A Thermochemical Approach to Thermophysical Properties - Modelling Surface and Interfacial Tension of Liquids

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Multiphase models for (liquid) surfaces and interfaces

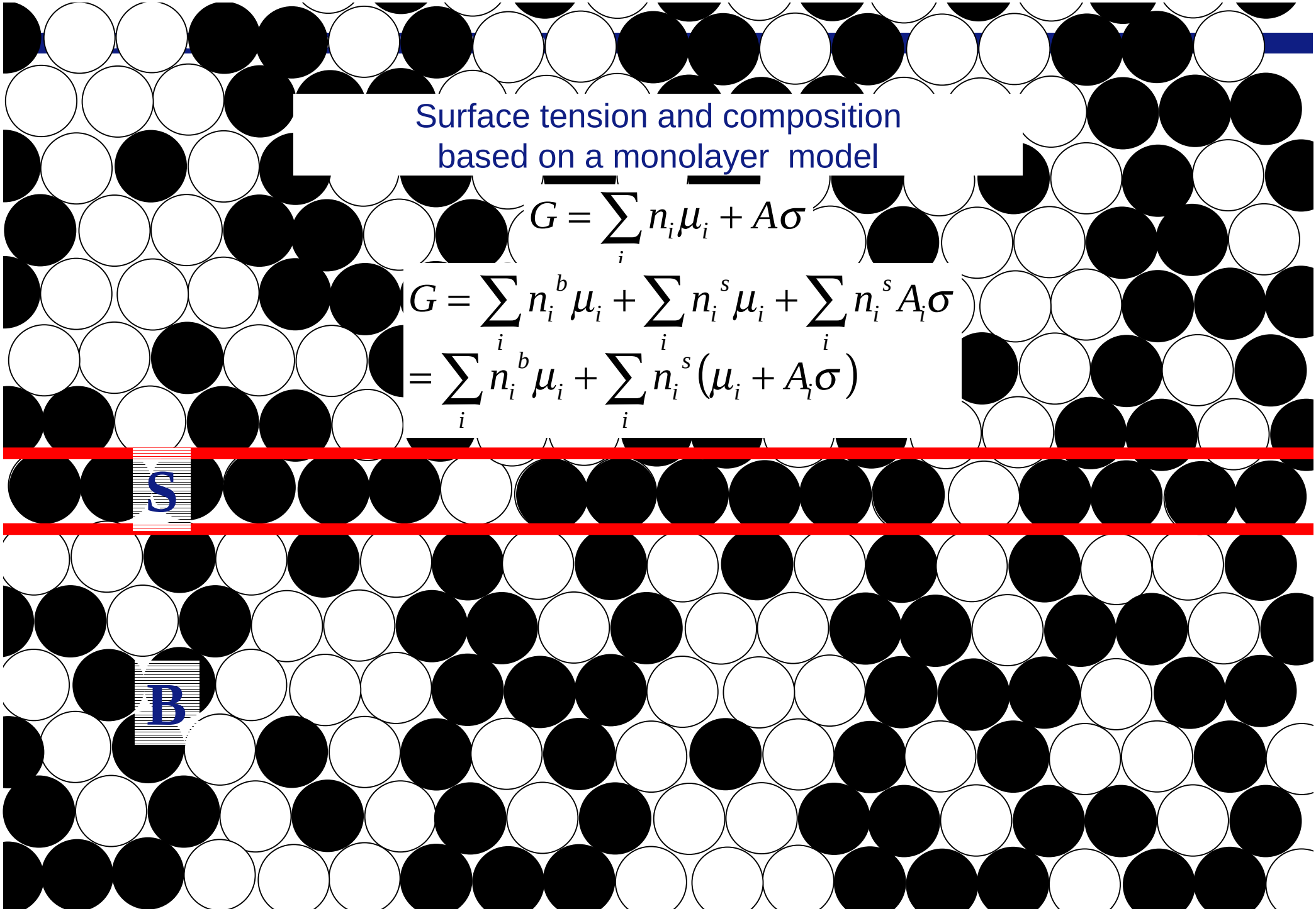
- Surfaces and interfaces modelled as one or more layers (phases)
- Strong adsorption can be included as a separate adsorption layer
- Aim to rely as much as possible on bulk thermodynamics (assumed to be known)
- Calculations done ChemSheet (based on ChemApp)

Surface tension and composition based on a monolayer model

$$G = \sum_i n_i \mu_i + A\sigma$$

$$G = \sum_i n_i^{\,b} \mu_i + \sum_i n_i^{\,s} \mu_i + \sum_i n_i^{\,s} A_i \sigma$$

$$= \sum_i n_i^{\,b} \mu_i + \sum_i n_i^{\,s} \left(\mu_i + A_i \sigma\right)$$



		Component(1)	Component(2)	•••	Component(M)	Area
bulk	Species (1)	ν_{11}	ν_{12}	•••	ν_{1M}	0
	Species (2)	ν_{21}	ν_{22}	•••	ν_{2M}	0
	⋮	⋮	⋮	⋱	⋮	⋮
	Species (N)	ν_{N1}	ν_{N2}	•••	ν_{NM}	0
surface	Species (1)	ν_{11}	ν_{12}	•••	ν_{1M}	A_1/A_0
	Species (2)	ν_{21}	ν_{22}	•••	ν_{2M}	A_2/A_0
	⋮	⋮	⋮	⋱	⋮	⋮
	Species (N)	ν_{N1}	ν_{N2}	•••	ν_{NM}	A_N/A_0

(A_i is the molar surface area of species i, A_0 a normalization factor with dimensions of m²/mol)

$$\sigma = \mu_{Area} / A_0 = \left(\mu_i^* - \mu_i\right) / A_i$$

(where $\mu_i^* = \mu_i^{0,s} + RT \ln a_i^s$) (Total molar Gibbs energy in the surface phase)

(and $\mu_i^{0,s} = \mu_i^{0,b} + A_i \sigma_i$) (Standard state for the surface layer)

