

Surface Effects on the Nanomechanics  
of Thin Films and Nanomaterials

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## Motivation

Principal microstructural characteristic of thin films and nanostructured materials: high density of interfaces.

Example of interface parameters that affect mechanical behavior:

- surface energy
- stacking fault energy
- grain boundary energy

Important to understand physical meaning of these surface thermodynamic quantities and how they relate to mechanics of materials

Bulk Thermodynamics:  $dU = TdS - PdV + \sum_i \mu_i dn_i$

Gibbs equilibrium condition: Virtual variation  $dU = 0$  for  $dS = 0$ ,  $dV = 0$ ,  $dn_i = 0$ .

Consider composite system composed of bulk phases  $\alpha$ ,  $\beta$ :

$$dU = dU^\alpha + dU^\beta = T^\alpha dS^\alpha + T^\beta dS^\beta - P^\alpha dV^\alpha - P^\beta dV^\beta + \sum_i (\mu_i^\alpha dn_i^\alpha + \mu_i^\beta dn_i^\beta)$$

Variational constraints:

$$dS = dS^\alpha + dS^\beta = 0; \quad dV = dV^\alpha + dV^\beta = 0; \quad dn_i = dn_i^\alpha + dn_i^\beta = 0$$

can be conducted independently.

$\Rightarrow \therefore dU = 0$  for arbitrary variations when:

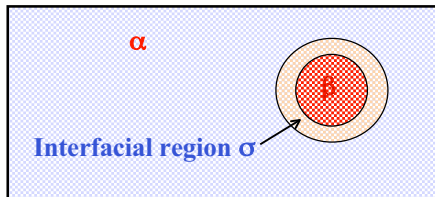
- $T^\alpha dS^\alpha + T^\beta dS^\beta = 0$  and  $dS^\alpha + dS^\beta = 0 \Rightarrow T^\alpha = T^\beta$
- $-P^\alpha dV^\alpha - P^\beta dV^\beta = 0$  and  $dV^\alpha + dV^\beta = 0 \Rightarrow P^\alpha = P^\beta$
- $\mu_i^\alpha dn_i^\alpha + \mu_i^\beta dn_i^\beta = 0$  and  $dn_i^\alpha + dn_i^\beta = 0 \Rightarrow \mu_i^\alpha = \mu_i^\beta$

## Thermodynamics of Systems With Interfaces

Consider multicomponent fluid system composed of spherical phase  $\beta$  in much larger phase  $\alpha$ .

J.W. Gibbs formulated two approaches to incorporate effects of interface:

First approach: Treat interfacial region as “third phase”



Choose boundaries such that:

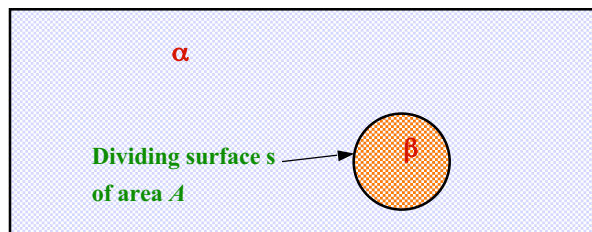
- $\alpha, \beta$  uniform up to boundaries
- Between boundaries is nonuniform interfacial region  $\sigma$

For completely fluid system at equilibrium, Gibbs showed that:

- $T^\alpha = T^\beta = T^\sigma$
- $\mu_i^\alpha = \mu_i^\beta = \mu_i^\sigma$

Cannot say anything about relation among  $P^\alpha, P^\beta, P^\sigma$

Second approach: Treat interface as two-dimensional “dividing surface.”



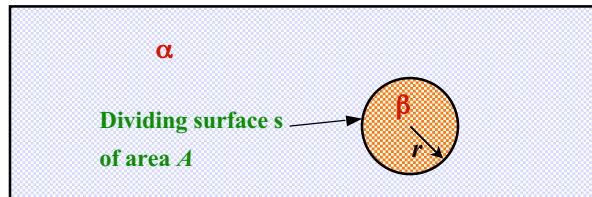
Completely fluid system

- Define “surface” amount of extensive quantity by:

$$U^s \equiv U - U^\alpha - U^\beta,$$

where  $U$  is actual internal energy of system;  $U^\alpha, U^\beta$ , evaluated taking  $\alpha, \beta$  phases as if uniform (ignore variation near surface).

