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

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6th Lecture

The excess entropy production
Integral relations for the resistivities

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11. The excess entropy production

The excess entropy production is given by:

$$\sigma^{\mathrm{S}} = \int_{x_{in}}^{x_{out}} dx \left\{ J_q'(x) \frac{d}{dx} \left[\frac{1}{T(x)} \right] - J_q'^{\mathrm{g}}(x) \frac{d}{dx} \left[\frac{1}{T^{\mathrm{g}}(x)} \right] \theta(x^{\mathrm{S}} - x) \right.$$

$$\left. - J_q'^{\mathrm{l}}(x) \frac{d}{dx} \left[\frac{1}{T^{\mathrm{l}}(x)} \right] \theta(x - x^{\mathrm{S}}) \right\}$$

In order to write this in the proper form we use $J_q'(x) = J_q - H(x)J$ where we neglect the small kinitic energy term.

$$\sigma^{\mathrm{S}} = J_q \int_{x_{in}}^{x_{out}} dx \left\{ \frac{d}{dx} \left[\frac{1}{T(x)} \right] - \frac{d}{dx} \left[\frac{1}{T^{\mathrm{g}}(x)} \right] \theta(x^{\mathrm{S}} - x) \right.$$

$$\left. - \frac{d}{dx} \left[\frac{1}{T^{\mathrm{l}}(x)} \right] \Theta(x - x^{\mathrm{S}}) \right\} - J \int_{x_{in}}^{x_{out}} dx \left\{ H(x) \frac{d}{dx} \left[\frac{1}{T(x)} \right] \right.$$

$$\left. - H^{\mathrm{g}}(x) \frac{d}{dx} \left[\frac{1}{T^{\mathrm{g}}(x)} \right] \Theta(x^{\mathrm{S}} - x) - H^{\mathrm{l}}(x) \frac{d}{dx} \left[\frac{1}{T^{\mathrm{l}}(x)} \right] \theta(x - x^{\mathrm{S}}) \right\}$$

Integrating the first term gives:

$$\sigma^{s} = J_{e}\left[\frac{1}{T^{l}(x^{s})} - \frac{1}{T^{g}(x^{s})}\right] - J\int_{x_{in}}^{x_{out}} dx\left\{H(x)\frac{d}{dx}\left[\frac{1}{T(x)}\right]\right.$$

$$\left. -H^{g}(x)\frac{d}{dx}\left[\frac{1}{T^{g}(x)}\right]\Theta(x^{s}-x) - H^{l}(x)\frac{d}{dx}\left[\frac{1}{T^{l}(x)}\right]\theta(x-x^{s})\right\}$$

The Gibbs-Helmholtz equation for constant pressure is:

$$H(x)\frac{d}{dx}\left(\frac{1}{T(x)}\right) = \frac{d}{dx}\left(\frac{\mu(x)}{T(x)}\right)$$

This results in:

$$\sigma^{s} = J_{q}\left[\frac{1}{T^{l}(x^{s})} - \frac{1}{T^{g}(x^{s})}\right] - J\int_{x_{in}}^{x_{out}} dx\left\{\frac{d}{dx}\left(\frac{\mu(x)}{T(x)}\right)\right.$$

$$\left. -\frac{d}{dx}\left(\frac{\mu^{g}(x)}{T^{g}(x)}\right)\Theta(x^{s}-x) - \frac{d}{dx}\left(\frac{\mu^{l}(x)}{T^{l}(x)}\right)\Theta(x-x^{s})\right\}$$

