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

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2nd Lecture

Excess densities of an interface.
Thermodynamic relations for heterogeneous systems

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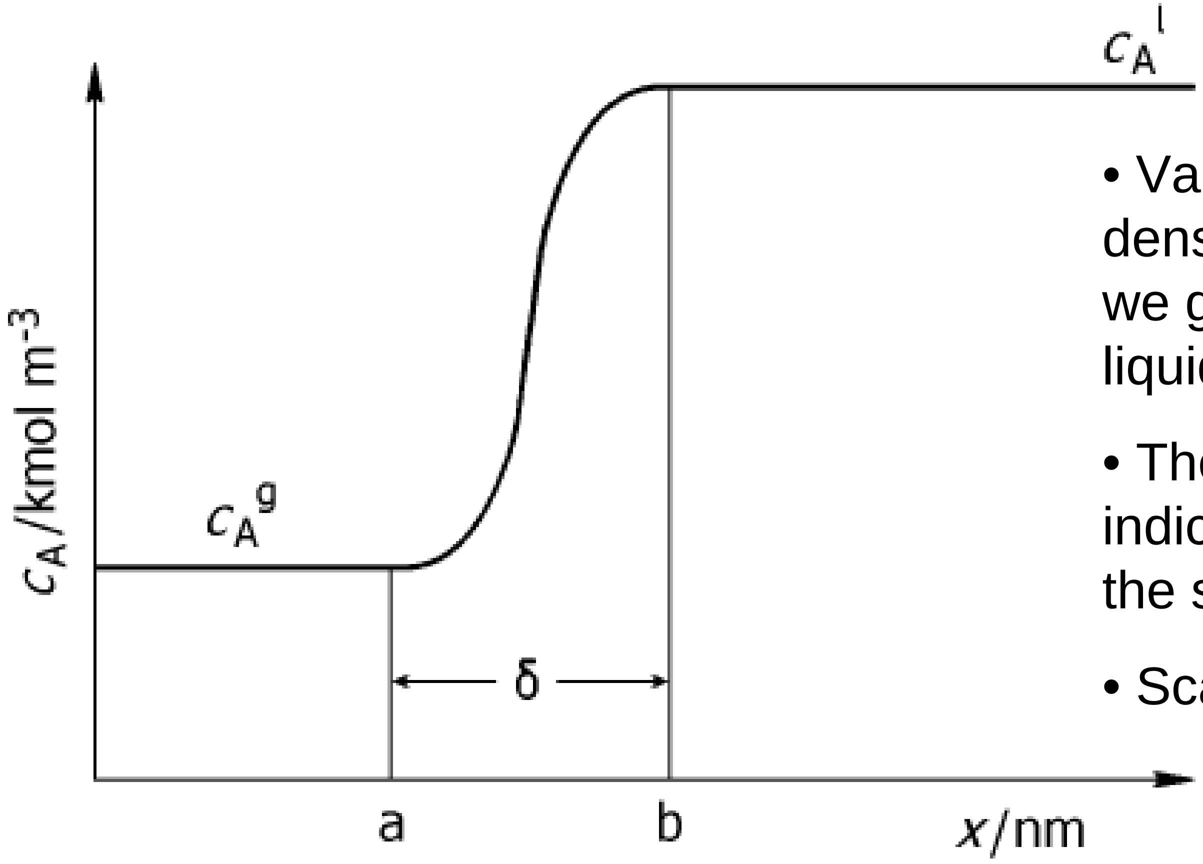
3. Excess densities of an interface

