

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

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4th Lecture

The entropy production, the force-flux relations
and the Onsager relations.

Numerical solution method for stationary states.

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7. The entropy production and the force-flux relations for the square gradient model

In order to verify the properties that are hopefully true for the description in terms of excess densities, we must carry the analysis further for the continuous square gradient model and proof these properties. We only consider flow normal to the surface in a one-component system to begin with.

Balance equations

Conservation of matter:
$$\frac{\partial c(x,t)}{\partial t} = -\frac{\partial J(x,t)}{\partial x} = -\frac{\partial c(x,t)v(x,t)}{\partial x}$$

The barycentric time derivative is:
$$\frac{d}{dt} \equiv \frac{\partial}{\partial t} + v(x,t) \frac{\partial}{\partial x}$$

For the molar volume it follows that:
$$c(x,t) \frac{dV(x,t)}{dt} = \frac{\partial v(x,t)}{\partial x}$$

For a system without gravitational forces or viscous friction we have:

$$M c(x, t) \frac{dv(x, t)}{dt} = M \left[\frac{\partial J(x, t)}{\partial t} + \frac{\partial J(x, t) v(x, t)}{\partial x} \right] = - \frac{\partial p_{\perp}(x, t)}{\partial x}$$

where M is the molar mass.

The total molar energy is the sum of internal and kinetic energy:

$$E(x, t) = U(x, t) + \frac{1}{2} M v^2(x, t)$$

The total molar energy is conserved: $\frac{\partial c(x, t) E(x, t)}{\partial t} = - \frac{\partial J_e(x, t)}{\partial x}$

The heat flux is defined by: $J_e(x, t) \equiv J(x, t) E(x, t) + p_{\parallel}(x, t) v(x, t) + J'_q(x, t)$

Substitution in the energy conservation law gives:

$$c(x, t) \frac{dE(x, t)}{dt} = - \frac{\partial}{\partial x} [p_{\parallel}(x, t) v(x, t) + J'_q(x, t)]$$

For the kinetic energy we have:

$$c(x, t) \frac{d}{dt} \left(\frac{1}{2} M v^2(x, t) \right) = - v(x, t) \frac{\partial}{\partial x} p_{\perp}(x, t)$$

Combining the last two equations gives for the internal energy:

$$\begin{aligned} \frac{\partial c(x,t) U(x,t)}{\partial t} + \frac{\partial}{\partial x} [J(x,t) H(x,t) - p_{\perp}(x,t) v(x,t)] \\ = -\frac{\partial J'_q(x,t)}{\partial x} - p_{\perp}(x,t) \frac{\partial v(x,t)}{\partial x} \end{aligned}$$

The entropy production

The entropy balance is:

$$\begin{aligned} c(x,t) \frac{dS(x,t)}{dt} &= \frac{\partial c(x,t) S(x,t)}{\partial t} + \frac{\partial J(x,t) S(x,t)}{\partial x} \\ &= -\frac{\partial J_s(x,t)}{\partial x} + \sigma(x,t) \end{aligned}$$

Now we should substitute the balance equations into the Gibbs relation to obtain explicit expressions for the entropy flux and the entropy production.

The Gibbs relation

In order to further proceed we now **postulate** the Gibbs relation. The only way to verify its validity is that the further results make sense in the thermodynamic description.

$$T(x, t) \frac{dS(x, t)}{dt} = V(x, t) \left\{ \frac{\partial c(x, t) U(x, t)}{\partial t} + \frac{\partial}{\partial x} [J(x, t) (H(x, t) - p_{\perp}(x, t) V(x, t))] \right\} + p_{\perp}(x, t) \frac{dV(x, t)}{dt}$$

In the homogeneous phases $p_{\perp} = p_{\parallel}$ so that the first term on the right hand side reduces to the usual form dU/dt .

In the interfacial region the difference between the parallel and the normal pressure leads to a difference.

It is definitely not correct to use the above expression with the parallel pressure. The description is then found to make no sense.

