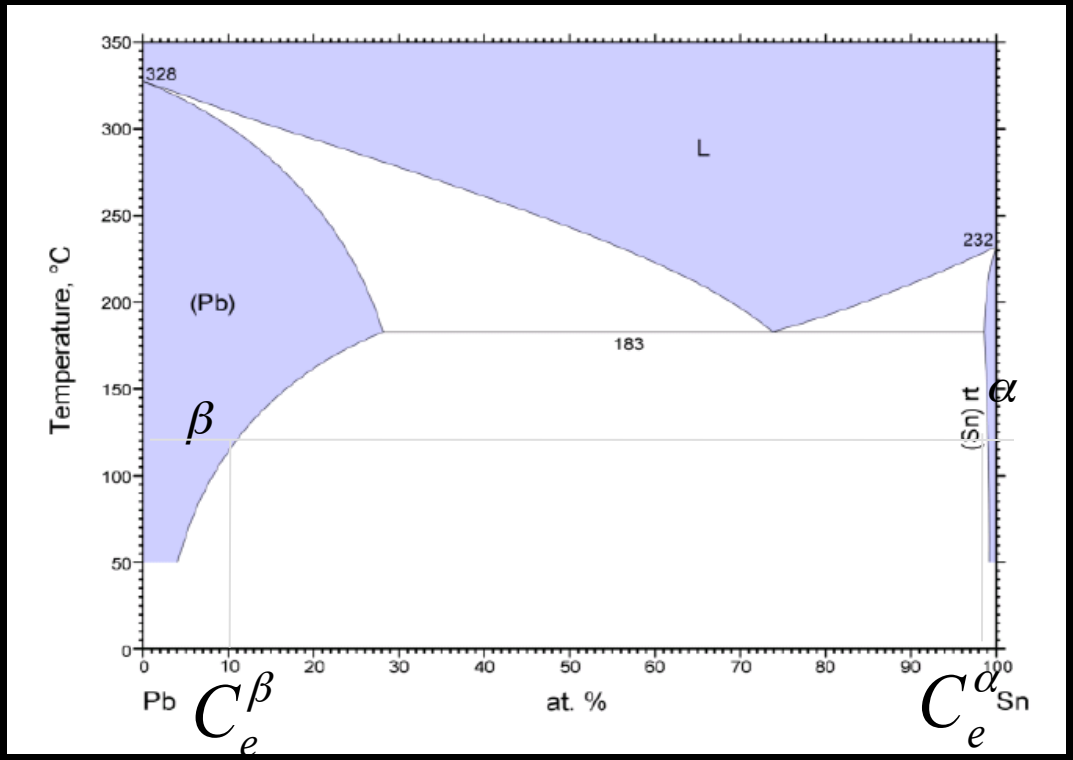
along with the conditions at a planar interface,

$$C^{\alpha}(R) = C_e^{\alpha} + \frac{2V_m^{\alpha}(C_e^{\beta})\gamma}{\left(C_e^{\alpha} - C_e^{\beta}\right)G_m^{''\alpha} R}$$

$$G_m^{''} = \left(\frac{\partial^2 G_m}{\partial C^2}\right)_{C_e, P_o}$$

$$C^{\beta}(R) = C_e^{\beta} + \frac{2V_m^{\alpha}(C_e^{\alpha})\gamma}{\left(C_e^{\alpha} - C_e^{\beta}\right)G_m^{''\beta} R}$$

