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

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9th Lecture

Local equilibrium for mixtures.
Definition of temperature and chemical potentials independent of the location of the dividing surface.

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16. Local equilibrium for mixtures

Non-equilibrium Gibbs surface

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

$$\downarrow ?$$

$$\hat{u} = T^s \hat{s} - \widehat{p_{||}} + \mu_1^s \widehat{c_1} + \mu_2^s \widehat{c_2}$$

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

$$\hat{u} = T^s \hat{s} - \widehat{p_{||}} + \mu_1^s \widehat{c_1} + \mu_2^s \widehat{c_2}$$

- 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 potentials independent of the location of the dividing surface

$$\gamma = -\widehat{p_{\|}}(x^s)$$ - surface tension

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

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

$\Rightarrow$ good quantities to use

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

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

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

$$\Rightarrow$$

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

non-equilibrium

$$\gamma(x^s)$$
$$\Gamma(x^s)$$

$\Rightarrow$ need to incorporate all surfaces together

Temperature and chemical potential of a surface

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

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least square method

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

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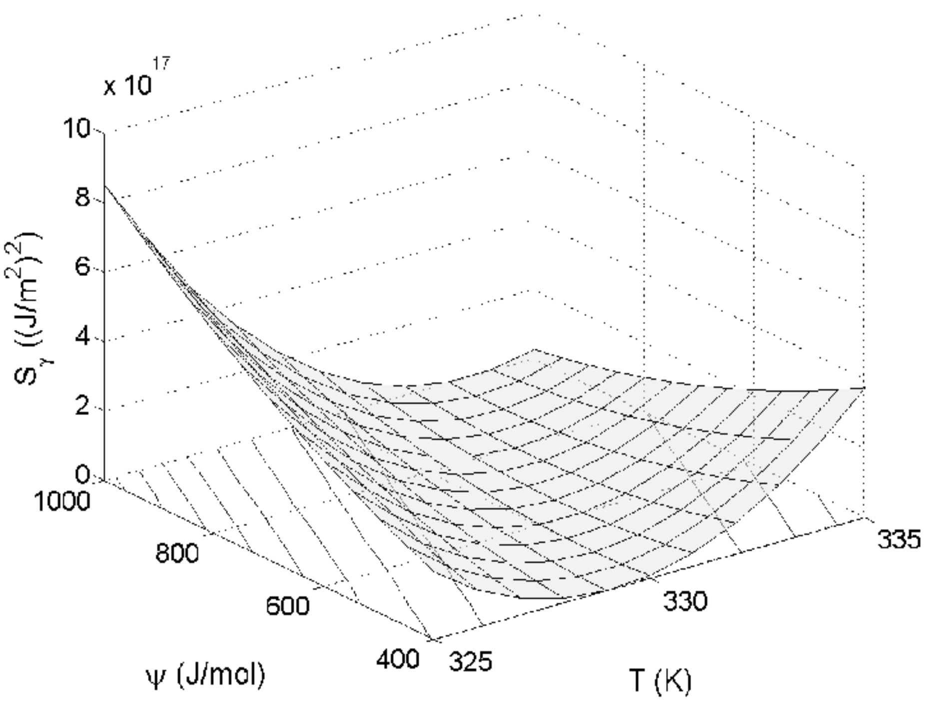

Temperature and chemical potential of a surface

	$T^{\ell} = 1.02\,T_{eq}$	
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