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

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5. Balance equations with flow. Excess fluxes along the surface

When we describe the system using excess densities, we need balance equations in the homogeneous phases and for the surface.

The balance equations for the homogeneous phases these are the same as those given for the square gradient model and will be presented later.

For the surface we need to account for excess fluxes along the surface and for fluxes into and out of the surface.

For the excess mass density of component j in a mixture we have for instance:

$$\frac{\partial \rho_j^s}{\partial t} = -\nabla_{\|} . \rho_j^s \mathrm{v}_{j,\|}^s + \rho_j^g \left(\mathrm{v}_{j,\perp}^g - \mathrm{v}_{\perp}^s \right) - \rho_j^l \left(\mathrm{v}_{j,\perp}^l - \mathrm{v}_{\perp}^s \right)$$

Here $\rho_j^s \mathrm{v}_{j,\|}^s$ is the excess mass flux of component j along the surface.

Addition over the components gives:

$$\frac{\partial \rho^s}{\partial t} = -\nabla_{\|} . \rho^s \mathrm{v}_{\|}^s + \rho^g \left(\mathrm{v}_{\perp}^g - \mathrm{v}_{\perp}^s \right) - \rho^l \left(\mathrm{v}_{\perp}^l - \mathrm{v}_{\perp}^s \right)$$

where: $\rho^s = \sum_{j=1}^{n} \rho_j^s$ and $\rho^s \mathrm{v}_{\|}^s = \sum_{j=1}^{n} \rho_j^s \mathrm{v}_{j,\|}^s$

Postulates:

- The normal velocity of the surface is independent of the choice of the dividing surface.
- The normal velocity of the surface is the same for all components and energy densities.

Remarks

- The description of transport phenomena parallel to the surface is important and interesting. Because of 2-dimensional isotropy these phenomena do not usually effect the transport through and into the surface directly.
- We shall restrict ourselves to transport normal to the surface.
- In that case the excess fluxes along the surface are zero.
- For the component densities and the total density this gives:

$$\frac{\partial \rho_j^s}{\partial t} = \rho_j^g \left(\mathrm{v}_{j,\perp}^g - \mathrm{v}_\perp^s \right) - \rho_j^l \left(\mathrm{v}_{j,\perp}^l - \mathrm{v}_\perp^s \right)$$

$$\frac{\partial \rho^s}{\partial t} = \rho^g \left(\mathrm{v}_\perp^g - \mathrm{v}_\perp^s \right) - \rho^l \left(\mathrm{v}_\perp^l - \mathrm{v}_\perp^s \right)$$

Remarks continued

- We shall usually use a coordinate frame in which the surface is not moving. The balance equations then become:

$$\frac{\partial \rho_j^s}{\partial t} = \rho_j^g \mathrm{v}_{j,\perp}^g - \rho_j^l \mathrm{v}_{j,\perp}^l \qquad \text{and} \qquad \frac{\partial \rho^s}{\partial t} = \rho^g \mathrm{v}_{\perp}^g - \rho^l \mathrm{v}_{\perp}^l$$

- For the balances of the excess internal energy and entropy for the surface for transport in the normal direction one finds:

$$\frac{\partial u^s}{\partial t} = J_{q,\perp}^g - J_{q,\perp}^l \quad \text{and} \quad \frac{\partial s^s}{\partial t} = J_{s,\perp}^g - J_{s,\perp}^l + \sigma^s \quad \text{where} \quad J_s = \frac{1}{T}\left(J_q - \sum_{j=1}^{n} \mu_j J_j \right)$$

S. Kjelstrup and D. Bedeaux, Series on Advances in Statistical Mechanics-Vol. 16, Non-Equilibrium Thermodynamics of Heterogeneous Systems, World Scientific, Singapore, 2008.

- For the general case where also transport along the surface is involved we refer to:

D. Bedeaux, Non-Equilibrium Thermodynamics and Statistical Physics of Surfaces,

Advances of Chemical Physics 64 (1986) 47 – 109.

6.The local equilibrium assumption for the surface

It assumes that the thermodynamic relations remain valid if the system is away from equilibrium

$$du^s(y,z,t) = T^s(y,z,t)ds^s(y,z,t) + \sum_{j=1}^{n} \mu_j^s(y,z,t)d\Gamma_j(y,z,t)$$

$$u^s(y,z,t) = T^s(y,z,t)s^s(y,z,t) + \gamma(y,z,t) + \sum_{j=1}^{n} \mu_j^s(y,z,t)\Gamma_j(y,z,t)$$

$$0 = s^s(y,z,t)dT^s(y,z,t) + d\gamma(y,z,t) + \sum_{j=1}^{n} \Gamma_j(y,z,t)d\mu_j^s(y,z,t)$$

One may now wonder how quantities like the temperature and the chemical potentials for the surface are defined if the system is not in equilibrium.

Are they equal to the value in one of the adjacent phases?

Such questions have discouraged most workers in the field. It was even said that thermodynamics for the surface was only possible for equilibrium systems when the temperature and the chemical potentials are uniform.

Even the concept of a surface tension for non-equilibrium surfaces was questioned.

It is clear that we will have to be more brave than that!!!

The intensive thermodynamic variables for the surface are:

$$T^s = \left(\frac{du^s}{ds^s}\right)_{\Gamma_j} \quad \text{and } \mu_j^s = \left(\frac{du^s}{d\Gamma_j}\right)_{s^s,\Gamma_k}$$

We find that these variables are perfectly well defined and that they are discontinuous at the surface!!!

All properties of the surface, like the surface tension, the internal energy, the enthalpy, the adsorptions, the diffusion coefficients and the thermal conductivity along the surface, etc., are a function of the surface temperature and chemical potentials.

They do not depend on the temperature and chemical potentials of the adjacent phases!

Postulate:
The temperature and chemical potentials of the surface are independent of the choice of the dividing surface.

It is clear that there are a lot of properties to verify using the continuous square gradient model!