- Include contributions from surface terms  $T^s dS^s$  and  $\mu_i^s dn_i^s$  in expression for  $dU$ .
- Note: “surface” volume  $V^s = 0 \Rightarrow$  no “ $-PdV$ ” term for surface  $\Rightarrow$  instead include surface work term to vary surface area  $A$ .



Completely fluid system

Can vary area keeping excess surface concentration fixed in two ways:

1. Vary area keeping number of moles of components at surface fixed (elastically strain surface):

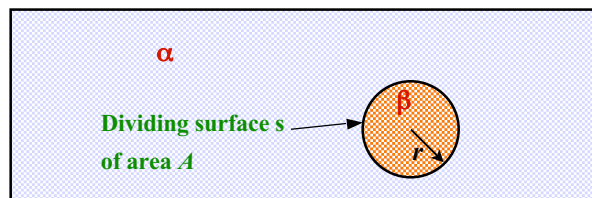
surface work  $dw^s \equiv f dA$ , where  $f \equiv$  "surface stress"

Consider this type of area variation  $\Rightarrow$  need to vary volume of bulk phases:

$$dV^\beta = -dV^\alpha = (r/2) dA$$

$\Rightarrow$  Equilibrium condition:  $dU = -P^\alpha dV^\alpha - P^\beta dV^\beta + f dA = -(P^\beta - P^\alpha) dV^\beta + f dA = 0$

$\Rightarrow$  "Laplace pressure"  $P^\beta - P^\alpha = 2f/r$



Completely fluid system

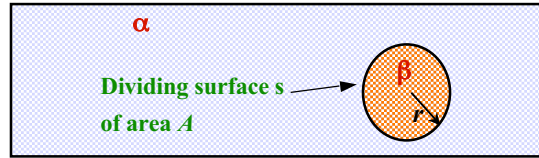
2. Vary area by creating new surface (add atoms or molecules to surface)

Surface work  $dw^s \equiv \gamma dA + \sum \mu_i^s dn_i^s$ , where  $\gamma \equiv$  "surface energy"

Gibbs showed for completely fluid system:

$$\mu_i^\alpha = \mu_i^\beta = \mu_i^s \Rightarrow f = \gamma \Rightarrow P^\beta - P^\alpha = 2\gamma/r$$

Consider new system: Single component crystal sphere  $\beta$  in large multicomponent fluid  $\alpha$



- Let solid be composed of component 1 with atomic volume  $\Omega$ .
- Fluid, surface contain components 1, 2, 3 ...
- Locate dividing surface so that number of moles of component 1 at surface is fixed  $n_1^s = 0$ .

Gibbs showed that at equilibrium:

$$T^\alpha = T^\beta = T^s$$

$$P^\beta - P^\alpha = 2f/r; f \neq \gamma \text{ in general}$$

$$\mu_1^\beta - \mu_1^\alpha = 2(f - \gamma)\Omega/r \neq 0 \text{ in general}$$

Difficulties in trying to generalize to multicomponent solid with nonplanar interface.

Relationship between  $f$  and  $\gamma$  for single component solid:

- Reversible work to *create* new surface area  $dw \equiv \gamma dA \Rightarrow w = \gamma A$ .
- Reversible work to *stretch* pre-existing area  $\equiv f dA = d(\gamma A) = A d\gamma + \gamma dA$
- Surface strain  $d\varepsilon^s = dA/A \Rightarrow \boxed{f = \gamma + \partial\gamma/\partial\varepsilon^s}$  “Shuttleworth-Herring equation”

Generalize for anisotropic surface:  $f_{ij} = \gamma \delta_{ij} + \partial\gamma/\partial\varepsilon_{ij}^s$

