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From coherent to incoheren interfaces: A generalized continuum formulation of surface stresses

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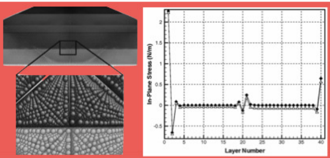
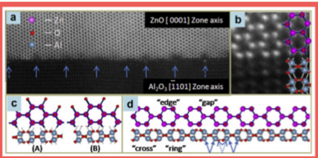
Nanostructure performance inherently dependent on interfacial properties and interfacial structure

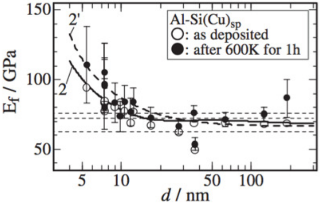


[Mi; PRB (2008)]



[Narayan; Acta Mater. (2013)]

Elasticity



[Kabe; Mat. Trans. (2004)]

Electrochemistry

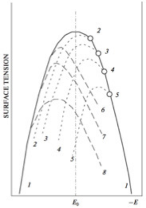
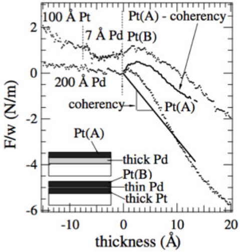


Fig. 1. Schematic view of electrocapillary curves of the mercury electrode in 0.5 M KNO$_3$ (1–5) with additions of 0.3 M of surface active anions: (1)—none, (2)—Cl$^-$, (3)—Br$^-$, (4)—I$^-$, (5)—S$_2$—, and cation Tl$^+$ as TlNO$_3$ (M): (1)—none, (6)—0.005, (7)—0.03, (8)—0.1.

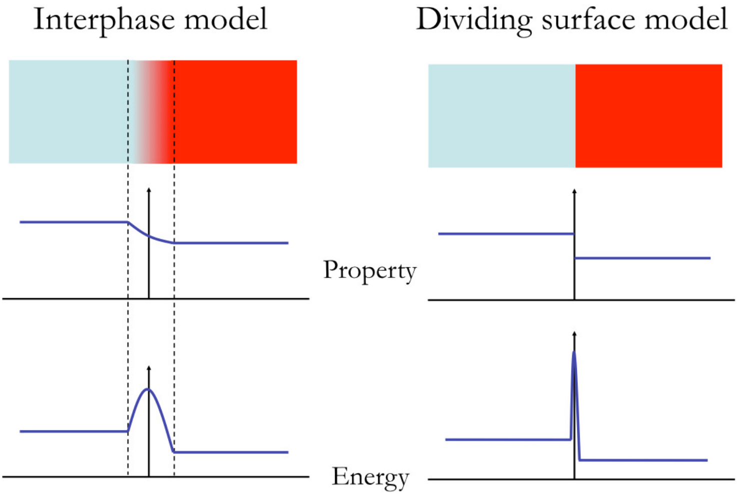
[Marichev; PMPCM (2012)]

Epitaxy growth



[Ramaswamy; Scripta Mat. (2004)]

Gibbs (1928): The interface is a mathematical surface of zero thickness over which the thermodynamic properties change discontinuously from one bulk phase to the other



Gibbs (1928): The interface is a mathematical surface of zero thickness over which the thermodynamic properties change discontinuously from one bulk phase to the other

Gibbs dividing surface thermodynamic framework:

- **Shuttleworth relation**:
  - $\boldsymbol{\Sigma}^S = \boldsymbol{\Sigma}_0^S + \partial\Gamma/\partial\boldsymbol{\epsilon}^S$.
- **Liquid interface:**
  - High atomic mobility.
  - Interfacial configuration preserved.
  - Surface free energy invariant to deformation loading path: $\partial\Gamma/\partial\boldsymbol{\epsilon}^S = 0$.
- **Solid interface:**
  - Long range correlation in atomic positions.
  - When solid crystal interfaces deform, their area may change.
  - No mass addition, rather **change of surface free energy with deformation**: $\partial\Gamma/\partial\boldsymbol{\epsilon}^S \neq 0$.