Modified excess energy expression for the surface layer, such as:

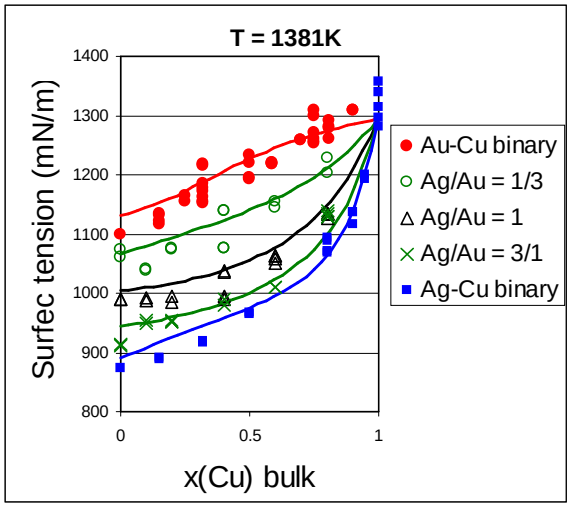
$$G_{Ex}^b = f\left(x_1^b, ..., x_n^b, T\right)$$
$$G_{Ex}^s = \beta \cdot f\left(x_1^s, ..., x_n^s, T\right)$$

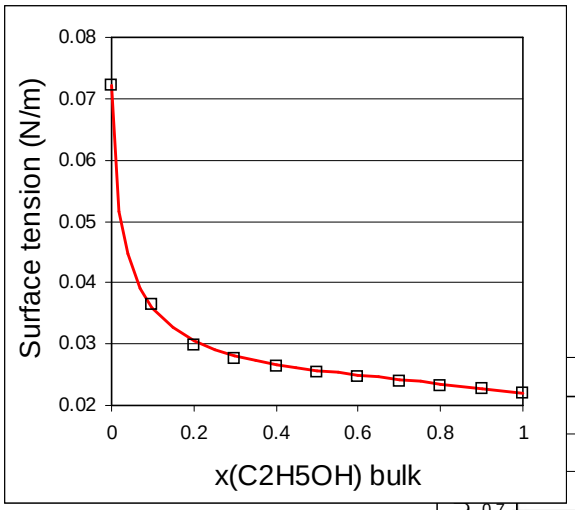
Simple example : Iron – Copper binary

		Fe	Cu	Area
bulk	Fe(l)	1	0	0
	Cu(l)	0	1	0
surface	Fe(l)	1	0	3.672
	Cu(l)	0	1	3.780

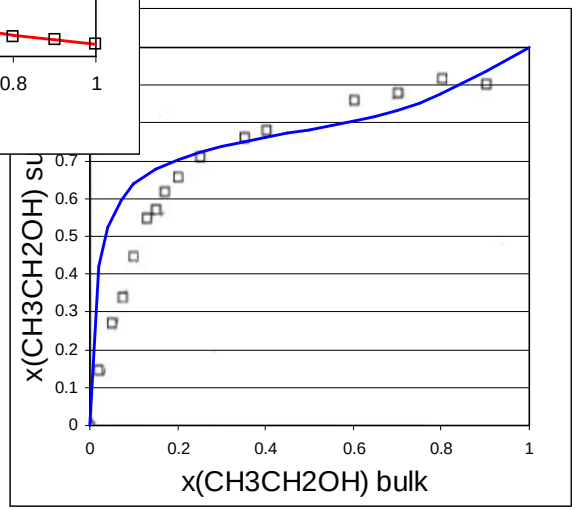
Example cases

Binary and ternary alloys: (Ag,Au-Cu)