Lagrangian coordinates:  $f'_{ij} = \partial\gamma'/\partial\varepsilon_{ij}^s$

### Summary of equilibrium conditions:

#### Bulk composite $\alpha/\beta$ systems (no surface effects)

Equilibrium conditions:  $T^\alpha = T^\beta$   
 $\mu_i^\alpha = \mu_i^\beta$   
 $P^\alpha = P^\beta$

#### Small fluid phase $\beta$ in large fluid phase $\alpha$

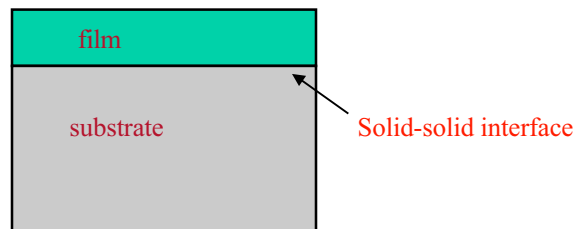
Equilibrium conditions:  $T^\alpha = T^\beta$   
 $\mu_i^\alpha = \mu_i^\beta$   
 $P^\alpha + 2f/r = P^\beta$   
 $f = \gamma$

#### Small single component solid phase $\beta$ in large fluid phase $\alpha$

Equilibrium conditions:  $T^\alpha = T^\beta$   
 $\mu_l^\alpha + 2(f - \gamma)\Omega/r = \mu_l^\beta$   
 $P^\alpha + 2f/r = P^\beta$   
 $f = \gamma + \partial\gamma/\partial\varepsilon$

### Solid-Solid Interface (planar)

Consider solid thin film (single component)-substrate system:



Can identify three surface work terms:

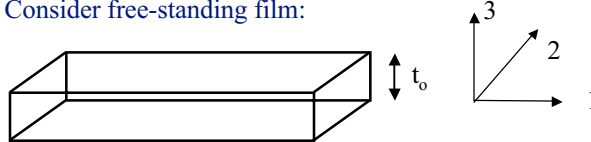
- work to create new surface  $\equiv \Gamma dA$ ;
- surface work to deform film (in-plane) keeping substrate fixed  $\equiv g dA$   
 $\Rightarrow$  associated with changing interface dislocation density.
- surface work to deform film and substrate by same amount (in-plane)  $\equiv h dA$ .

$$\Gamma \equiv \text{“interface energy”} \quad g, h \equiv \text{“interface stress”}$$

## Surface Effects on Mechanical Behavior (isothermal)

### 1. Elastic Behavior and Internal Friction

Consider free-standing film:



Work to elastically strain film and surfaces by amount  $d\varepsilon_{11}$ :

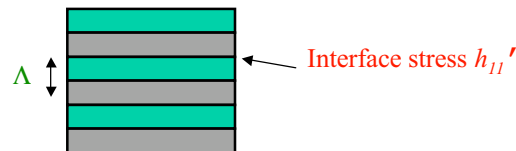
$$dF' = V_o C_{11}' \varepsilon_{11} d\varepsilon_{11} + 2A_o f_{11}' d\varepsilon_{11}; \quad F' = \text{Helmholtz free energy}$$

$$C_{11}' = \text{film elastic constant}$$

Effective elastic constant including surface effects =  $(V_o)^{-1} (\partial^2 F' / \partial \varepsilon_{11}^2) =$

$$C_{11}' + (2/t_o) (\partial f_{11}' / \partial \varepsilon_{11})$$

Similar analysis for multilayered film



Effective in-plane elastic constant =  $C_{11}' + (2/\Lambda) (\partial h_{11}' / \partial \varepsilon_{11})$

Typical values (metals):  $(\partial f_{11}' / \partial \varepsilon_{11}) \sim (\partial h_{11}' / \partial \varepsilon_{11}) \sim \pm 1 \text{ N/m}$  (Streitz, Sieradzki, RCC)

$$C_{11}' \sim 10^{11} \text{ Pa}$$

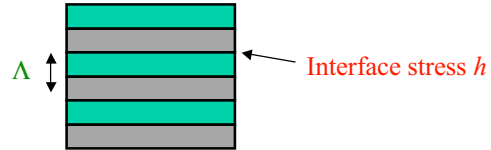
$\Rightarrow$  For  $\Lambda = 2 \text{ nm}$ :  $(2/\Lambda) (\partial h_{11}' / \partial \varepsilon_{11}) \sim \pm 10^{-2} C_{11}'$