Some of the concerns (among many!) when assessing the role of interface in the Gibbsian sense

1. **“3D” nature of interface:** Theories based on such two-dimensional framework cannot account for the flexural stiffness.
2. **Effect of mismatch:** Shuttleworth-Herring relation does not account for the interfacial mismatch structure.
3. **Coupling effects:** Is there any synergistic effects between loading path and interfacial structure?
4. **From a discrete description to a continuum framework:** What is the relationship between the atomistic description of the interface and its thermomechanical description?

Today's reflection and overview

1. **Where surface matters...**
   - Needs for Gibbs dividing surface thermodynamic framework.
2. **Thermodynamic framework for an incoherent interface**
   - Interfacial kinematics.
   - Generalization of the Shuttleworth relation.
   - Insight on interfacial elasticity.
3. **Illustration from atomistic simulations of Cu/Cu2O interfaces**
4. **Summary**

Two measures of the Lagrangian interfacial in-plane strain tensors $(\epsilon^S, \epsilon^{*,S})$ are necessary to define the interfacial kinematics

Coherent surface strain: Measure associated with deforming both phases by the same amount

$$\boldsymbol{\epsilon}^S = \boldsymbol{\epsilon}^S_+ = \boldsymbol{\epsilon}^S_- = \frac{1}{2}\left(\nabla^S \mathbf{u}_\pm + \nabla^S {\mathbf{u}_\pm}^T\right)$$

Medium “+” chosen as our reference phase.

Incoherent surface strain: In-plane eigenstrain related to the change of the interface structure

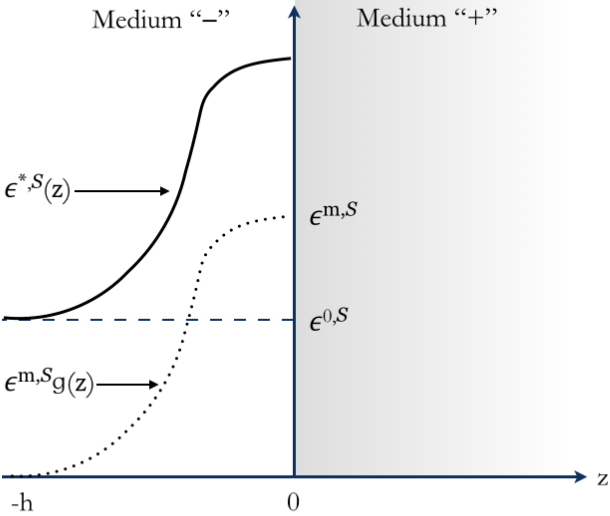
$$\boldsymbol{\epsilon}^{*,S}\left(\mathbf{x}\right) = \boldsymbol{\epsilon}^{0,S} + \boldsymbol{\epsilon}^{m,S} g\left(\mathbf{x}\right)$$

$\boldsymbol{\epsilon}^{0,S}$: change in molar volume between medium “+” and “-”.
$\boldsymbol{\epsilon}^{m,S}$: misfit strain.

Misfit strain and molar volume change eigenstrain

$$\epsilon^{m,S}_{\alpha\beta} = 2\frac{\lambda_+ - \lambda_-}{\lambda_+ + \lambda_-}\delta_{\alpha\beta}\ ,\ V^0_- = \left[1 + \epsilon^{0,S}_{kk}\right]^3 V^0_+ \approx \left[1 + 3\epsilon^{0,S}_{kk}\right] V^0_+$$

Decomposition of the in-plane eigenstrain $\epsilon^{*,S}$ related to the change of the interface structure



The Gibbs dividing surface thermodynamic framework is used to define the interfacial excess free energy, interfacial excess stress and interfacial excess strain for a coherent and a incoherent interface

Interfacial thermodynamic framework

$$\Gamma = \hat{\Gamma}\left(\boldsymbol{\epsilon}^S, \boldsymbol{\epsilon}^{m,S}, \boldsymbol{\sigma}^{\perp}\right) = \int_0^{\infty} \left(\Psi(\mathbf{x}) - \Psi_+\right) d\mathbf{x} + \int_{-\infty}^{0} \left(\Psi(\mathbf{x}) - \Psi_-\right) d\mathbf{x}$$

$$p^{(S)} = \boldsymbol{\Sigma}^S : \dot{\boldsymbol{\epsilon}}^S + \mathbb{D}^{\perp} \cdot \dot{\boldsymbol{\sigma}}^{\perp} + \boldsymbol{\Upsilon}^S : \dot{\boldsymbol{\epsilon}}^{m,S}$$

Γ: interfacial excess energy (Gibbsian sense).
$p^{(S)}$: interfacial power density.