Scientific papers of J.W. Gibbs, Dover, New York, 1961



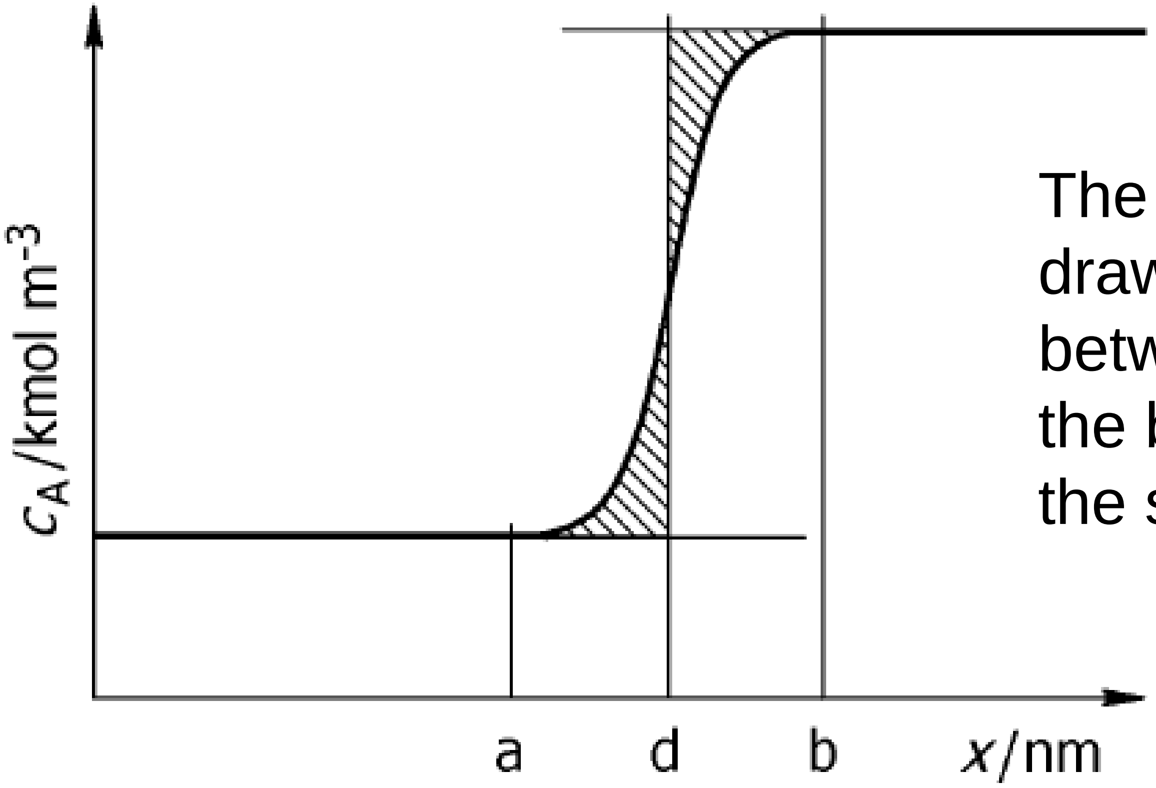
- Variation in the molar density of component A if we go from the gas to the liquid state.
- The vertical lines indicate the extension of the surface.
- Scale in nanometers

The excess density of component A

$$\Gamma_A(y,z) = \int_a^b \left[c_A(x,y,z) - c_A^g(a,y,z)\theta(d-x) - c_A^l(b,y,z)\theta(x-d) \right] dx$$