- For a simple eutectic phase diagram



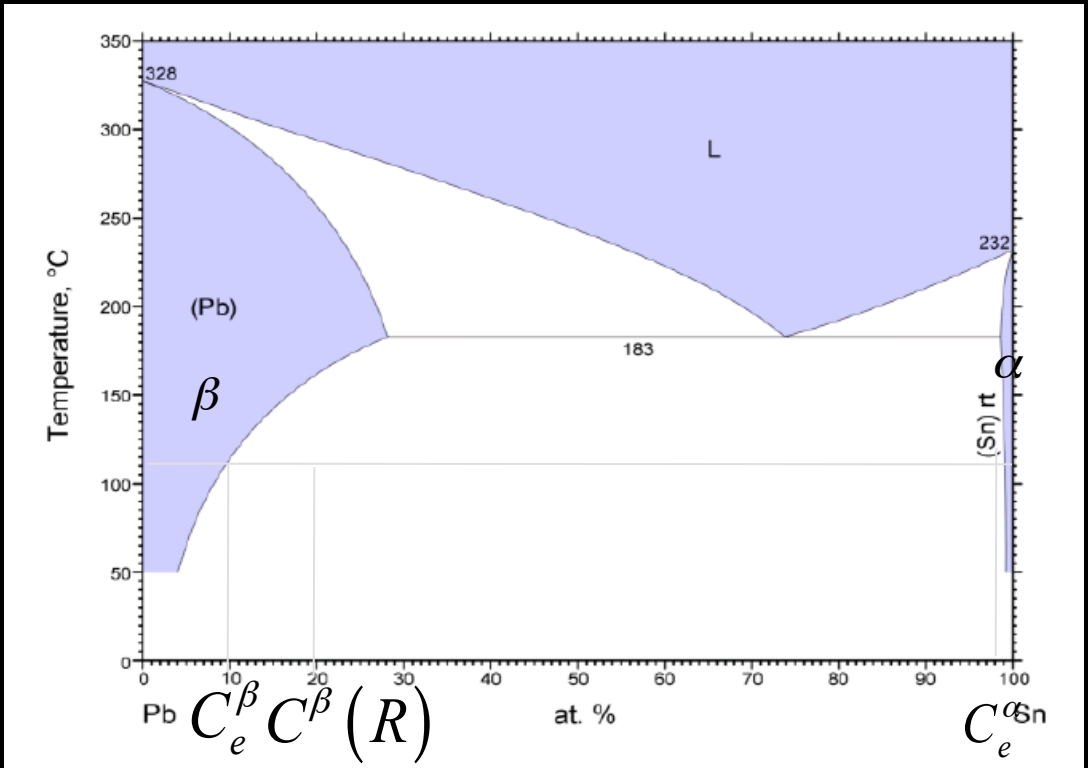
- Consider the case of spherical Sn-rich α particles in a Pb-rich β matrix.

$$C_e^{\alpha} > C_e^{\beta}$$

$$G_m^{\alpha''} > 0 \quad \text{(since the phase is thermodynamically stable)}$$

$$G_m^{\beta''} > 0 \quad \text{(since the phase is thermodynamically stable)}$$

- For a simple eutectic phase diagram



$$C^\alpha(R) = C_e^\alpha + \frac{2V_m^\alpha(C_e^\beta)\gamma}{\left(C_e^\alpha - C_e^\beta\right)G_m^{''\alpha}R}$$

$$C^\beta(R) = C_e^\beta + \frac{2V_m^\alpha(C_e^\alpha)\gamma}{\left(C_e^\alpha - C_e^\beta\right)G_m^{''\beta}R}$$

- Thus $C^\alpha(R) > C_e^\alpha$

  $C^\beta(R) > C_e^\beta$

- The particle is *purer: nanoscale objects in many cases are purer than their bulk counterparts*

- Where can we get the second derivatives of the free energy?
- Use the evaluated phase diagram that gives $G_m(C)$
- Approximations to give an estimate of the composition shift. For an ideal solution:

$$G_m'' = \frac{R_g T}{C_e(1 - C_e)}$$

and thus,

$$C^{\alpha}(R) = C_e^{\alpha} + \frac{2C_e^{\alpha}(1 - C_e^{\alpha})V_m^{\alpha}\gamma}{\left(C_e^{\alpha} - C_e^{\beta}\right)R_g TR}$$

$$C^{\beta}(R) = C_e^{\beta} + \frac{2C_e^{\beta}(1 - C_e^{\beta})V_m^{\alpha}\gamma}{\left(C_e^{\alpha} - C_e^{\beta}\right)R_g TR}$$