The entropy flux and production

Substitution of the balance equations for the internal energy and the molar volume gives:

$$\begin{aligned}c(x, t) \frac{dS(x, t)}{dt} &= -\frac{1}{T(x, t)} \frac{\partial J'_q(x, t)}{\partial x} \\ &= -\frac{\partial}{\partial x} \left[\frac{J'_q(x, t)}{T(x, t)} \right] + J'_q(x, t) \frac{\partial}{\partial x} \left[\frac{1}{T(x, t)} \right]\end{aligned}$$

It follows that the entropy flux and production are given by:

$$J_s(x, t) = \frac{J'_q(x, t)}{T(x, t)}$$

$$\sigma = J'_q(x, t) \frac{\partial}{\partial x} \left[\frac{1}{T(x, t)} \right] = -\frac{J'_q(x, t)}{T^2(x, t)} \frac{\partial T(x, t)}{\partial x}$$

This are the usual expressions in a 1-component system

The force-flux relation

In non-equilibrium thermodynamics it follows from the entropy production that the force-flux relation is given by:

$$\frac{\partial T(x, t)}{\partial x} = -r(x, t) J'_q(x, t)$$

Alternatively we may write this as:

$$J'_q(x, t) = -\frac{1}{r(x, t)} \frac{\partial T(x, t)}{\partial x} = -\lambda(x, t) \frac{\partial T(x, t)}{\partial x}$$

This is Fourier's law. λ is the thermal conductivity. We will refer to r as the thermal resistivity. In order to satisfy the second law both r and λ are positive.

We note that we adsorbed a factor T^{-2} from the thermodynamic force in the resistance.

The continuous thermal resistivity

For the numerical analysis we need explicit values of the resistivity. In view of the fact that all thermodynamic quantities may depend on the spacial derivatives of the molar density we now have:

$$r(x, t) = r \left(T(x, t), c(x, t), \frac{dc(x, t)}{dx}, \frac{d^2c(x, t)}{dx^2}, \dots \right)$$

The expression must be such that $r > 0$ to satisfy the 2nd law.

$$r(x, t) = r_{coex}^g(T(x, t)) + \left(r_{coex}^l(T(x, t)) - r_{coex}^g(T(x, t)) \right) \left(\frac{c(x, t) - c_{coex}^g(T(x, t))}{c_{coex}^l(T(x, t)) - c_{coex}^g(T(x, t))} \right) + \alpha(T(x, t), c(x, t)) m \left(\frac{dc(x, t)}{dx} \right)^2$$

The first two terms give a contribution which changes smoothly from the vapor to the liquid value through the interfacial region. The last term contributes a peak in the interfacial region.

For the values along the coexistence one should preferably use experimental data when these are available.

In molecular dynamics simulations a small peak was found on the vapor side of the surface. We therefore used the following expression for alpha:

$$\alpha(T(x), c(x)) = \alpha \left(\frac{c_{coex}^1(T_{eq})}{c(x)} \right)^2$$

In the outset we expected the contribution due to the peak to increase with the surface tension. This is the reason for the factor m . This was not correct. In the work with Glavatskiy we therefore changed the choice of αm .

J-M. Simon, S. Kjelstrup, D. Bedeaux, and B. Hafskjold,
Thermal Flux through a Surface of n-Octane. A Non-Equilibrium Molecular Dynamics Study,
J. Phys. Chem. B 108 (2004) 7186-7195.

8. Numerical solution method for stationary states

As it is not possible to solve the various equations analytically we have to use numerical methods. For stationary states it follows from the balance equations that

$$J(x), p_{\perp}(x) + MJv(x) \text{ and } J_q(x) + \frac{1}{2}MJv^2(x)$$

are independent of the position. Furthermore we need a scaling length for which we use: $x_S \equiv 7\xi_W^1(p_{eq})$

where the correlation length in the liquid is given by:

$$\begin{aligned} \xi^1(p_{eq}) &= c_{eq}^1(p_{eq}) \sqrt{m\kappa_{eq}^1(p_{eq})} \\ &= c_{eq}^1(p_{eq}) \sqrt{m} \left[\frac{c_{eq}^1(p_{eq})RT_{eq}(p_{eq})}{(1 - Bc_{eq}^1(p_{eq}))^2} - 2A (c_{eq}^1(p_{eq}))^2 \right]^{-1/2} \end{aligned}$$