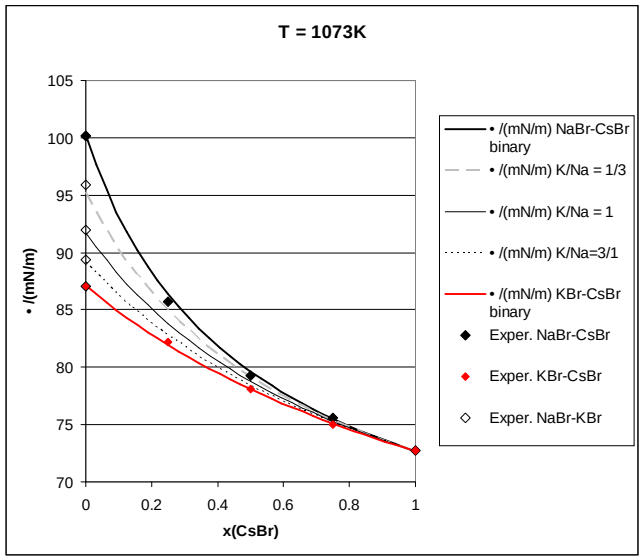




Organics/aqueous: Ethanol-Water

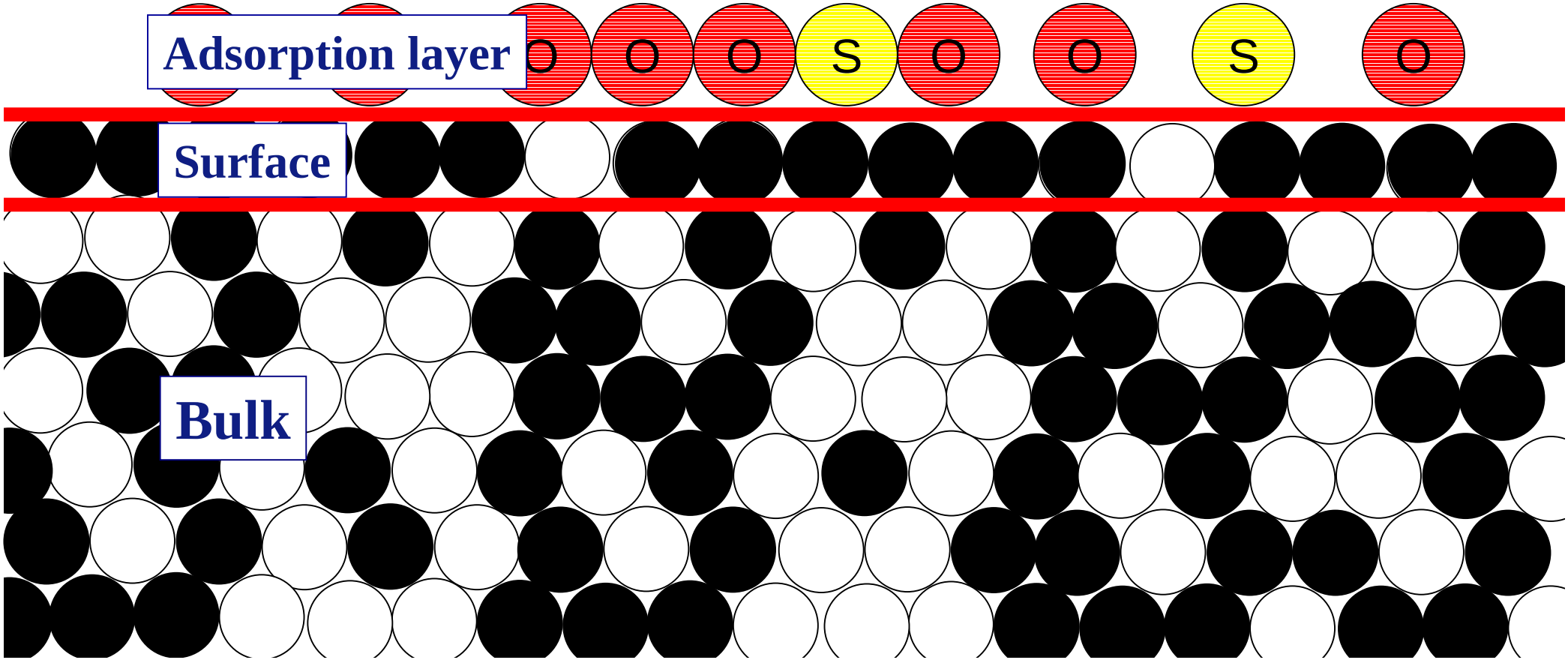


Molten salts: (Na/K/CsBr)



The three layer (phase) adsorption model

- Three phases: bulk, surface layer and adsorption layer



Simple Langmuir adsorption equilibrium model:

		Fe	O	Adsorption location
Bulk	Fe O	1	 1	
Adsorption layer	(Fe)[] (Fe)O		 1	1 1

- Standard states of the species on the adsorption layer have been set using the Langmuir adsorption constant $\mu^0_{(Fe)[\ ]} \equiv 0$, $\mu^0_{(Fe)O} - \mu^0_{(Fe)[\ ]} = \mu^0_{(Fe)O} = \mu^0_{O_{bulk}} - RT \ln K$
  and the total molar amount of adsorption locations based on the maximum adsorbed amount $n_{\text{Adsorption location}} = n_{(Fe)[]} + n_{(Fe)O} = n_{(Fe)O}^{MAX}$
- Model gives Langmuir model type dependency for the surface coverage as a function of the activity of the adsorbing species
- It can be further combined to surface layer model for calculating the effect of adsorption on surface energy

Langmuir type model with a surface energy contribution

		Fe	O	Area	Adsorption area
Bulk	Fe O	1	 1		
Surface	Fe	1		A_{Fe}/A_0	$-A_{Fe}/A_0$
Adsorption layer	(Fe)[] (Fe)O		 1		$A_{O/}A_0$ $A_{O/}A_0$

For basic Langmuir model type behaviour the adsorption layer is modelled as an ideal mixture

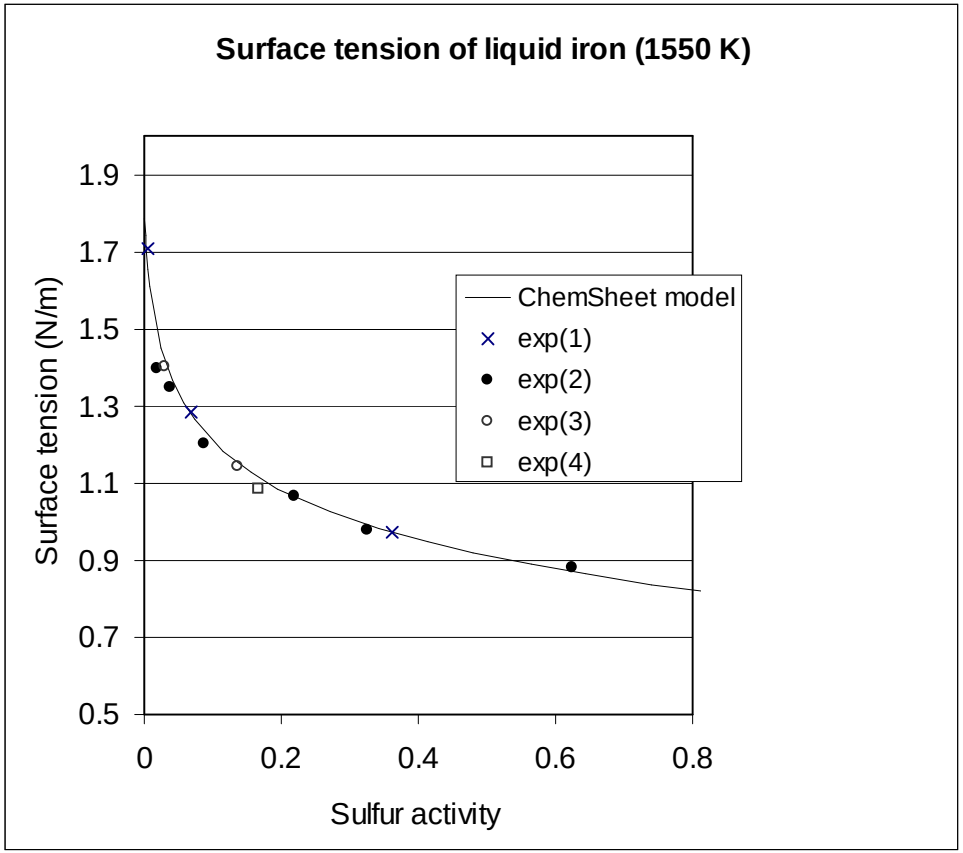
$$\mu^0_{(Fe)[\ ]} \equiv 0 \text{ (definition)}$$