- In many cases,

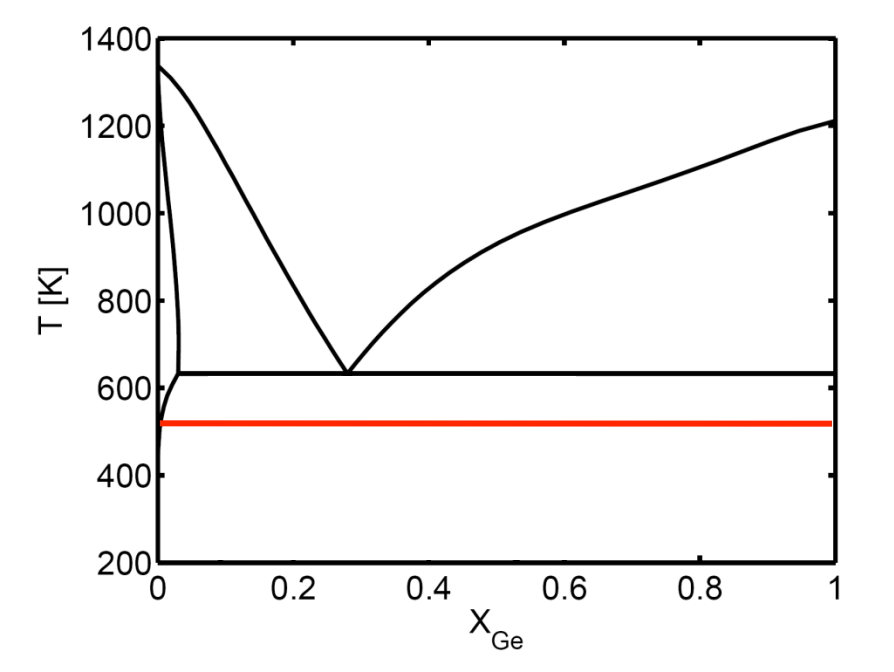
$$\frac{2C_e^{\alpha}(1-C_e^{\alpha})V_m^{\alpha}\gamma}{\left(C_e^{\alpha}-C_e^{\beta}\right)R_gT} \approx 0.1nm \text{ to } 1nm$$

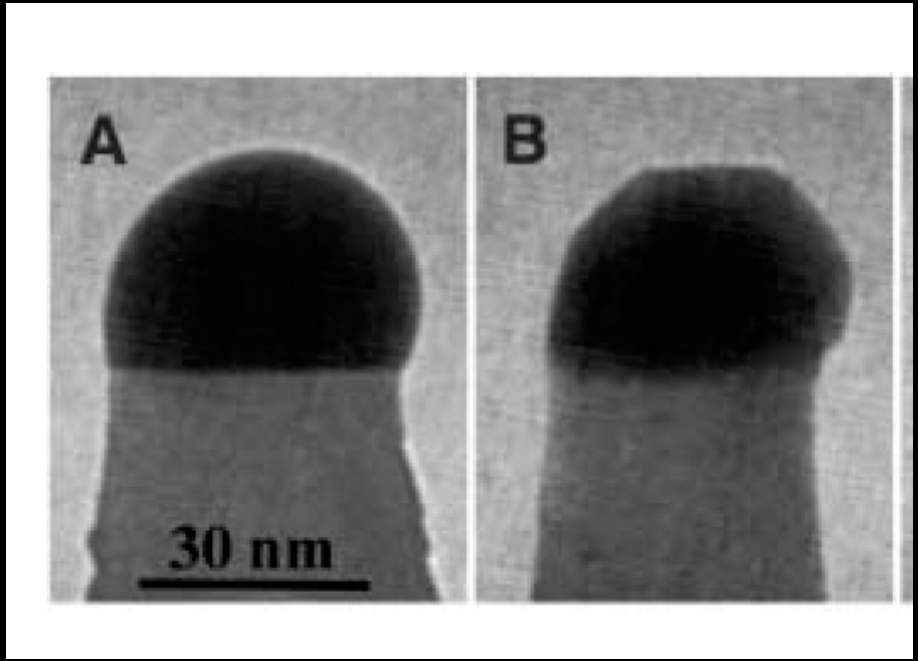
so,

$$C^{\alpha}(R) \approx C_e^{\alpha} + \frac{0.1nm}{R} \text{ to } \frac{1nm}{R}$$

Thus the changes are small except for nanoscale objects

Growth Below the Eutectic Temperature?