Internal friction:

Cu-Ni multilayered films with  $\Lambda$  below 100 nm showed order of magnitude enhancement in internal friction over bulk metals  $\Rightarrow$  attributed to

“imaginary part” of interface contribution elastic constant. (M. Wuttig, RCC)

Multilayered film:



In-plane Laplace pressure for multilayered film =  $2h/\Lambda$

Hooke's law:  $-2h/\Lambda = M\varepsilon$

a. Equilibrium in-plane strain relative to bulk  $\varepsilon = -2h/M\Lambda$

Typical values (metals):  $h \sim \pm 1\text{N/m}$ ;  $M \sim 10^{11}\text{ Pa}$

$\Rightarrow$  For  $\Lambda = 2\text{ nm}$ :  $\varepsilon \sim \pm 1\%$   $\Rightarrow$  can lead to nonlinear elastic effects

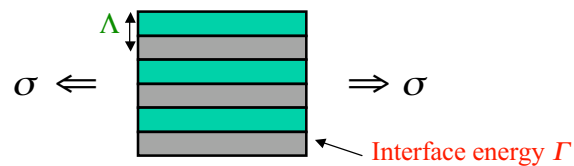
b. Can also use multilayered films to measure  $h$ :

Measure in-plane strain  $\varepsilon$  for given  $\Lambda \Rightarrow h = -M\Lambda/2\varepsilon$ .

For Ag-Ni (111),  $h = -2\text{ N/m}$  (F. Spaepen; J. Bottiger; D. Josell and RCC)

## 2. Creep

Zero creep measurements in multilayered thin films (D. Josell, T.P. Weihs)

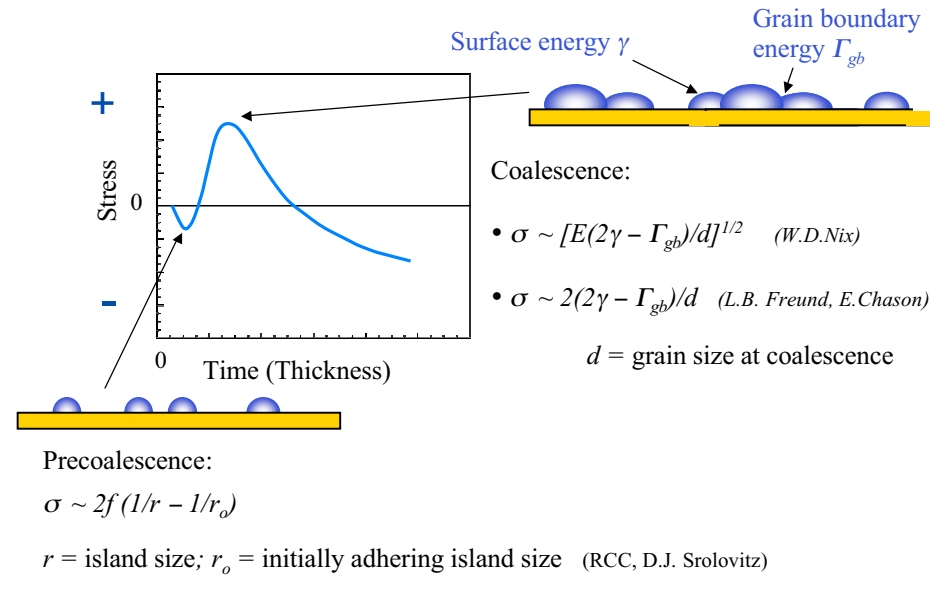


Can analyze creep behavior by taking as effective net stress  $\sigma = \sigma_{app} + \sigma_o$