- Interfacial elastic tensors derived using "T-decomposition" and general anisotropic elasticity with eigenstrains due to lattice mismatch:

Excess thermodynamical quantities are formulated by combining the “T”-decomposition with the Gibbs dividing surface concept

Interfacial excess stress:

$$\boldsymbol{\Sigma}^S = \int_0^\infty \left(\boldsymbol{\sigma}^S(\mathbf{x}) - \boldsymbol{\sigma}^S_+\right) d\mathbf{x} + \int_{-\infty}^0 \left(\boldsymbol{\sigma}^S(\mathbf{x}) - \boldsymbol{\sigma}^S_-\right) d\mathbf{x}$$

$$\boldsymbol{\sigma}^S(\mathbf{x}) = \hat{\boldsymbol{\tau}}^S(\mathbf{x}) + \underline{\underline{\mathbb{C}}}^S(\mathbf{x}) : \left[\boldsymbol{\epsilon}^S(\mathbf{x}) - \boldsymbol{\epsilon}^{*,S}(\mathbf{x})\right] + \boldsymbol{\sigma}^\perp \cdot \underline{\gamma}(\mathbf{x})$$

$$\boldsymbol{\Sigma}^S = \boldsymbol{\Sigma}^S_0 - \underline{\underline{\boldsymbol{\Phi}}} : \boldsymbol{\epsilon}^{m,S} + \underline{\underline{\boldsymbol{\Gamma}}}^{(2)} : \boldsymbol{\epsilon}^S + \boldsymbol{\sigma}^\perp \cdot \underline{\mathbb{H}}$$

Transverse interfacial excess strain:

$$\boldsymbol{\Delta}^\perp = \int_0^\infty \left(\boldsymbol{\epsilon}^\perp(\mathbf{x}) - \boldsymbol{\epsilon}^\perp_+\right) d\mathbf{x} + \int_{-\infty}^0 \left(\boldsymbol{\epsilon}^\perp(\mathbf{x}) - \boldsymbol{\epsilon}^\perp_-\right) d\mathbf{x}$$

$$\boldsymbol{\epsilon}^\perp(\mathbf{x}) = \boldsymbol{\epsilon}^{*,\perp}(\mathbf{x}) - \mathbb{M}^\perp(\mathbf{x}) \cdot \boldsymbol{\tau}^\perp(\mathbf{x}) + \mathbb{M}^\perp(\mathbf{x}) \cdot \sigma^\perp$$
$$-\underline{\gamma}(\mathbf{x}) : \left[\boldsymbol{\epsilon}^S(\mathbf{x}) - \boldsymbol{\epsilon}^{*,S}(\mathbf{x})\right]$$

$$\boldsymbol{\Delta}^\perp = \boldsymbol{\Lambda}^\perp_0 + \underline{\mathbb{K}} : \boldsymbol{\epsilon}^{m,S} + \boldsymbol{\Lambda}^{(2)} \cdot \boldsymbol{\sigma}^\perp - \underline{\mathbb{H}} : \boldsymbol{\epsilon}^S$$

Generalized Shuttleworth relationships define the connection between the interface thermodynamic quantities and the interface structure

Generalized Shuttleworth relationship

$$\boldsymbol{\Sigma}^S = \left.\frac{\partial \Gamma}{\partial \boldsymbol{\epsilon}^S}\right|_{\boldsymbol{\epsilon}^{m,S},\boldsymbol{\sigma}^{\perp}} + \boldsymbol{\sigma}^{\perp} \cdot \underline{\mathbb{H}}$$

$$\mathbb{D}^{\perp} = \boldsymbol{\Delta}^{\perp} - \boldsymbol{\Lambda}_0^{(\perp)} = \left.\frac{\partial \Gamma}{\partial \boldsymbol{\sigma}^{\perp}}\right|_{\boldsymbol{\epsilon}^S,\boldsymbol{\epsilon}^{m,S}} - \underline{\mathbb{H}} : \boldsymbol{\epsilon}^S + \underline{\mathbb{K}} : \boldsymbol{\epsilon}^{m,S}$$

$$\boldsymbol{\Upsilon}^S = \left.\frac{\partial \Gamma}{\partial \boldsymbol{\epsilon}^{m,S}}\right|_{\boldsymbol{\epsilon}^S,\boldsymbol{\sigma}^{\perp}} - \boldsymbol{\sigma}^{\perp} \cdot \underline{\mathbb{K}} + \underline{\underline{\boldsymbol{\Upsilon}}}^{(2)} : \boldsymbol{\epsilon}^S$$

$\boldsymbol{\Sigma}^S$: coherent interfacial stress.