$$\mu^0_{(Fe)ads} - \mu^0_{(Fe)[\ ]} \equiv \mu^0_{(Fe)O} = \mu^0_{O_{bulk}} - RT \ln K_O^{ads}$$

$$A_O = \frac{1}{\Gamma_O^{MAX}}$$

$$\sigma \equiv \frac{\partial G}{\partial A} \equiv \mu_{Area} \Big/ A_0 = \left(\mu_i^{*(surface)} + \frac{A_i}{A_O} \mu_{(i)[]} - \mu_i \right) \Big/ A_i$$

Example of Langmuir type adsorption (S on liquid Fe)



(Experimental values taken from *Metallurgical transactions B* 7B(1976)35)

System with a mixed solvent

		Fe	Cr	O	Area	Fe-adsorption area	Cr-adsorption area
Bulk	Fe	1					
	Cr		1				
	O			1			
	S						
Surface	Fe	1			A_{Fe}/A_0	$-A_{Fe}/A_0$	
	Cr		1		A_{Cr}/A_0		$-A_{Cr}/A_0$
Adsorption layer	(Fe)[]					A_{Fe}/A_0	
	(Fe)O			1		$A_{O(on\ Fe)}/A_0$	
	(Cr)[]						A_{Cr}/A_0
	(Cr)O			1			$A_{O(on\ Cr)}/A_0$

- Compared to the earlier case there is now one separate ‘adsorption area’ component for each solvent species into which adsorption can happen
- Fe and Cr adsorption places are located in separate sublatices, if non-ideal interactions within adsorption layer are not considered they can formally be divided to two separate phases

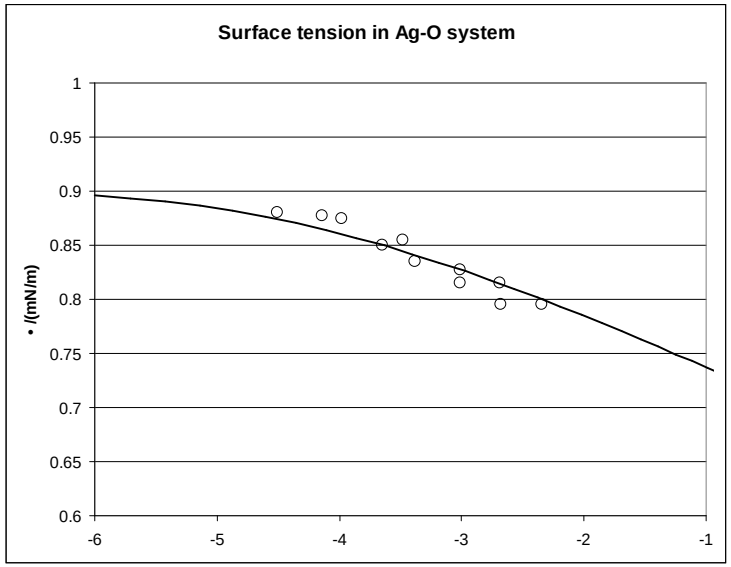
Competing adsorption of several species (of unequal size)

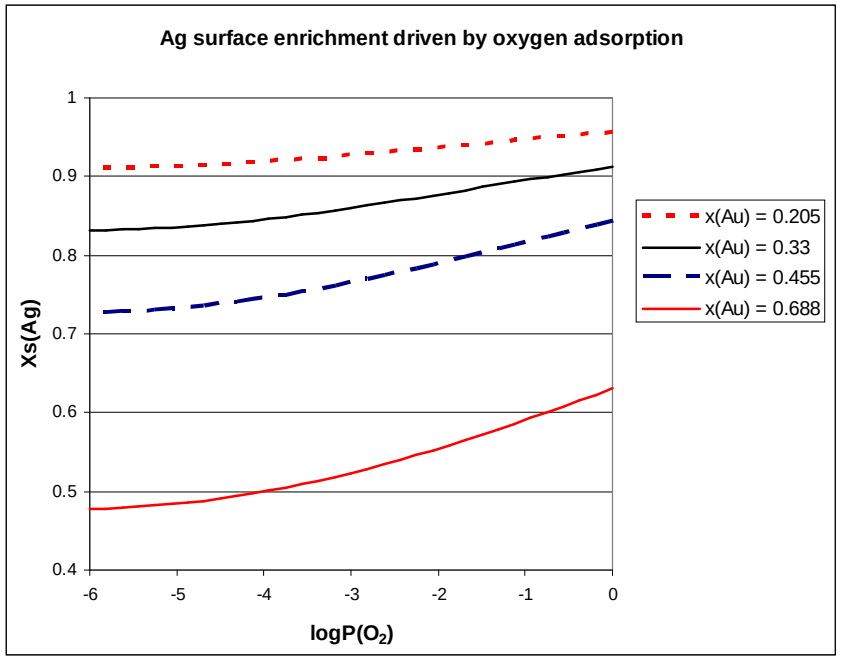
		Fe	Cr	O	S	Area	Fe-adsorption area	Cr-adsorption area
Bulk	Fe	1						
	Cr		1					
	O			1				
	S				1			
Surface	Fe	1				A_{Fe}/A_0	$-A_{Fe}/A_0$	
	Cr		1			A_{Cr}/A_0		$-A_{Cr}/A_0$
Adsorption layer	(Fe)[]						A_{Fe}/A_0	
	(Fe)O			1			$A_{O(on\ Fe)}/A_0$	
	(Fe)S				1		$A_{S(on\ Fe)}/A_0$	
	(Cr)[]							A_{Cr}/A_0
	(Cr)O			1				$A_{O(on\ Cr)}/A_0$
	(Cr)S				1			$A_{S(on\ Cr)}/A_0$