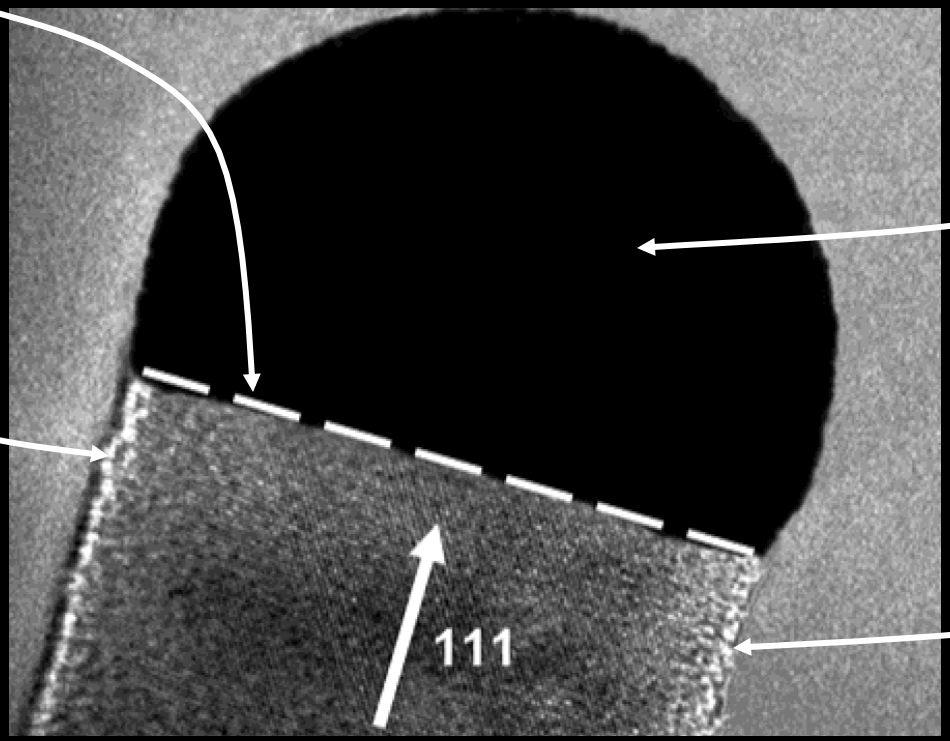


608K 528K

Kodambaka, Tersoff, Reuter and Ross, Science, Sept 2007

(See also Adhikari, Marshall, Goldthorpe, Chidsey & McIntyre. *ACS Nano.* **2007**, *1*, 415.)

A Phase Diagram for Nanowires



Equilibrium Conditions

At the solid-liquid interface:

$$\rho_s \mu_i^s (c_i, 0) + W_e + c_i \eta \mathrm{Tr}\mathbf{T} + P_l + \frac{2\gamma_{sv}}{R_w} = \rho_s \mu_i^l (c_i, P_l)$$

for both components

Equilibrium Conditions

$$\rho_s \mu_i^s (c_i, 0) + W_e + c_i \eta \mathrm{Tr}\mathbf{T} + P_l + \frac{2\gamma_{sv}}{R_w} = \rho_s \mu_i^l (c_i, P_l)$$

Chemical potentials in the absence of stress

Equilibrium Conditions

$$\rho_s \mu_i^s (c_i, 0) + W_e + c_i \eta \mathrm{Tr}\mathbf{T} + P_l + \frac{2\gamma_{sv}}{R_w} = \rho_s \mu_i^l (c_i, P_l)$$