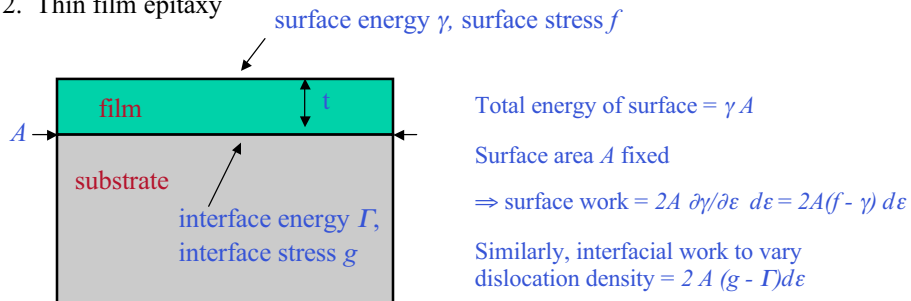
where  $\sigma_{app}$  = applied stress and  $\sigma_o$  = "effective creep stress"  $\sim 2\Gamma/\Lambda$ .

## Applications

### 1. Residual stress $\sigma$ generated during island growth.



### 2. Thin film epitaxy



Total work to introduce in-plane film strain  $d\epsilon$  is:

$$dF = At\sigma d\epsilon + 2A(f - \gamma) d\epsilon + 2A(g - \Gamma) d\epsilon; \quad \sigma = \text{in-plane film (coherency) stress}$$

Equilibrium:  $dF = 0 \Rightarrow \sigma = -(f + g - \gamma - \Gamma)/t$ .

$\Rightarrow$  Can consider  $-(f + g - \gamma - \Gamma)/t$  = "surface pressure" that opposes film stress.

Hooke's law:  $\sigma = M\epsilon \Rightarrow$  In-plane coherency strain  $\epsilon = -(f + g - \gamma - \Gamma)/Mt$ .

Critical thickness for epitaxy:  $t_c = -(f + g - \gamma - \Gamma)/Mm$  where  $m$  = misfit strain.

Can generalize for anisotropic behavior:

$$\text{Force balance: } t \sigma_{ij} = (\gamma + \Gamma) \delta_{ij} - f_{ij} - g_{ij}$$

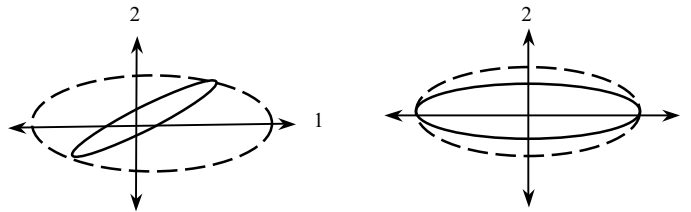
$$\text{Define "surface force" tensor } B_{ij} = (\gamma + \Gamma) \delta_{ij} - f_{ij} - g_{ij}$$

Let  $B_{ij}^c$  = surface force tensor for a completely lattice-matched film;

$\sigma_{ij}^c$  = stress state for a completely lattice-matched film.

Critical thickness occurs when a component of the tensor  $B_{ij}^c/t$  equals the corresponding component of  $\sigma_{ij}^c$ .

Representation ellipses for  $\sigma_{ij}^c$  (dashed) and  $B_{ij}^c/t$  (solid) at the critical thickness



#### Examples of other applications:

- Surface stress effects on fracture. (K. Sieradzki)
- Interface stress effects phase transformations. (Z. Suo)
- Surface stress effects on metal surface reconstructions.  
(T.M. Trimble, RCC)
- Interface thermodynamics effects on fatigue in multilayers. (RCC)

## SUMMARY

Fundamental surface quantities

- Free surface: surface energy  $\gamma$ , surface stress  $f$ .
- Solid-solid interface: interface energy  $\Gamma$ , surface stresses  $g, h$ .

Consider thin film of thickness  $t$  (or nanostructured material with characteristic length scale  $t$ ):

“Creep stress”	Free surface: $\sim \gamma/t$ Interface: $\sim \Gamma/t$
“Laplace pressure”	Free surface: $\sim f/t$ Interface: $\sim h/t$
“Surface pressure” for epitaxy	Free surface: $\sim (f - \gamma)/t$ Interface: $\sim (g - \Gamma)/t$
“Surface modulus”	Free surface: $\sim (\partial f' / \partial \epsilon)/t$ Interface: $\sim (\partial h' / \partial \epsilon)/t$