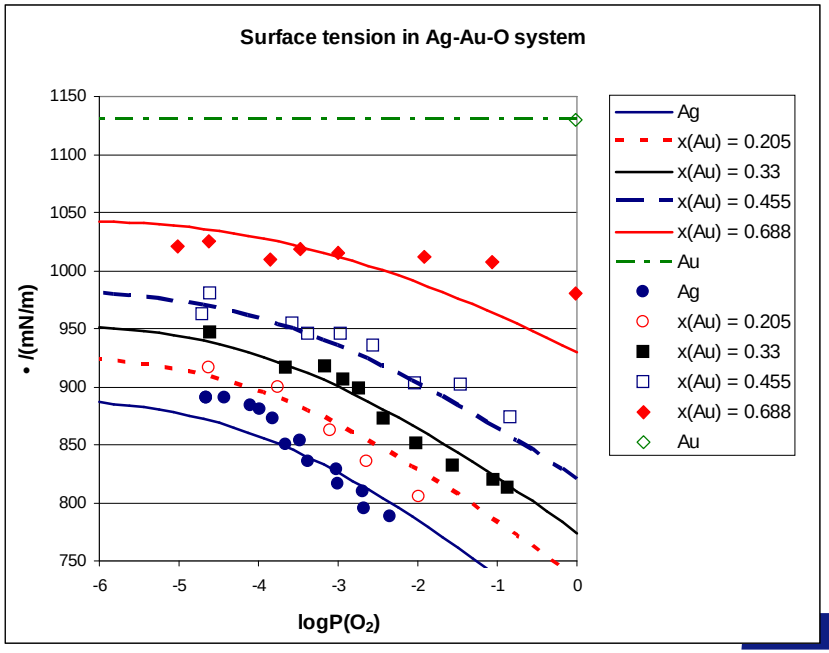
- The 'Adsorption area' of an empty adsorption place has been tentatively set same as the surface area of the corresponding metal

$$\sigma \equiv \frac{\partial G}{\partial A} \equiv \mu_{Area} \Big/ A_0 = \left(\mu_i^{*(surface)} + \mu_{(i)[]} - \mu_i\right) \Big/ A_i$$

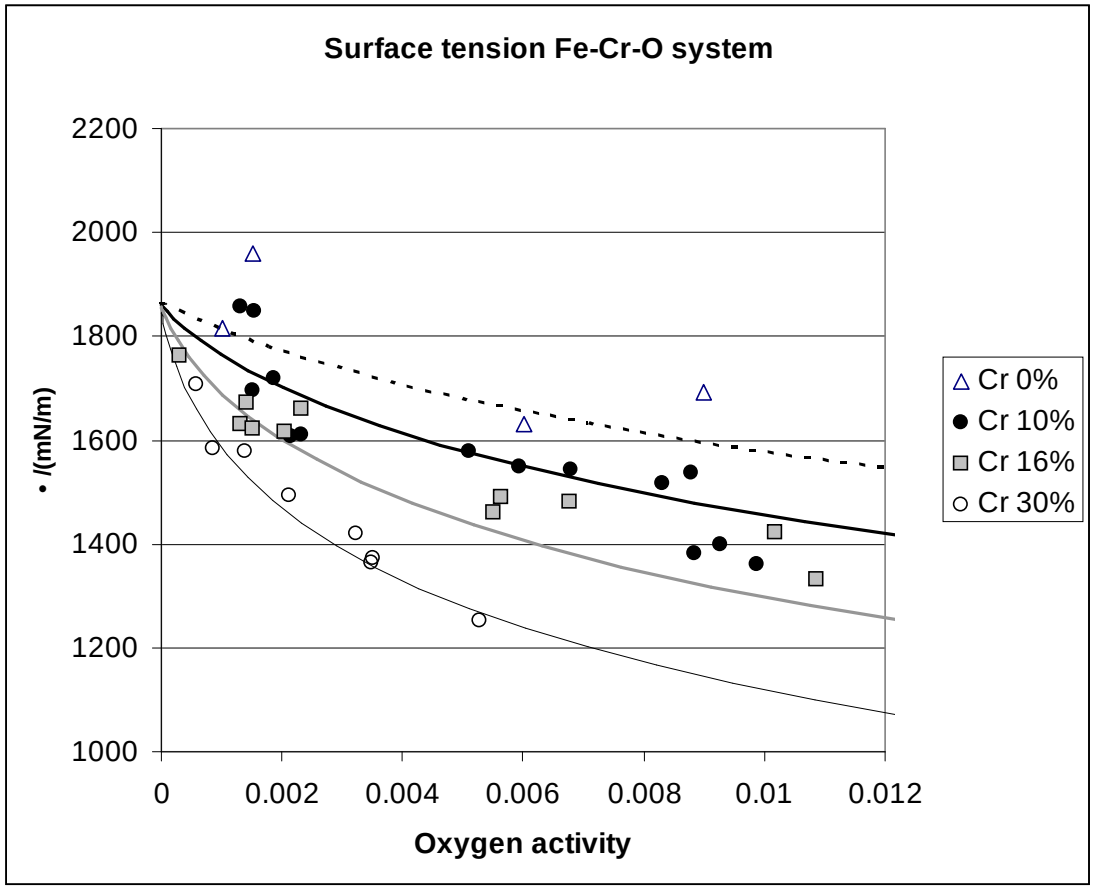
Ag+O – Ag/Au+O (1381K)