Elastic stress

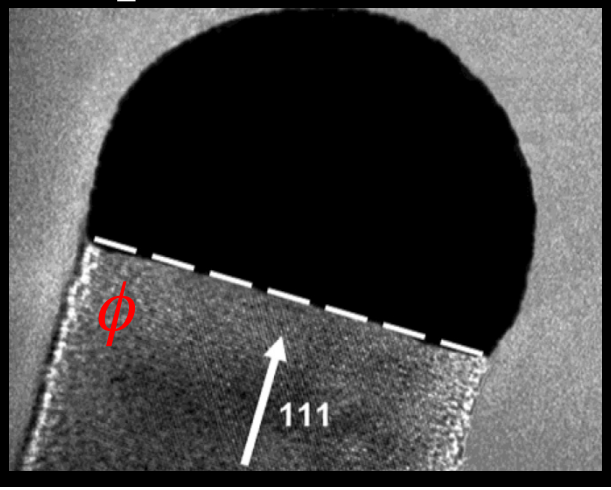
Equilibrium Conditions

$$\rho_s \mu_i^s (c_i, 0) + W_e + c_i \eta \mathrm{Tr}\mathbf{T} + P_l + \frac{2\gamma_{sv}}{R_w} = \rho_s \mu_i^l (c_i, P_l)$$

Due to the presence of a faceted solid liquid interface

$$\mu_i = \mu_i^o + \frac{V_m}{A_{facet}} \int \left[\gamma_{sv} \csc\phi - \gamma_{sl} \cot\phi \right] ds$$

(Herring, Phys. Powder Metall.)