$\boldsymbol{\Upsilon}^S$: incoherent interfacial stress.

$\mathbb{D}^{\perp}$: interfacial transverse strain.

Physical interpretation:

$\boldsymbol{\Sigma}^S$and $\boldsymbol{\Delta}^{\perp}$: Thermodynamic driving forces deforming the interface.

$\boldsymbol{\Upsilon}^S$: Work of stretching one crystal holding the other fixed i.e. altering the structure of the interface.

Deforming a coherent or a incoherent interface does not always increase its interfacial excess energy

Interfacial thermo-elastic properties

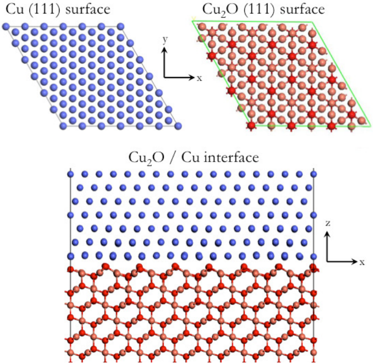
$$\epsilon^{m,S}_{\alpha\beta} = \alpha^S \delta_{\alpha\beta} \Delta T$$

$$\begin{bmatrix} \frac{\Gamma^{(1)}_{11}}{2} \\ \Lambda^{(1)}_3 \end{bmatrix} + \begin{bmatrix} 2K^S & \frac{2K^S\nu^S}{E^\perp} & -d^*_0 \\ -\frac{4K^S\nu^S}{E^\perp} & \frac{1}{E^{*,\perp}} & \frac{2d^*_0\nu^{*,S}}{E^{*,\perp}} \end{bmatrix} \cdot \begin{bmatrix} \epsilon^S \\ \sigma^\perp \\ \Delta T \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

Thermal-mechanical structural connection: $d^*_0 = 2K^{*,S}\alpha^S$.

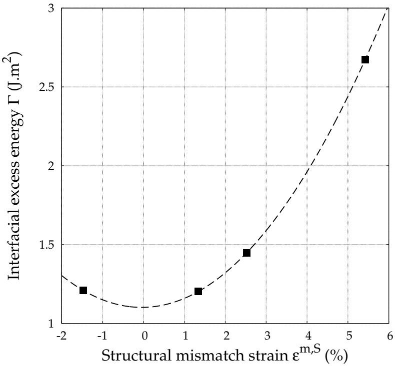
- One can construct a loading path $(\epsilon^S, \sigma^\perp)$ that would minimize the impact of the interface on the behavior of a material system separated by it or construct a loading path for which the surface to volume ratio is significant

Illustration from atomistic simulations of Cu/Cu_2O interfaces



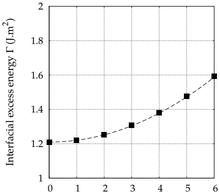
- **Interfacial structural mismatch:**
$$\epsilon^{m,S}_{\alpha\beta} = 2\frac{n\lambda_{\mathrm{Cu}} - m\lambda_{\mathrm{Cu_2O}}}{n\lambda_{\mathrm{Cu}} + m\lambda_{\mathrm{Cu_2O}}}\delta_{\alpha\beta}.$$
- **Interatomic potential:**
  1. Cu-Cu: EAM potential.
  2. Cu-CuO_2: (i) LJ potential for the interaction between copper metallic atoms and copper atoms from the oxide, and (ii) a Morse potential linking copper metallic atoms with the oxygen atoms [Hallil, 2014].
- **Loading:**
  1. Biaxial deformation: $\epsilon^S_{xx} = \epsilon^S_{yy} = \epsilon^S$ and $\sigma^\perp = 0$.
  2. Transverse loading: $\sigma^\perp = \sigma_{zz}$ and $\epsilon^S = 0$.

