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

Dick Bedeaux

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

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## Balance equations with flow for continuous description of mixtures
## The Gibbs relation, entropy production and force-flux relations

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# 13. Balance equations with flow for the continuous description of mixtures

Balance of mass of the components:

$$\frac{d\rho}{dt} = -\rho\nabla\cdot\mathbf{v}$$

$$\rho\frac{d\xi_k}{dt} = -\nabla\cdot\mathbf{J}_k, \quad k = \overline{1, n-1}$$

The barycentric velocity is given by:

$$\mathbf{v}(\mathbf{r}, t) = \frac{1}{\rho(\mathbf{r}, t)}\sum_{i=1}^{n}\rho_i(\mathbf{r}, t)\mathbf{v}_i(\mathbf{r}, t)$$

And the diffusion fluxes by:

$$\mathbf{J}_k \equiv \rho_k\left(\mathbf{v}_k - \mathbf{v}\right), \qquad k = \overline{1, n-1}$$

$\xi_k$ is the mass fraction and $v_k$ the velocity field of component k

Note that: $\sum_{k=1}^{n} J_k = 0$ and $\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{v}\cdot\nabla$

The equation of motion is:

$$\rho \frac{d\mathrm{v}_\beta}{dt} = -\frac{\partial(\sigma_{\alpha\beta} + \pi_{\alpha\beta})}{\partial x_\alpha} + \rho g_\beta$$

where $\sigma_{\alpha\beta}$ is the pressure tensor, $\pi_{\alpha\beta}$ the viscous pressure tensor and $g_\beta$ the gravitational acceleration. The internal energy balance is:

$$\rho \frac{du}{dt} = -\nabla \cdot \mathbf{J}_q - \pi_{\alpha\beta}\,\mathrm{v}_{\beta\alpha} - p\,\nabla \cdot \mathrm{v} + \mathrm{v}_\beta \frac{\partial \gamma_{\alpha\beta}}{\partial x_\alpha}$$

The first term on the right hand side is a divergence of the heat flux, the 2nd a viscous work term and the last two are work terms due to the pressure tensor.

Here: $$\sigma_{\alpha\beta}(\mathrm{r}) = p(\mathrm{r})\,\delta_{\alpha\beta} + \gamma_{\alpha\beta}(\mathrm{r})$$

The important new term in the internal energy balance is the last term. This term will also feature in the Gibbs relation.

The papers and thesis of Glavatskiy give more details.

# References for mixtures:

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Non-equilibrium properties of a two-dimensional isotropic interface in a two-phase mixture as described by the square gradient model, Phys. Rev. E 77 (2008) 061101.
- K.S. Glavatskiy and D. Bedeaux,
Numerical solution and verification of local equilibrium for the flat interface in the two-phase binary mixture, Phys. Rev. E 79 (2009) 031608, 1-19.
- K.S. Glavatskiy,
Doctoral thesis at NTNU, Trondheim, Norway, 2009: 176, Multi-component interfacial transport as described by the square gradient model; evaporation and condensation.
- K.S. Glavatskiy, D. Bedeaux,
Transport of heat and mass in a two-phase mixture. From a continuous to a discontinuous description, arXiv:1006.5844v1 [cond-mat.soft], J. Chem. Phys., Accepted.
- The thesis of Glavatskiy will appear as a book in the Springer Thesis Series, Autumn 2010.
- K.S. Glavatskiy and D. Bedeaux,
Liquid-vapor interfacial resistances for a binary mixture, preprint.

# The balance of entropy in the continuous case

$$\rho \frac{ds}{dt} = -\nabla \cdot \mathbf{J}_s + \sigma_s$$

Where $J_s$ is the entropy flux and $\sigma_s$ the entropy production.

The aim is now to obtain explicit expressions for the entropy flux and the entropy production in the context of the square gradient model.

The reason that this is not trivial is that in the square gradient model the thermodynamic energy densities depend on the gradients. This implies that the value in a point depends on the densities in neighboring point via the gradient. The square gradient model is therefore not in local equilibrium. How this effects the excess densities is as a consequence a very important issue to be addressed.

# 14. The Gibbs relation for the square gradient model, the entropy production and the force-flux relations

The standard procedure to obtain the entropy flux and the entropy production is to use the Gibbs relation, which expresses the change in the entropy density in terms of the changes in the other thermodynamic densities.

In the square gradient model we postulate the following Gibbs relation:

$$T\rho\frac{ds}{dt} = \rho\frac{du}{dt} - \sum_{i=1}^{n-1}\rho\psi_i\frac{d\xi_i}{dt} + p\rho\frac{dv}{dt} - \mathrm{v}_\beta\frac{\partial\gamma_{\alpha\beta}}{\partial x_\alpha}$$

The important new term in this expression is the last term. It shows that due to the square gradient modifications to the pressure tensor, the divergence of $\gamma_{\alpha\beta}$ gives a contribution to the entropy change. The difference between the parallel and the normal pressure leads to this contribution.