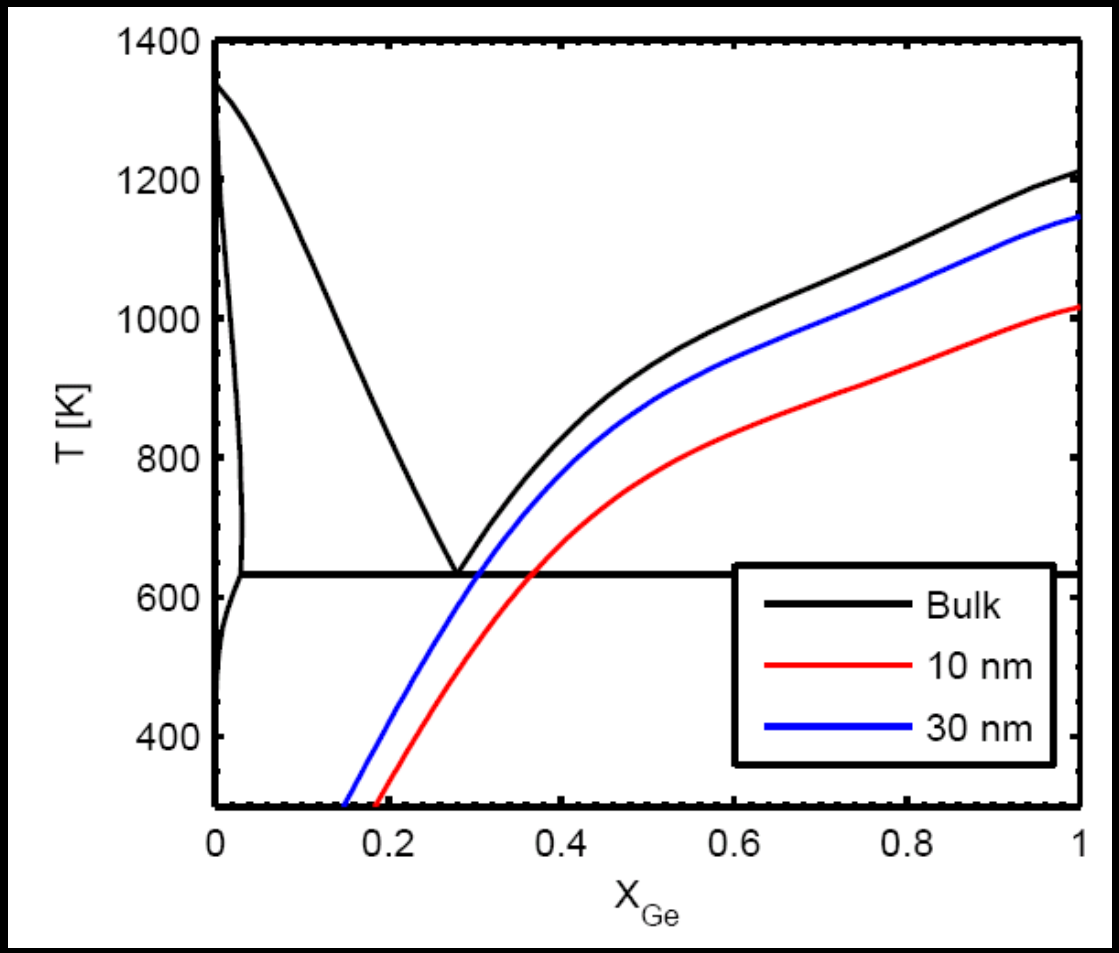
Analytical Solution

Assume a dilute solution of Au in the wire and wire diameter greater than 10nm,

$$x_A^l = \hat{x}_A^l + \frac{2\gamma_{sv}\hat{V}_m^s}{R^w \Delta\hat{x}_A \hat{G}_l''}\left[1+\xi\frac{\gamma_{lv}}{\gamma_{sv}}\left(1-\frac{\hat{V}_m^l\left(\hat{x}_A^s\right)}{\hat{V}_m^s}\right)\right]$$

$$x_A^s = \hat{x}_A^s + \frac{2\gamma_{sv}\hat{V}_m^s}{R^w \Delta\hat{x}_A \hat{G}_s''}\left[1+\xi\frac{\gamma_{lv}}{\gamma_{sv}}\left(1-\frac{\hat{V}_m^l}{\hat{V}_m^s}\right)-\frac{\Delta\bar{V}^s\,\Delta\hat{x}_A}{3\hat{V}_m^s\gamma_{sv}}\left(\xi\gamma_{lv}+2f_{sv}\right)\right]$$