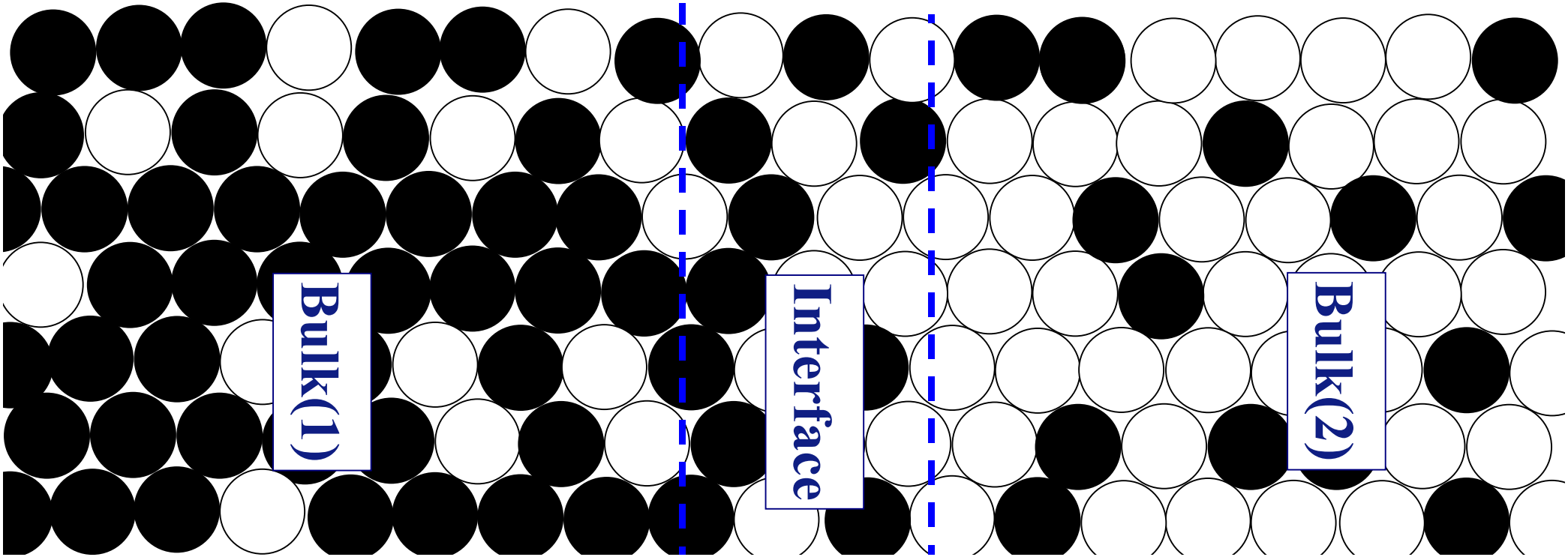
Fe/Cr/O (1823 K)



Experimental results from Metallurgical and Materials Transactions B, 36 (2005), 241

Interface model

- Interface modelled as one or more monolayers between two condensed bulk phases



Matrix representation

		Bi	Al	area
bulk(1)	Bi(l)	1	0	0
	Al(l)	0	1	0
Interface	Bi(l)	1	0	A_{Bi}/A_0
	Al(l)	0	1	A_{Al}/A_0
bulk(2)	Bi(l)	1	0	0
	Al(l)	0	1	0

$$G = \sum_i n_i^{bulk(1)} \mu_i + \sum_i n_i^{bulk(2)} \mu_i + \sum_i n_i^{interface} \mu_i^*$$

$$= \sum_i n_i \mu_i + \sum_i n_i^{interface} \left(\mu_i^* - \mu_i \right)$$

from differences in activity coefficients/excess energy only

$$= \sum_i n_i \mu_i + \sum_i n_i^{interface} \frac{A_i}{A_0} \mu_{area} = \sum_i n_i \mu_i + \frac{A}{A_0} \mu_{area}$$

$$\sigma^{interfacial} = \pi_{area} / A_0 = \left(\mu_i^* - \mu_i \right) / A_i$$

Interfacial energy model

- Fundamental requirement for the model is to have a reasonable expression for the activity coefficients in a atomic layer that has neighbouring layer of differing composition
- The actual implementation requires the usage of the *User defined* model features of ChemApp (as rather naturally in none of the GTT supplied ChemApp models is the excess energy of one phase dependent on the composition of another phase)
  - Equation used for activity coefficient for Redlich-Kister model for a system with one interfacial layer

$$RT\ln\gamma_1^i = \sum_j W_j \left[l\left(x_2^i\right)^2 \left[\left(x_1^i - x_2^i\right)^{j-1} + 2(j-1)\left(x_1^i - x_2^i\right)^{j-2} x_1^i \right] + m\left[\left(x_1^i - x_2^i\right)^{j-1} \left(\left(x_2^{b1}\right)^2 + \left(x_2^{b2}\right)^2 \right) \right.\right.$$
$$\left.\left. + (j-1)\left(x_1^i - x_2^i\right)^{j-2} 2x_2^i \left(2x_2^i \left(x_1^{b1} - x_2^{b2} \right) + x_2^{b1} x_2^{b1} + x_2^{b2} x_2^{b2} \right) \right] \right]$$

  (Reduces to the standard form when the bulk phases (and the interfacial layer) are of the same composition