Variation of the interfacial excess energy $\Gamma\big|_{\boldsymbol{\epsilon}^S=0,\boldsymbol{\sigma}^\perp=0}$ (1/3)

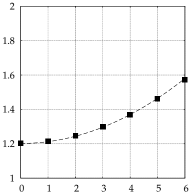


$$\Gamma\big|_{\boldsymbol{\epsilon}^S=0,\boldsymbol{\sigma}^\perp=0} = \Gamma^* = \Gamma_0 + \Upsilon^{(1)}_{\alpha\alpha}\epsilon^{m,S}_{\alpha\alpha} + \frac{1}{2}\epsilon^{m,S}_{\alpha\alpha}\Upsilon^{(3)}_{\alpha\alpha\beta\beta}\epsilon^{m,S}_{\beta\beta}$$

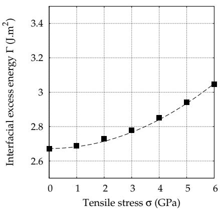
Variation of the interfacial excess energy $\Gamma\big|_{\epsilon^S=0}$ (2/3)



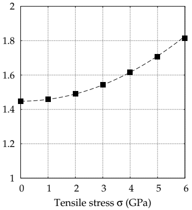
(a) $\epsilon^{m,S} = -1.476\%$



(b) $\epsilon^{m,S} = 1.34\%$



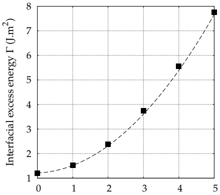
(c) $\epsilon^{m,S} = 5.421\%$



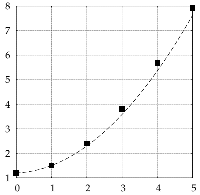
(d) $\epsilon^{m,S} = 2.524\%$

$$\Gamma\big|_{\epsilon^S=0} = \Gamma^* + \frac{1}{2}\sigma^\perp \Lambda^{(2)}_{zz} \sigma^\perp$$

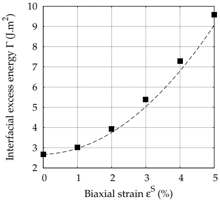
Variation of the interfacial excess energy $\Gamma\big|_{\boldsymbol{\sigma}^\perp=0}$ (3/3)



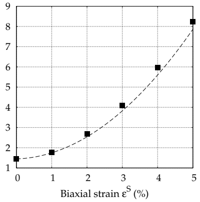
(e) $\epsilon^{m,S} = -1.476\%$



(f) $\epsilon^{m,S} = 1.34\%$



(g) $\epsilon^{m,S} = 5.421\%$



(h) $\epsilon^{m,S} = 2.524\%$

$$\Gamma\big|_{\boldsymbol{\sigma}^\perp=0} = \Gamma^* + \Gamma^{(1)}_{\alpha\alpha}\epsilon^S_{\alpha\alpha} + \frac{1}{2}\epsilon^S_{\alpha\alpha}\Gamma^{(2)}_{\alpha\alpha\beta\beta}\epsilon^S_{\beta\beta} - \epsilon^{m,S}_{\alpha\alpha}\Upsilon^{(2)}_{\alpha\alpha\beta\beta}\epsilon^S_{\beta\beta}$$

Summary: A generalized continuum formulation of surface stresses for incoherent mismatched interfaces

- **Complete formulation of the thermodynamic framework** relating the coherent surface stress, the incoherent surface stress and the transverse excess strain to the interface excess energy by means of the Gibbs dividing surface concept and "*T-decomposition*" of deformation path.
- Formulation not only **accounts for the three-dimensional nature of the interface in a Gibbsian sense** but also explicitly considers the interfacial structure.
- Origin of surface stresses and their coupling with the interfacial structural mismatch.
- Illustration with examples based on atomistic simulations for incoherent interfaces between Cu and its oxide Cu_2O under various loading configurations.
- Perspective: equilibrium condition of curved incoherent interfaces:account for interface curvature.

R. Dingreville, A. Hallil and S. Berbenni; "From coherent to incoherent mismatched interfaces: A generalized continuum formulation of surface stresses." *Journal of the Mechanics and Physics of Solids*, **72**, pp.40–60 (2014).