Au-Ge Phase Equilibrium



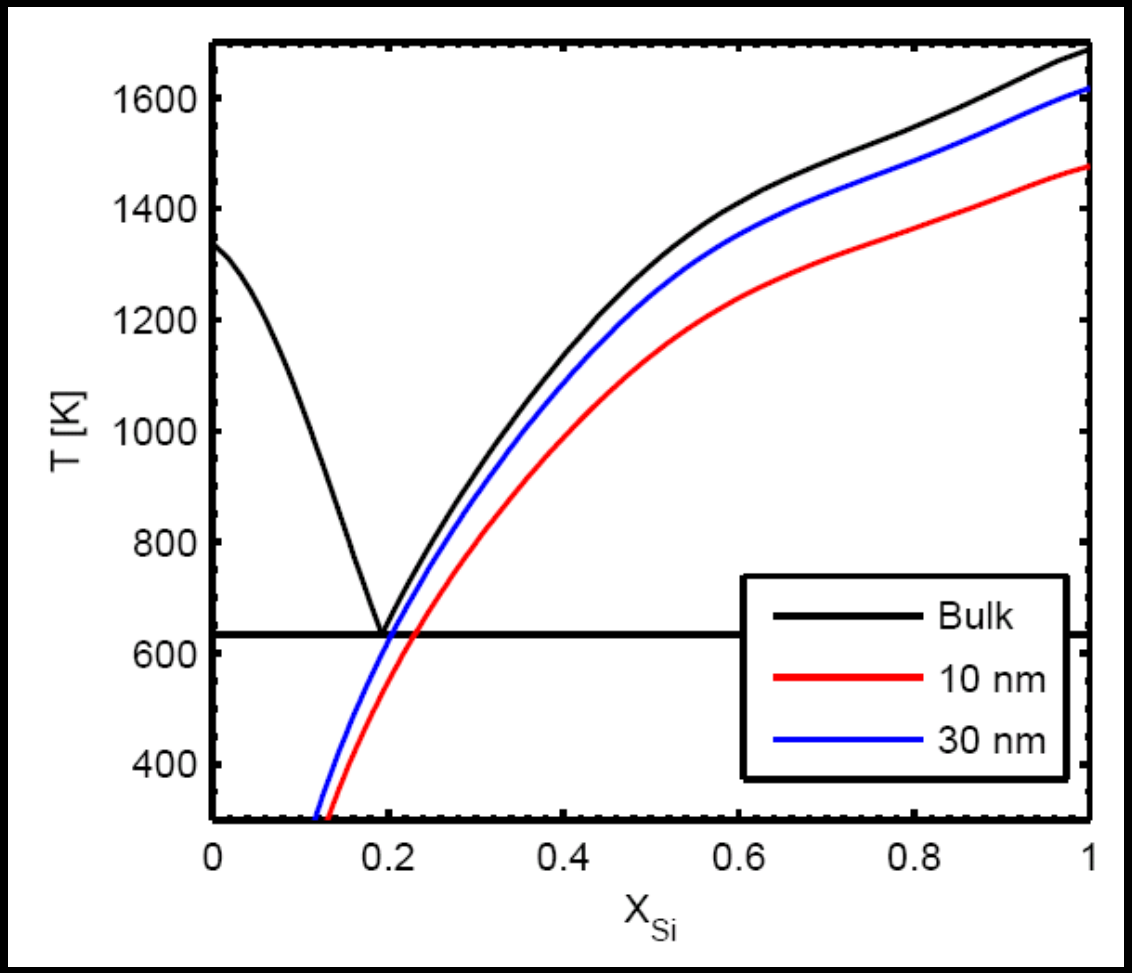
Bulk

30 nm diameter wire

10 nm diameter wire

- Modest shift for 30 nm diameter
- Significant shifts for wires less than 10 nm in diameter