$$= J_{q}\left[\frac{1}{T^{l}(x^{s})} - \frac{1}{T^{g}(x^{s})}\right] - J\left[\frac{\mu^{l}(x^{s})}{T^{l}(x^{s})} - \frac{\mu^{g}(x^{s})}{T^{g}(x^{s})}\right]$$
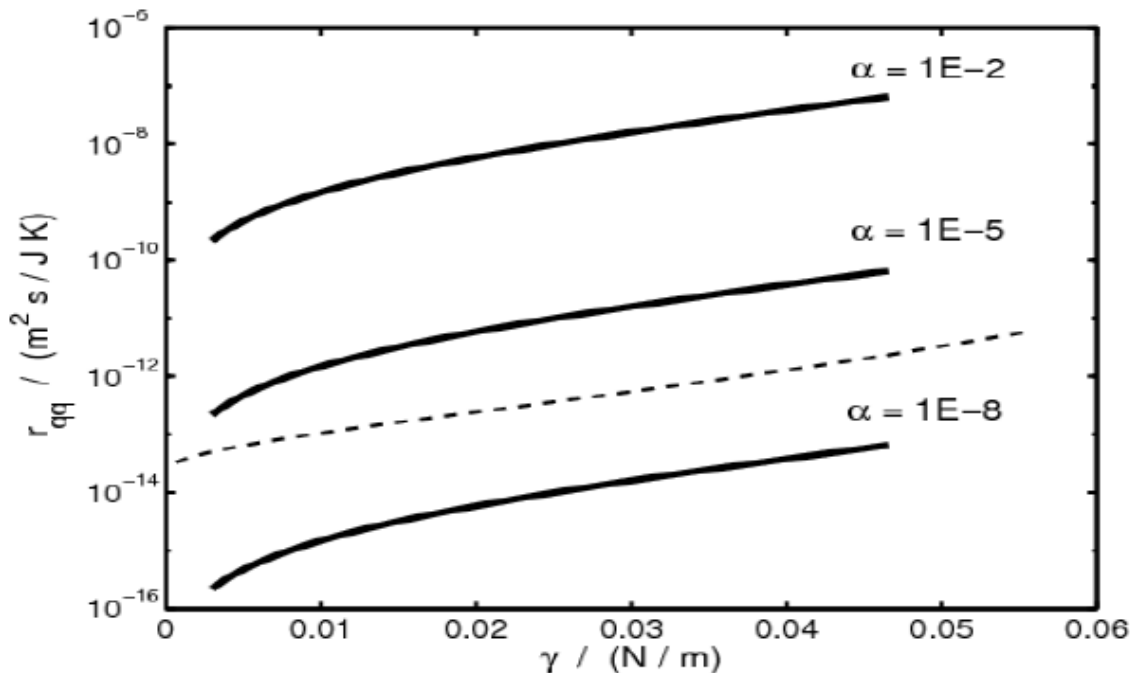
Reintroducing the measurable heat flux on the vapor side gives:

$$\sigma^s = J_q'^g(x^s)\left[\frac{1}{T^l(x^s)} - \frac{1}{T^g(x^s)}\right] - J\left[\frac{\mu^l(T^l(x^s)) - \mu^g(T^l(x^s))}{T^l(x^s)}\right]$$

The resulting force-flux relations are:

$$\frac{1}{T^l(x^s)} - \frac{1}{T^g(x^s)} = r_{qq}^s J_q'^g(x^s) + r_{q\mu}^s J$$

$$-\frac{\mu^l(T^l(x^s)) - \mu^g(T^l(x^s))}{T^l(x^s)} = r_{\mu q}^s J_q'^g(x^s) + r_{\mu\mu}^s J$$

The resulting values for the heat transfer resistivity for 3 choices of alpha. The dashed line are the kinetic theory values. One can fit alpha using the kinetic theory values.

Concluding remarks for the one component system

• The description using Gibbs excess densities has been shown to be robustly valid for excess densities obtained using the continuous square gradient description for stationary states.

• The temperature and chemical potential can be defined in a multitude of ways and are independent of the location of the dividing surface.

• The behavior of the various profiles through the stationary state interface resembles equilibrium behavior at the temperature and chemical potential of the surface to a surprising degree.

• Remains the task to verify all these properties for mixtures.

12. Integral relations for the resistivities

A convenient method to calculate the overall resistivities from the resistivities in the continuous description are integral relations. We will derive them for the one-component case. We have:

$$\frac{\partial}{\partial x}\frac{1}{T(x)} = -\frac{1}{T^2(x)}\frac{\partial T(x)}{\partial x} = \frac{r(x)}{T^2(x)}J'_q(x) \equiv r_{qq}(x)J'_q(x)$$

Integration of this equation from $x^{s,g}$ to $x^{s,l}$, which are just left and right of the interfacial region gives:

$$\frac{1}{T^l} - \frac{1}{T^g} = \int_{x^{s,g}}^{x^{s,l}} J'_q(x)r_{qq}(x)\,dx$$

$$= J_q \int_{x^{s,g}}^{x^{s,l}} r_{qq}(x)\,dx - J \int_{x^{s,g}}^{x^{s,l}} r_{qq}(x)h(x)\,dx$$

$$= J'_q(x^{s,g}) \int_{x^{s,g}}^{x^{s,l}} r_{qq}(x)\,dx + J \int_{x^{s,g}}^{x^{s,l}} r_{qq}(x)[h(x^{s,g}) - h(x)]\,dx$$

Comparing this with the result on a previous transparacy gives

the first two of the following equations:

$$r_{qq}^{s} = \int_{x^{s,\theta}}^{x^{s,l}} r_{qq}(x)\, dx$$

$$r_{q\mu}^{s} = r_{\mu q}^{s} = \int_{x^{s,\theta}}^{x^{s,l}} r_{qq}(x)[h(x^{s,\theta}) - h(x)]\, dx$$

$$r_{\mu\mu}^{s} = \int_{x^{s,\theta}}^{x^{s,l}} r_{qq}(x)[h(x^{s,\theta}) - h(x)]^{2}\, dx$$

This are the integral relations. To linear order in the deviation from equilibrium one may replace the enthalpy profile by the equilibrium profile. This implies that the overall coefficients can be obtained using only equilibrium simulations once one knows the continuous resistivity profile. This simplifies the analysis considerably.