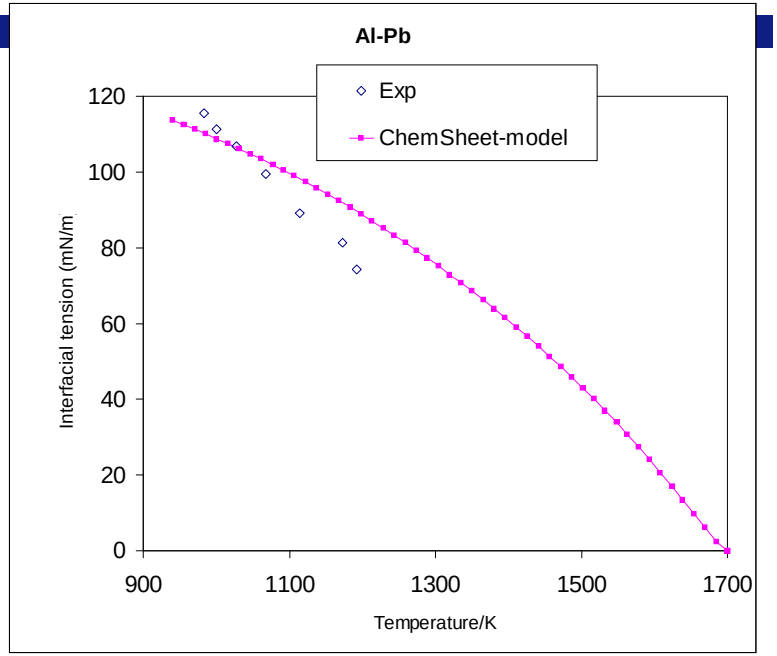
$$RT\ln\gamma_1^i = \sum_j W_j \left[(l+2m)\left(x_2\right)^2 \left[\left(x_1 - x_2\right)^{j-1} + 2(j-1)\left(x_1 - x_2\right)^{j-2} x_1 \right] \right]$$

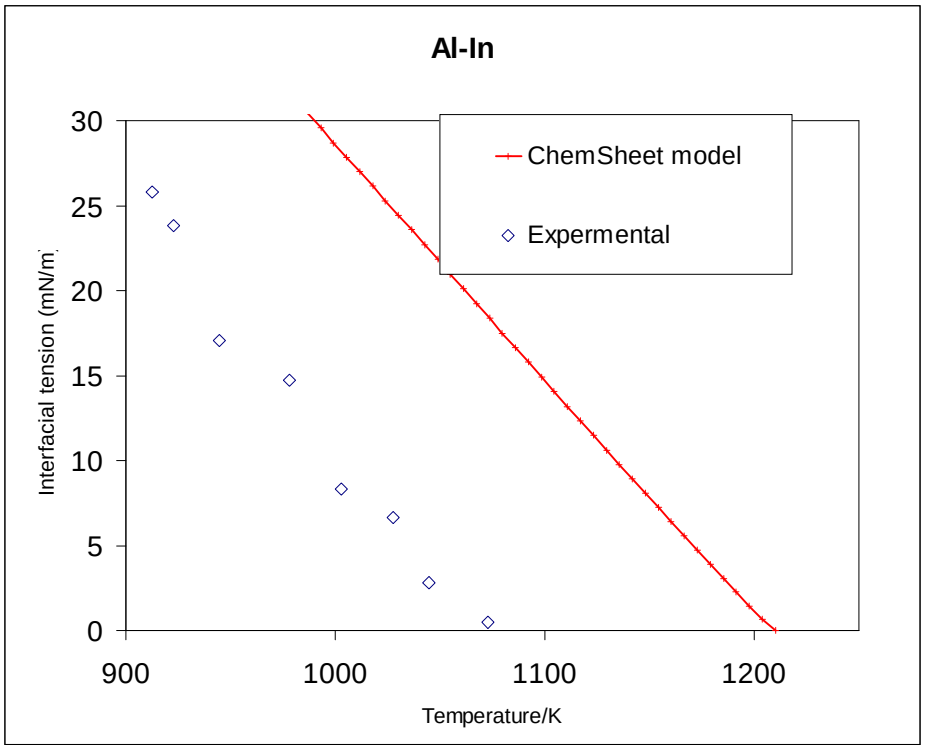
Example case of liquid-liquid metal interfacial energies

