

Non-Equilibrium Thermodynamics of Heterogeneous Systems: The square gradient model

Dick Bedeaux

Department of Chemistry, Norwegian University of Science
and Technology, Trondheim, Norway

9th Lecture

Università Degli Studi di Brescia, Italy,

13-16 September 2010

16. Local equilibrium for mixtures

Non-equilibrium Gibbs surface

$$u(x, t) = T(x, t)s(x, t) - p_{\parallel}(x, t) \\ + \mu_1(x, t)c_1(x, t) + \mu_2(x, t)c_2(x, t)$$

↓ ?

$$\hat{u} = T^s \hat{s} - \hat{p}_{\parallel} + \mu_1^s \hat{c}_1 + \mu_2^s \hat{c}_2$$

Local equilibrium

Local equilibrium

- Determine the surface temperature and chemical potentials independent of the choice of the dividing surface

$$T^s, \mu_1^s, \mu_2^s$$

- Verify the relation

$$\hat{u} = T^s \hat{s} - \hat{p}_{\parallel} + \mu_1^s \hat{c}_1 + \mu_2^s \hat{c}_2$$

- Verify that non-equilibrium excesses are given by equilibrium functions at the temperature and chemical potentials of the surface

$$\hat{u} = \hat{u}_{eq}(T^s, \mu_2^s)$$

$$\hat{c}_1 = \hat{c}_{1,eq}(T^s, \mu_2^s)$$

Irrespective of the position of the dividing surface

17. Definition of temperature and chemical potential independent of the location of the dividing surface

$$\gamma = -\widehat{p}_{||}(x^s)$$

- surface tension

$$\Gamma = \widehat{c}_1(x^s) - \widehat{c}_2(x^s) \frac{c_1^l - c_1^g}{c_2^l - c_2^g}$$

- relative adsorption

γ_{eq} and Γ_{eq} are independent of the position of the dividing surface

\Rightarrow good quantities to use

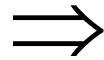
$$\begin{aligned} \gamma_{eq} &= \gamma_{eq}(T_q, \mu_{2,eq}) & \Leftrightarrow & & T_{eq} &= T_{eq}(\gamma_{eq}, \Gamma_{eq}) \\ \Gamma_{eq} &= \Gamma_{eq}(T_q, \mu_{2,eq}) & & & \mu_{2,eq} &= \mu_{2,eq}(\gamma_{eq}, \Gamma_{eq}) \end{aligned}$$

Temperature and chemical potential of a surface

$$T_{eq} = T_{eq}(\gamma_{eq}, \Gamma_{eq})$$

$$\mu_{2,eq} = \mu_{2,eq}(\gamma_{eq}, \Gamma_{eq})$$

equilibrium



$$T^s = T_{eq}(\gamma(x^s), \Gamma(x^s))$$

$$\mu_2^s = \mu_{2,eq}(\gamma(x^s), \Gamma(x^s))$$

non-equilibrium

$$\gamma(x^s)$$

$$\Gamma(x^s)$$

\Rightarrow need to incorporate all surfaces together

Temperature and chemical potential of a surface

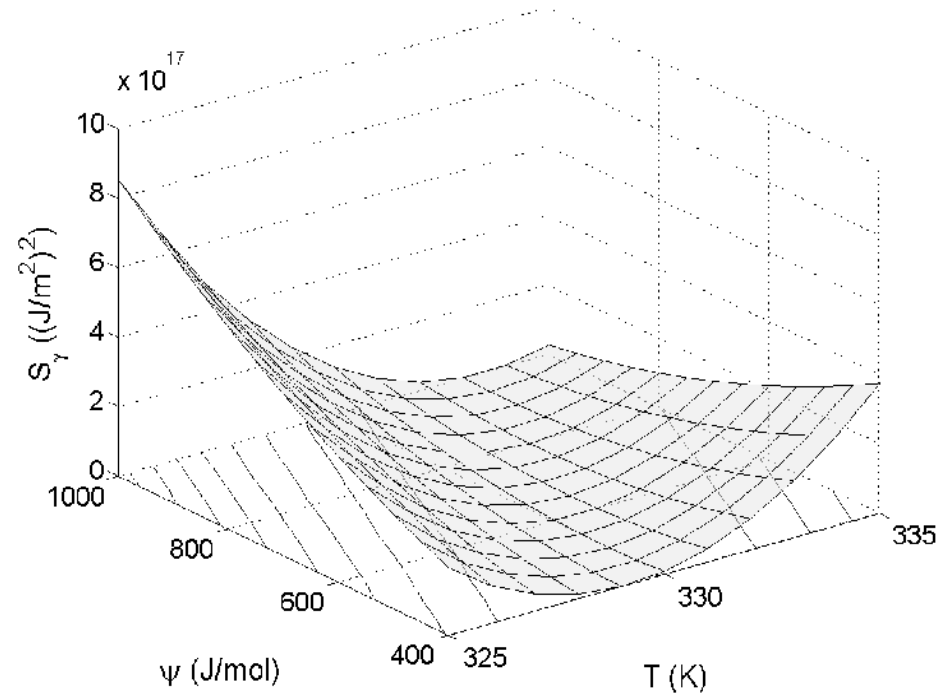
$$S_\gamma(T, \mu_2) = \sum \left[\gamma(x^s) - \gamma_{eq}(T, \mu_2) \right]^2$$

$$S_\Gamma(T, \mu_2) = \sum \left[\Gamma(x^s) - \Gamma_{eq}(T, \mu_2) \right]^2$$

least square method

$$S_\gamma(T^s, \mu_2^s) = \min$$

$$S_\Gamma(T^s, \mu_2^s) = \min$$



Temperature and chemical potential of a surface

$T^{\ell} = 1.02 T_{eq}$		
surface	T^s	ψ^s
$\{x^s\}$	331.831	770.53
x^c	331.823	769.51
x^{γ}	331.828	770.22
x^{c1}	331.814	767.97
x^{c2}	331.838	771.86

$p^g = 1.02 p_{eq}$		
surface	T^s	ψ^s
$\{x^s\}$	330.796	683.87
x^c	330.8	684.68
x^{γ}	330.799	684.44
x^{c1}	330.804	685.19
x^{c2}	330.795	683.93