If one has done molecular dynamics simulations of heat transport such information is often available.

# We have verified this for simulations of Argon like particles
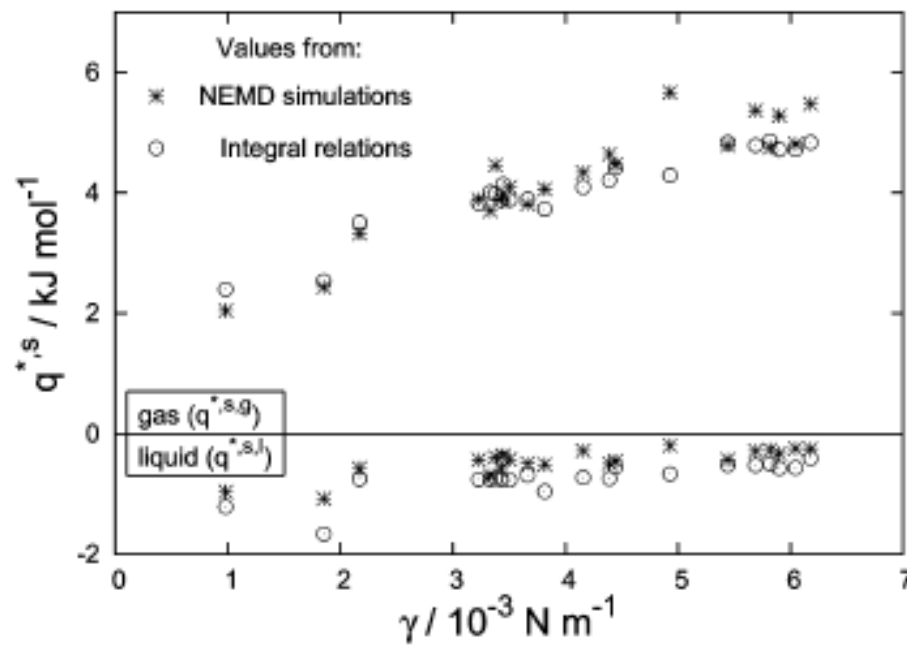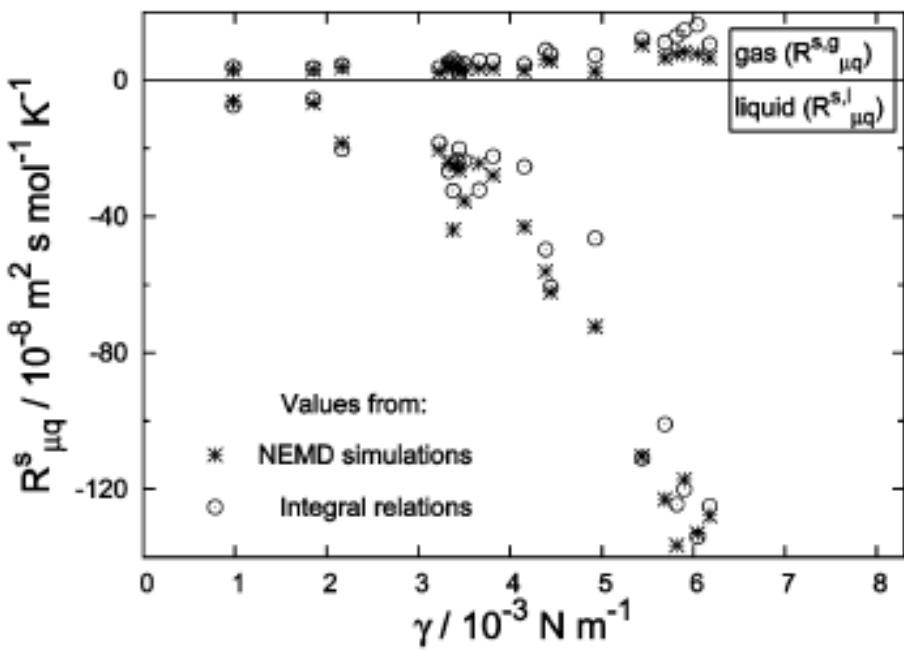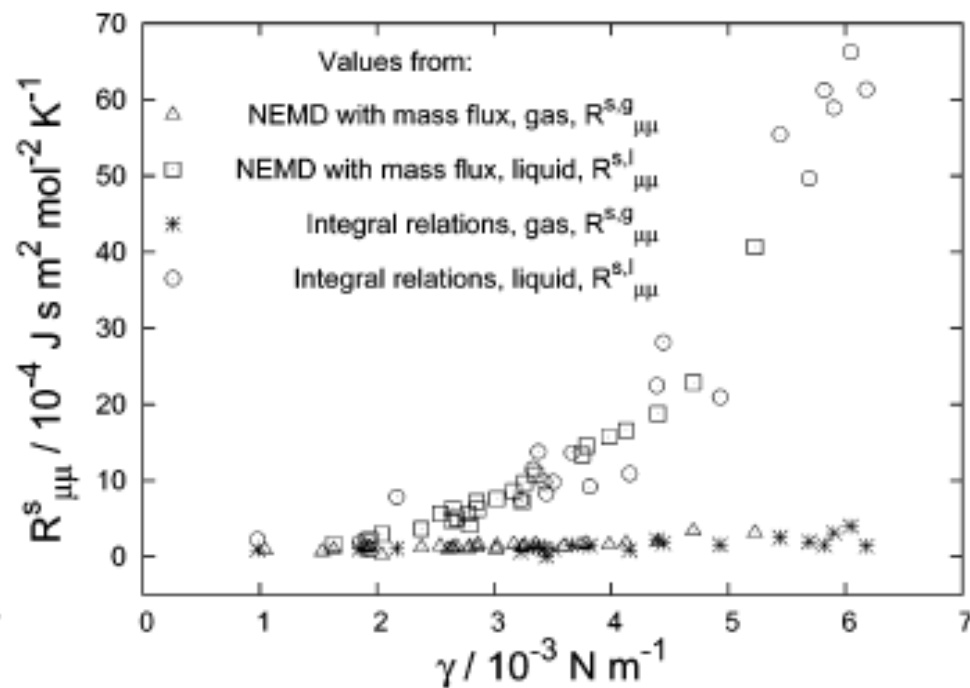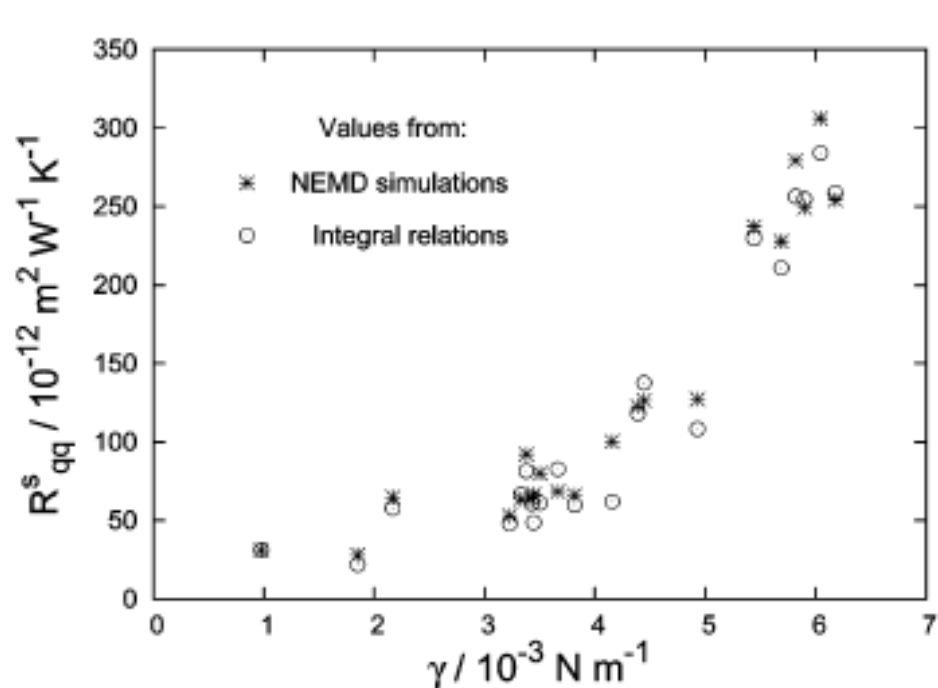
• We have also verified it for simulations of two phase octane. This also worked well. In that case we had only been able to obtain 2 resistivities from the simulations, which were rather time consuming. The integral relations gave us also the third independent resistivity.