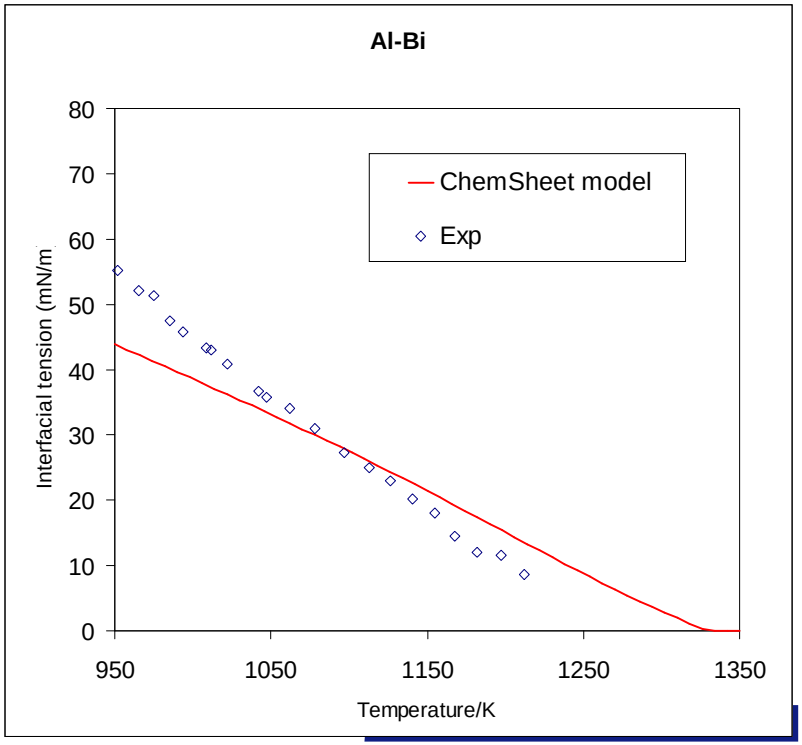
Thermodynamic data from SGTE database

Experimental interfacial energy values from

Journal of Optoelectronics and Advanced Materials **5** (2003) 1069

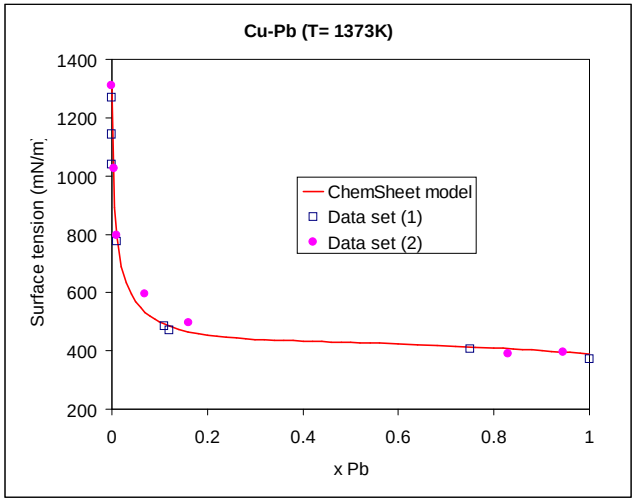


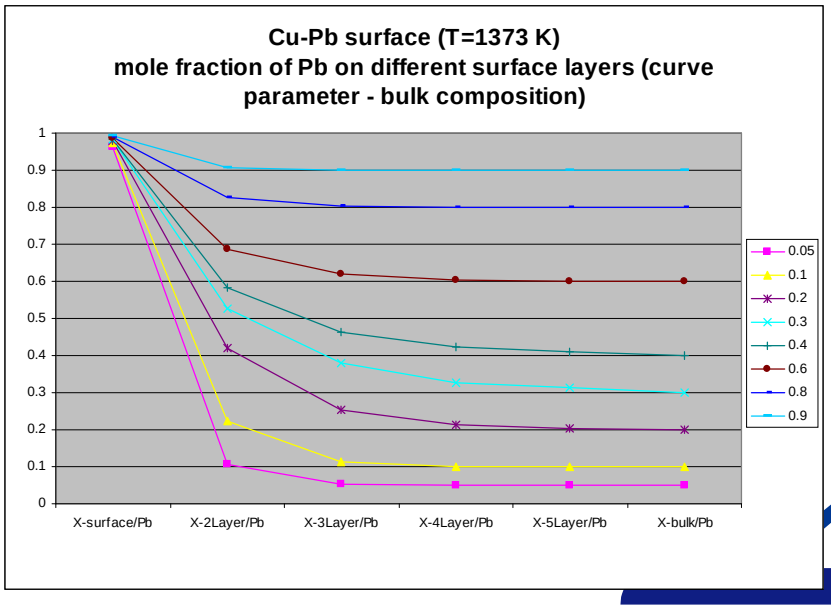




Extension to more than one surface/interfacial layers

- Requires a model for interacting layers
  - For surfaces, a prediction for the composition as a function of depth is derived; the surface tension values remain practically unchanged

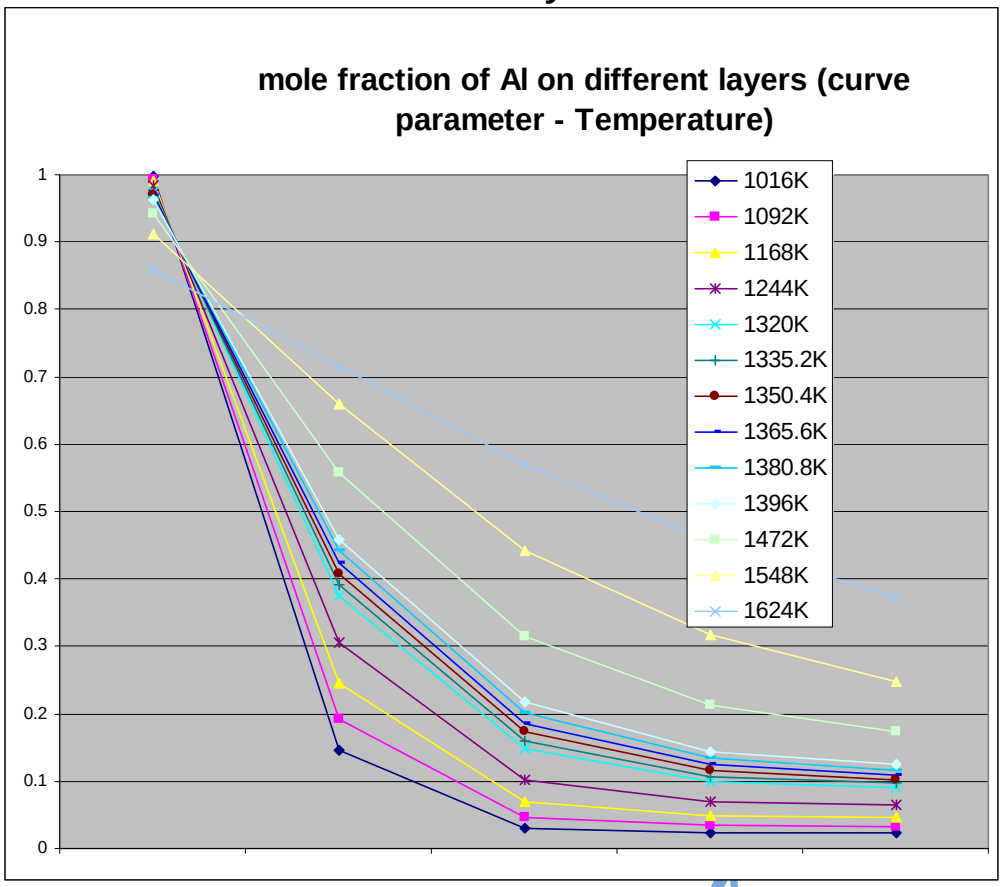




Extension to more than one surface/interfacial layers

- Requires a model for interacting layers
  - For interfaces, similarly a the composition profiles for the interfacial region are received as a result. The received interfacial energies are (as one would expect) slightly lowered (but here I should actually still actually do some checking of the equations used)

Al-Pb system



Thank you for your attention!