The relation is equivalent to the one given for the 1-component system!

Bedeaux, Johannessen, Røsjorde, Physica A 330 (2003) 329-353

After substitution of the balance equations into the Gibbs relation we find for the entropy flux and production:

$$\mathbf{J}_s = \frac{1}{T}\left(\mathbf{J}_q - \sum_{k=1}^{n-1} \psi_k \mathbf{J}_k\right)$$

$$\sigma_s = \mathbf{J}_q \cdot \nabla \frac{1}{T} - \sum_{k=1}^{n-1} \mathbf{J}_k \cdot \nabla \frac{\psi_k}{T} - \frac{1}{T} \pi_{\alpha\beta} \mathrm{v}_{\beta\alpha}$$

These expressions are identical to the usual expressions. The contributions are due to the heat, the diffusion and the viscous fluxes.

Using that the surface layer is thin compared to the surface, one may use the two-dimensional isotropy of the surface.

The entropy production can be written as the sum of a scalar, a two-dimensional vectorial and a 2x2 tensorial contribution:

$$\sigma_{s,\,scal} = J_{q,\perp}\,\nabla_\perp \frac{1}{T} - \sum_{k=1}^{n-1} J^{m}_{i,\perp}\,\nabla_\perp \frac{\psi_k}{T} - (\nabla_\perp \mathrm{v}_\perp)\,\frac{1}{T}\,\pi_{\perp\perp} - \frac{1}{2}\,(\nabla_\parallel \cdot \mathrm{v}_\parallel)\,\frac{1}{T}\,(\mathrm{Tr}\,\pi_{\parallel\parallel})$$

$$\sigma_{s,\,vect} = \mathbf{J}_{q,\,\parallel} \cdot \nabla_\parallel \frac{1}{T} - \sum_{k=1}^{n-1} \mathbf{J}_{i,\,\parallel} \cdot \nabla_\parallel \frac{\psi_k}{T} - 2\,\mathbf{v}_{\#} \cdot \frac{1}{T}\,\pi_{\#}$$

$$\sigma_{s,\,tens} = (\overset{\circ}{\nabla_\parallel \mathbf{v}_\parallel}) : \frac{1}{T}\,\mathring{\pi}_{\parallel\parallel}$$

where $\mathbf{v}_{\#} \equiv \frac{1}{2}(\nabla_\parallel \mathbf{v}_\perp + \nabla_\perp \mathbf{v}_\parallel)$

Restricting ourselves to fluxes normal to the surface one has:

$$\sigma_{s,\,scal} = J_{q,\perp}\,\nabla_\perp \frac{1}{T} - \sum_{k=1}^{n-1} J^{m}_{i,\perp}\,\nabla_\perp \frac{\psi_k}{T} - (\nabla_\perp \mathrm{v}_\perp)\,\frac{1}{T}\,\pi_{\perp\perp}$$

For transport through and into the surface there are therefore only scalar contributions.

We note that, due to the 2-dimensional isotropy of the surface, fluxes and forces of a different tensorial nature do not couple.

The resulting linear force flux relations are:

$$\nabla_\perp \frac{1}{T} = R_{qq,\perp\perp} J_{q,\perp} - \sum_{k=1}^{n-1} R_{qk,\perp\perp} J^m_{k,\perp} - R_{q\pi,\perp\perp} \pi_{\perp\perp}$$

$$\nabla_\perp \frac{\psi_i}{T} = R_{iq,\perp\perp} J_{q,\perp} - \sum_{k=1}^{n-1} R_{ik,\perp\perp} J^m_{k,\perp} - R_{i\pi,\perp\perp} \pi_{\perp\perp}$$

$$\frac{1}{T} \nabla_\perp \mathrm{v}_\perp = R_{\pi q,\perp\perp} J_{q,\perp} - \sum_{k=1}^{n-1} R_{\pi k,\perp\perp} J^m_{k,\perp} - R_{\pi\pi,\perp\perp} \pi_{\perp\perp}$$

It follows from the Onsager reciprocal relations that the resistance matrix is symmetric.

To simplify the analysis, and because it is expected that these contributions are small, we neglect the viscous term.

$$\nabla_\perp \frac{1}{T} = R_{qq,\perp\perp} J_{q,\perp} - \sum_{k=1}^{n-1} R_{qk,\perp\perp} J^m_{k,\perp}$$

$$\nabla_\perp \frac{\psi_i}{T} = R_{iq,\perp\perp} J_{q,\perp} - \sum_{k=1}^{n-1} R_{ik,\perp\perp} J^m_{k,\perp}$$

This still leaves us with 0.5 n(n+1) independent resistances.

For binary mixtures, which is our main concern, this are 3 terms.

In the application the question arises how do we obtain these resistances. On the vapor side we have some help from kinetic theory. On the liquid side we can use experimental values when available. In the interfacial region there is some evidence from molecular dynamics simulations that there is a small peak. We will return to this.

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