All excess densities can be defined in this way

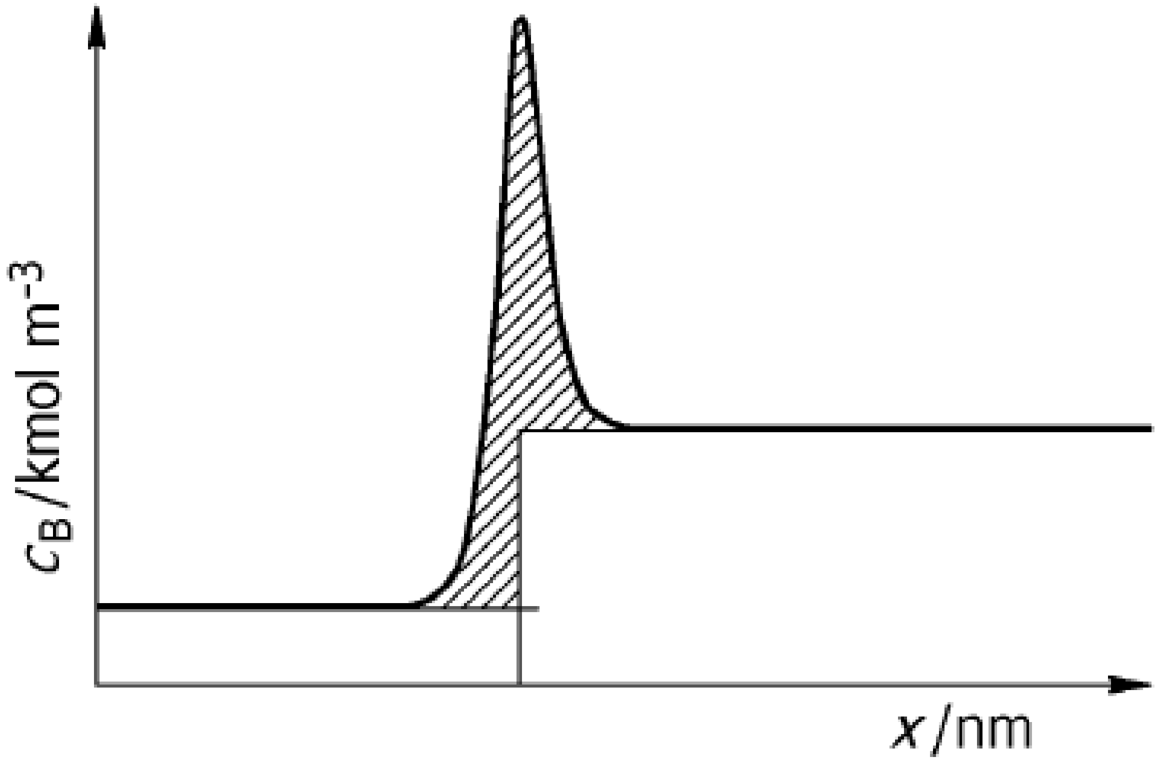
Equimolar surface of component A



The vertical line is drawn so that the areas between the curve and the bulk densities are the same.

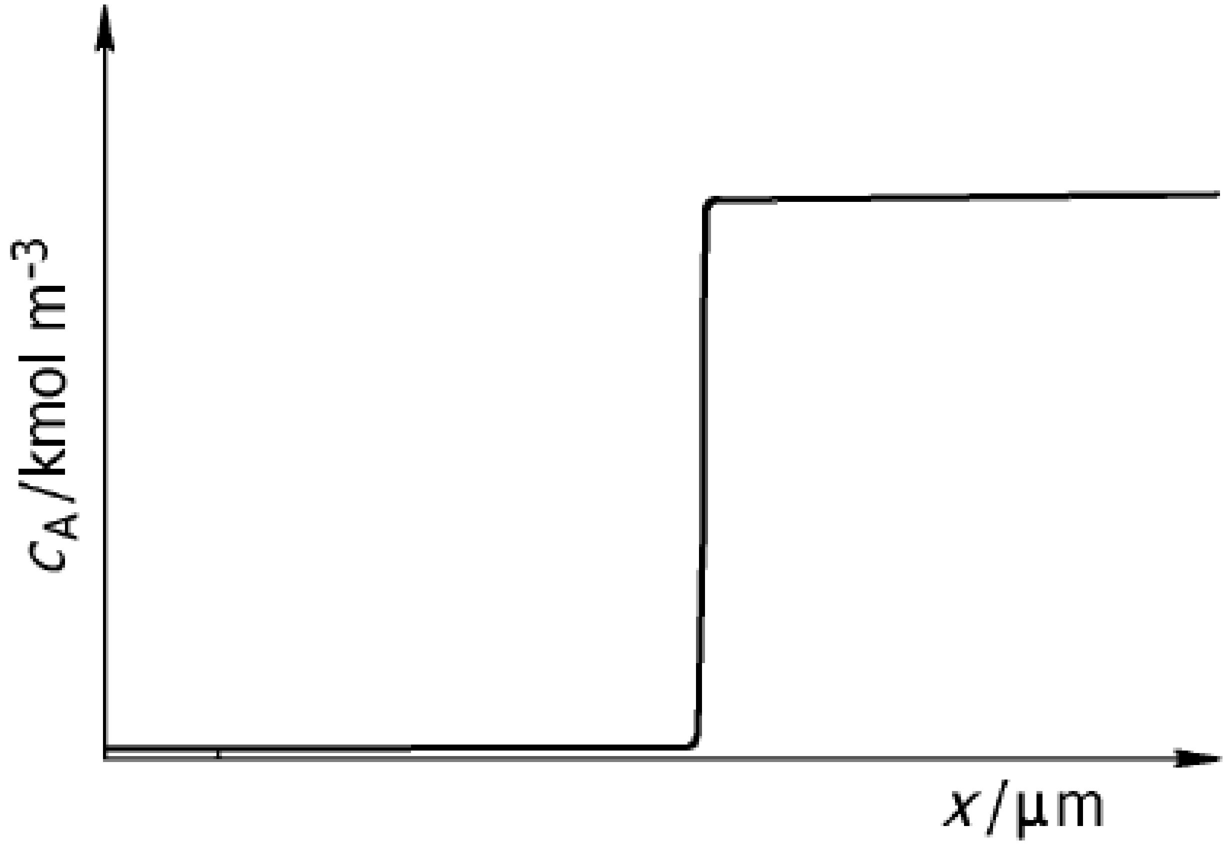
$$\int_a^d \left[c_{\mathrm{A}}(x,y,z) - c_{\mathrm{A}}^{\mathrm{g}}(a,y,z)\right] dx = -\int_d^b \left[c_{\mathrm{A}}(x,y,z) - c_{\mathrm{A}}^{\mathrm{l}}(b,z,y)\right] dx$$