For 200 bar we find $x_S = 2.8062 \text{ nm}$

The temperature, pressure and molar density were scaled with

$$T_S \equiv T_{eq}(p_{eq}), \quad p_S \equiv p_{eq} \quad \text{and} \quad c_S \equiv c_{eq}^l(p_{eq})$$

When $p_{eq} = 200$ bar, the scaling parameters are

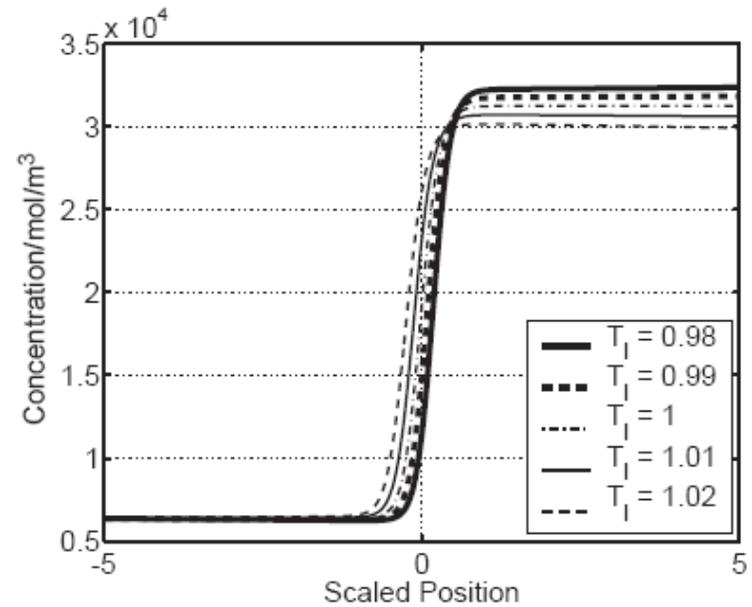
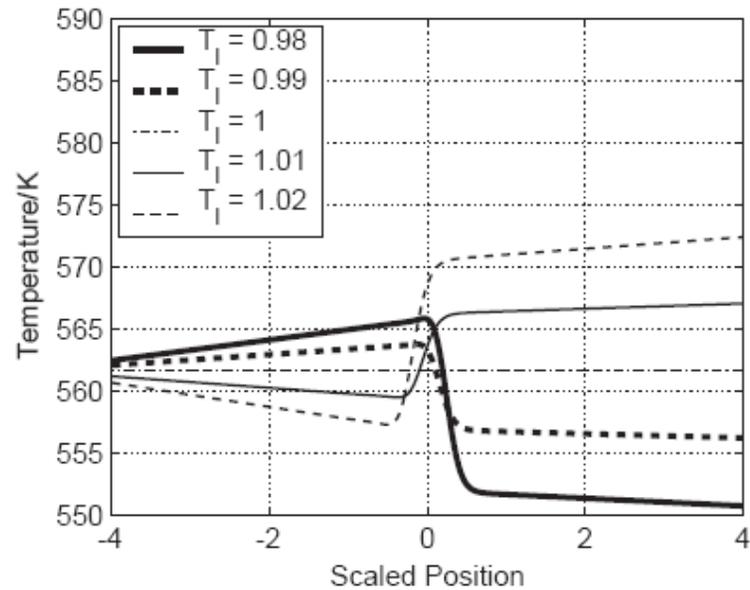
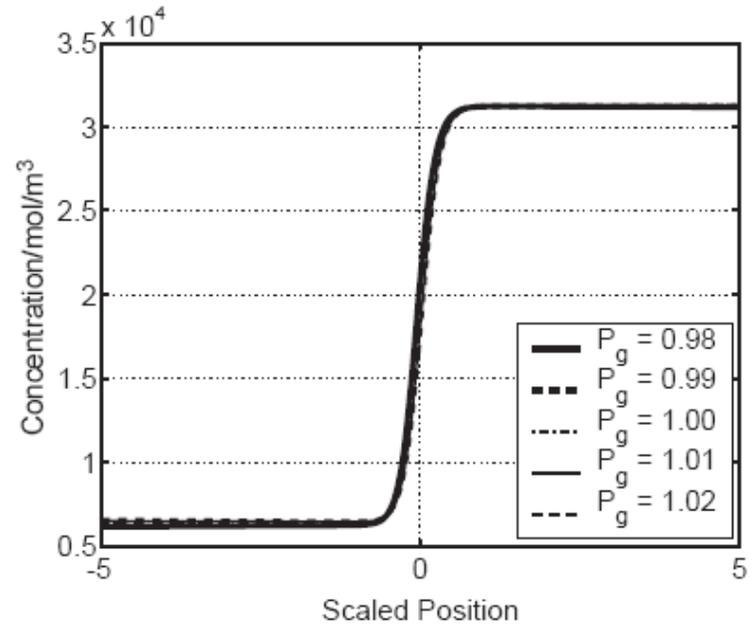
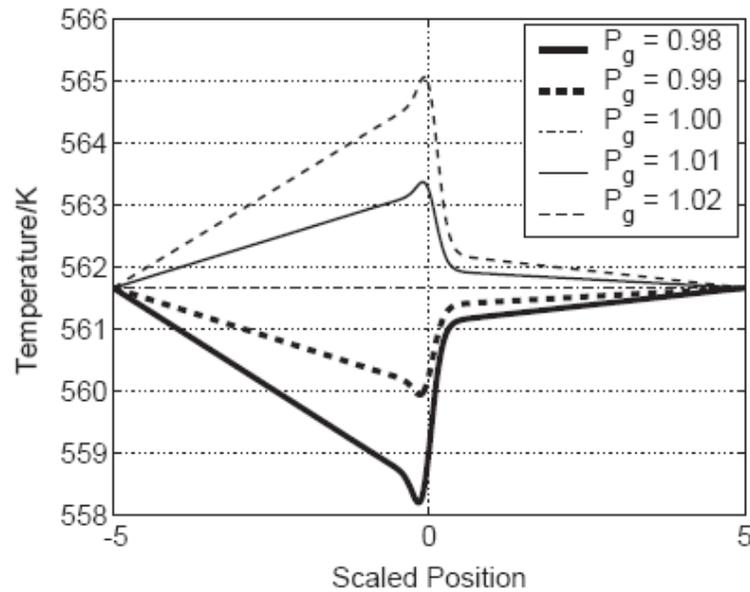
$$x_S = 2.8062 \text{ nm}, \quad T_S = 561.65 \text{ K}, \quad p_S = 200 \text{ bar}, \quad c_S = 3.1243 \times 10^4 \text{ mol/m}^3$$