Au-Si Phase Equilibrium



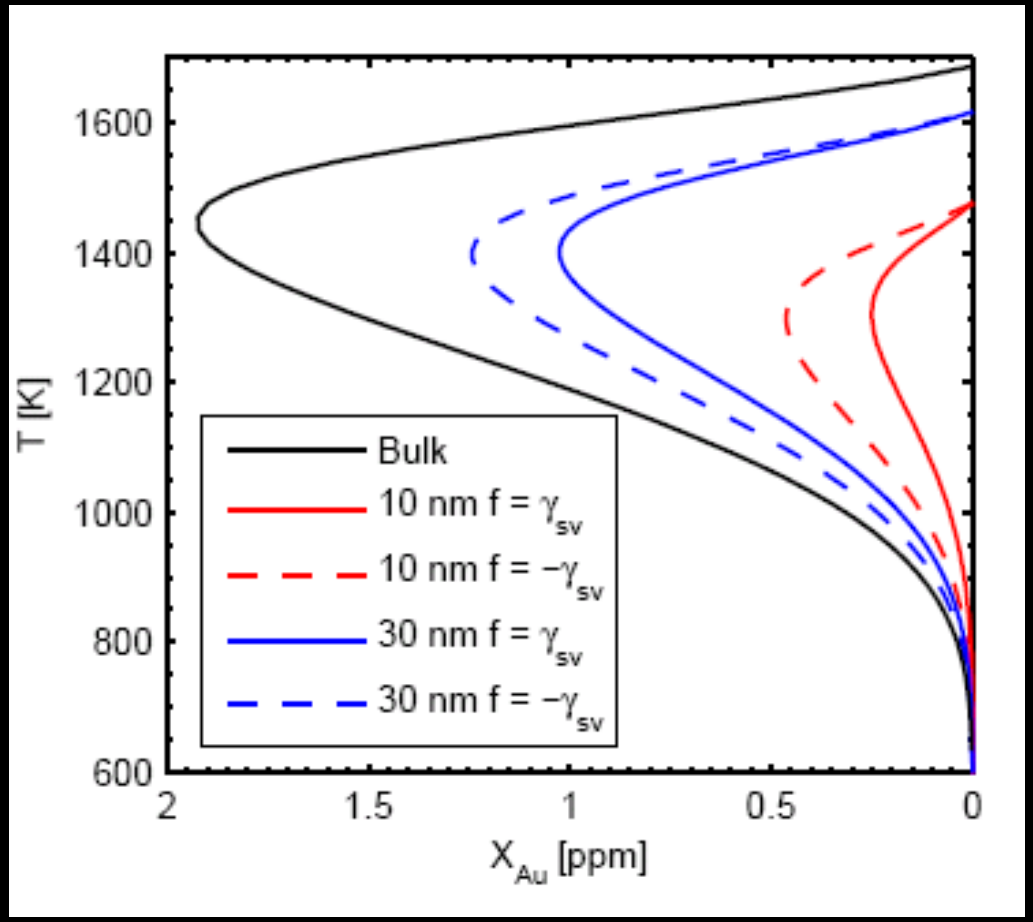
Bulk

30 nm diameter wire

10 nm diameter wire

- Smaller shifts in phase boundaries than in Ge-Au

Au-Si Solidus



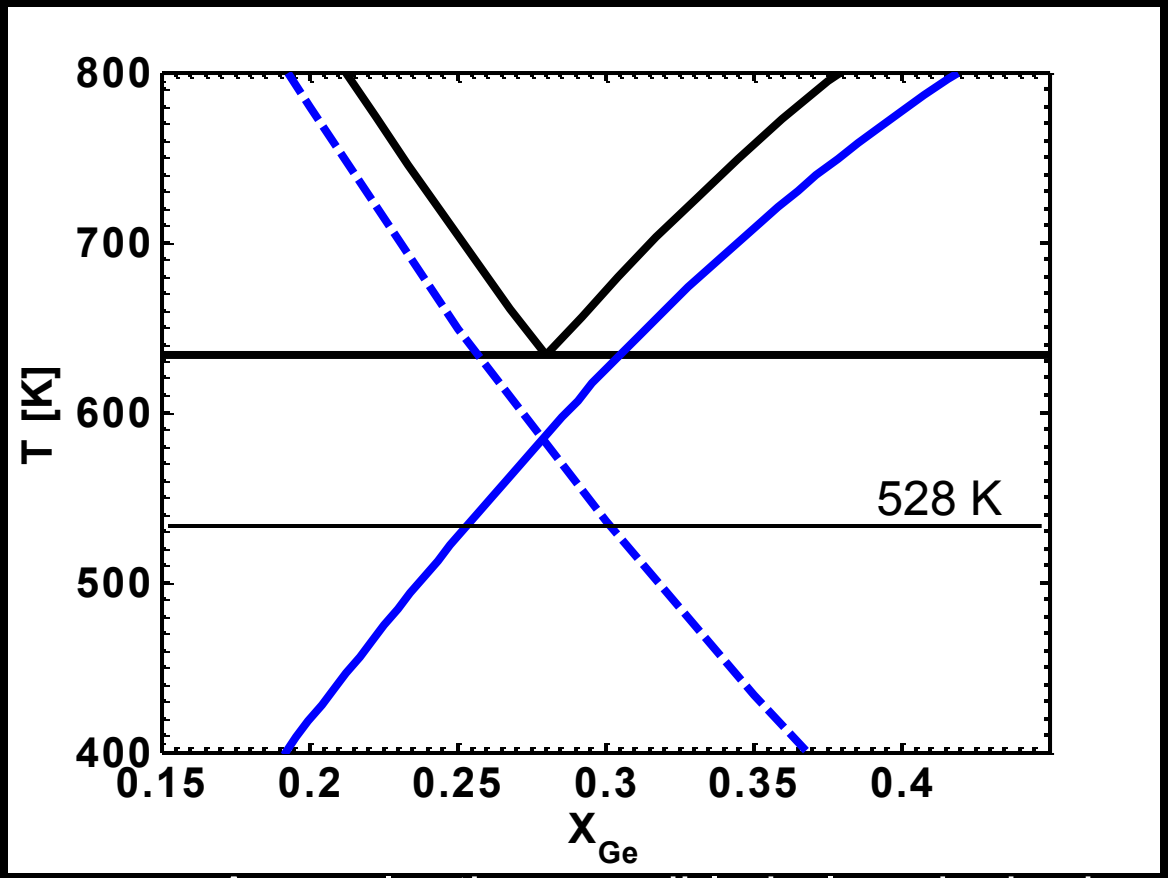
Bulk

30 nm diameter wire

10 nm diameter wire

- Thermodynamic data on solid solution of Au in Si
- Solid becomes more pure with decreasing radius

T^* on the Phase Diagram



Bulk
30 nm liquidus
30 nm T* vs. Alloy comp.
10 nm liquidus
10 nm T* vs. Alloy comp.

- Au nucleation possible below dashed curves
- Not a phase boundary

Kodambaka, Tersoff, Reuter & Ross. Science. **2007**, 316, 729.