Variation in the density of a surface active component B across the surface



- The excess surface concentration of component B is the integral under the curve in the figure.
- Not advisable to use the equimolar surface for this component

On a micrometer scale

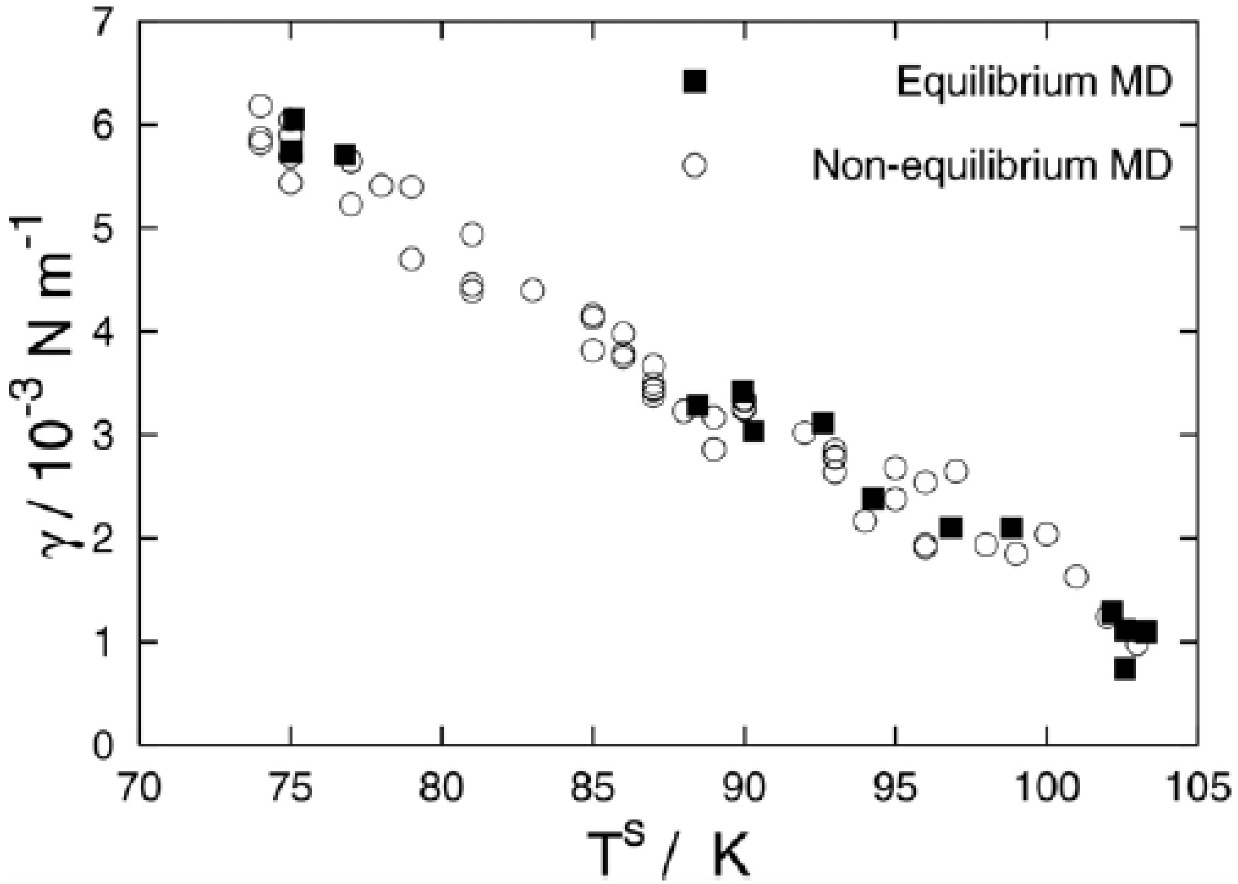


- density profile of component A looks like a Heaviside function
- density profile of component B looks like a generalized function

Remarks about non-equilibrium

- All excess densities can also be defined in non-equilibrium systems.
- The non-equilibrium square gradient model makes it possible to calculate profiles and from these profiles excess densities.
- Questions like how do we define the temperature and chemical potentials for a non-equilibrium surface can be answered.
- At important question to be answered is whether the non-equilibrium surface as described using excess densities is in local equilibrium? And what exactly does this imply?