The size of the box was $10x_S = 28.062$ nm.

In the first set of cases, the pressure at the vapor end of the box was changed to 0.98, 0.99, 1.01 or 1.02 times $p_S = p_{eq} = 200$ bar, while the temperatures at the ends were kept equal to $T_S = T_{eq}(p_{eq})$. In the second set of cases, the temperature at the liquid end was set to 0.98, 0.99, 1.01 or 1.02 times $T_S = 561.65$ K, while the pressure and the temperature at the other end were kept equal to $p_S = p_{eq} = 200$ bar and $T_S = T_{eq}(p_{eq})$. The four first cases were named PG98, PG99, PG101, PG102, and the four last were named TL98, TL99, TL101, and TL102 respectively.

We used $\alpha = 5 \times 10^{-4}$ for the figures on the following page

This enabled us to calculate stationary temperature and density profiles



- The temperature profiles are most interesting. They show large gradients of the temperature of up to 10^8 K/m.
- In the interfacial region we see that the profile may have a peak (or a dip) above (below) the extrapolated profiles from the homogeneous phases.
- The density profiles for the pressure changes have only rather small changes.
- The density profiles for the temperature changes in the liquid are due to the change of the coexistence density of the liquid with the temperature. The location of the interface has a corresponding change to keep the total mass in the box the same.

Using the profiles of the mass, energy and entropy densities one can calculate all the excess densities relative to a dividing surface x_s .

As one can see in the figure for the Helmholtz energy for TL102, one needs to **extrapolate** the densities from the bulk phases to the surface.

The vertical line is the equimolar surface. It is important to realise that

The extrapolation procedure leads to a certain numerical error in the excess densities obtained. This is a pity but it is unavoidable.

We have already discussed how to obtain excess densities.