Local equilibrium for surface tension in MD simulations



Equilibrium and non-equilibrium values are the same → Local equilibrium

A. Røsjorde, D.W. Fossmo, D. Bedeaux, S. Kjelstrup and B. Hafskjold,
J. of Colloid and Int. Science 232 (2000) 178-185; 240 (2001) 355-364.

Local equilibrium of a Gibbs surface under non-equilibrium conditions

Molecular dynamics simulations for 1-component systems

A. Røsjorde, D.W. Fossmo, D. Bedeaux, S. Kjelstrup and B. Hafskjold, J. of Colloid and Int. Science 232 (2000) 178-185; 240 (2001) 355-364
J-M. Simon, S. Kjelstrup, D. Bedeaux, and B. Hafskjold, J. Phys. Chem. B 108 (2004) 7186
J. Xu, S. Kjelstrup and D. Bedeaux, Phys. Chem. Chem. Phys. 8 (2006) 2017-2027
J. Ge, S. Kjelstrup, D. Bedeaux, J-M. Simon, B. Rousseaux, Phys. Rev. E 75 (2007) 061604
S. Kjelstrup, D. Bedeaux, I. Inzoli and J-M. Simon, Energy 33 (2008) 1185-1196.

The square gradient model for 1-component systems

E. Johannessen and D. Bedeaux, Physica A 330 (2003) 354-372

The square gradient model for mixtures

K.S. Glavatskiy and D. Bedeaux, Phys. Rev. E 77 (2008) 061101, 1-15.
K.S. Glavatskiy and D. Bedeaux, Phys. Rev. E 79 (2009) 021608, 1-19.

4. Thermodynamic relations for heterogeneous systems

In a two-phase system there are typically two homogeneous phases and a surface in between.

In the homogeneous phases one has:

- The Gibbs equation:

$$dU = TdS - pdV + \sum_{j=1}^{n} \mu_j dN_j$$

- Integration for constant temperature, pressure and chemical potentials gives:

$$U = TS - pV + \sum_{j=1}^{n} \mu_j N_j$$

- Gibbs-Duhem:

$$0 = SdT - Vdp + \sum_{j=1}^{n} N_j d\mu_j$$

Introduce densities per unit of volume:

$u = U/V$	$n_j = N_j/V$	$s = S/V$
Internal energy	adsorptions	entropy

These densities satisfy:

- Gibbs equation: $$du = Tds + \sum_{j=1}^{n} \mu_j dn_j$$
- Integrated: $$u = Ts - p + \sum_{j=1}^{n} \mu_j n_j$$
- Gibbs-Duhem: $$0 = sdT - dp + \sum_{j=1}^{n} n_j d\mu_j$$

Note that the densities per unit of volume are equal to the molar densities of the quantity considered times the molar dencity *c.*

In a heterogeneous system one does not only need thermodynamic relations in the homogeneous phases but also for the excess densities describing the surface.

- Gibbs equation for the surface:

$$dU^s = TdS^s + \gamma d\Omega + \sum_{j=1}^{n} \mu_j dN_j^s$$

- Integration for constant temperature, surface tension and chemical potentials gives:

$$U^s = TS^s + \gamma \Omega + \sum_{j=1}^{n} \mu_j N_j^s$$

- Gibbs-Duhem:

$$0 = S^s dT + \Omega d\gamma + \sum_{j=1}^{n} N_j^s d\mu_j$$

Introduce densities per unit of surface area:

$u^s = U^s/\Omega$

Internal energy

$\Gamma_j = N_j^s/\Omega$

adsorptions

$s^s = S^s/\Omega$

entropy

These interfacial densities satisfy:

- Gibbs equation:

$$du^s = Tds^s + \sum_{j=1}^{n} \mu_j d\Gamma_j$$

- Integrated:

$$u^s = Ts^s + \gamma + \sum_{j=1}^{n} \mu_j \Gamma_j$$

- Gibbs-Duhem:

$$0 = s^s dT + d\gamma + \sum_{j=1}^{n} \Gamma_j d\mu_j$$

The Gibbs and the Helmholtz energies per unit of surface area are given by:

$$g^s = u^s - Ts^s - \gamma \quad = \sum_{j=1}^{n} \mu_j \Gamma_j$$

$$f^s = u^s - Ts^s \qquad = \gamma + \sum_{j=1}^{n} \mu_j \Gamma_j$$