• Using the integral relations we were also able to verify the existence of the rather paradoxical inverted temperature profile found using kinetic theory. See next page.

• E. Johannessen and D. Bedeaux, Integral Relations for the Heat and Mass Transfer Resistivities of the Liquid-Vapor Interface. Physica A 370 (2006) 258-274

• Simon, J.M., Bedeaux, D., Kjelstrup, S., Xu , J., and Johannessen, E., 2006, Interface Film Resistivities for Heat and Mass Transfer, Integral Relations verified by Non-equilibrium Molecular Dynamics. *J. Phys. Chem. B*, Vol. 110, pp. 18528-18536.

Using the integral relations we could generally show that the temperature profile between a evaporating and condensing liquid is inverted.
This property was predicted by Pao using kinetic theory.
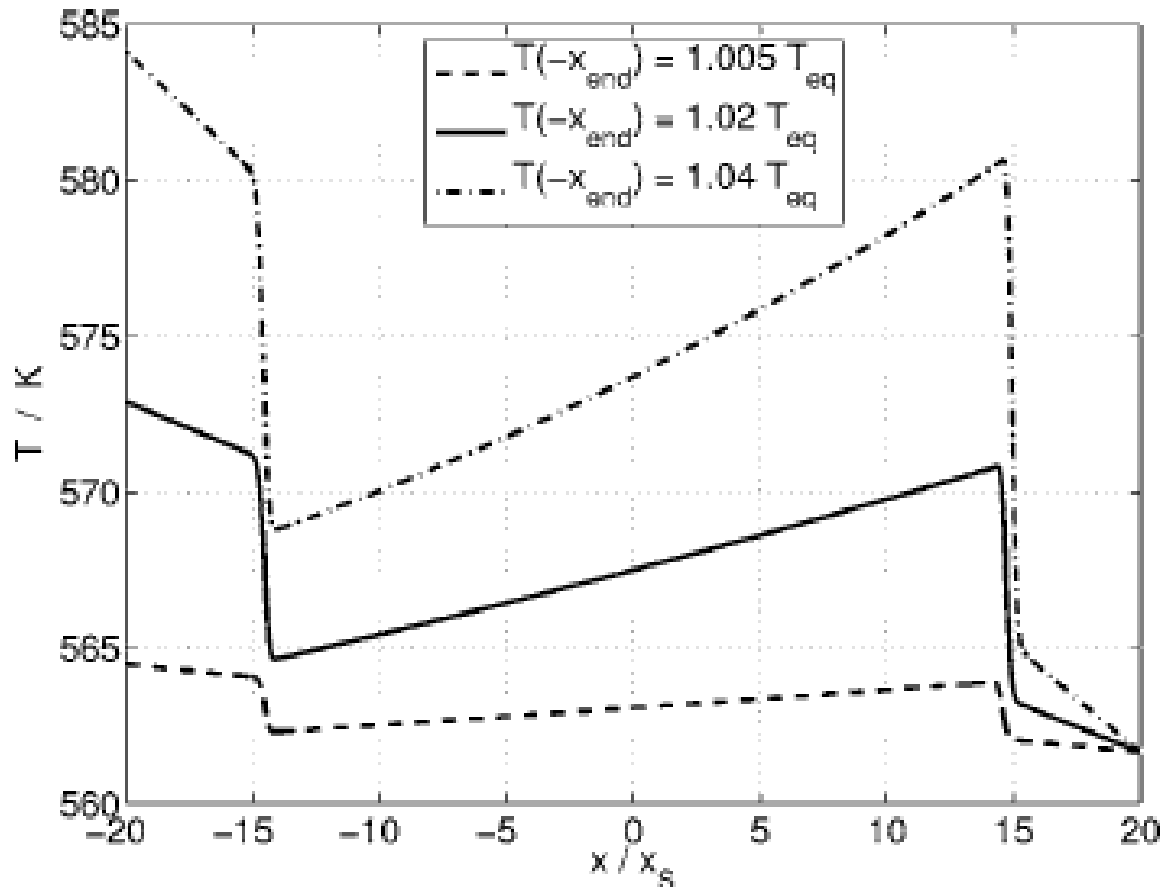
• Johannessen, E., and Bedeaux, D., 2007, Integral Relations for the Interfacial Heat and Mass Transfer Resistivities and the Inverted Temperature Profile. *Phys. of Fluids*, Vol. 19, pp. 017104, 1-7.
• Pao, Y.P., 1971a, Application of kinetic theory to problem of evaporation and condensation, *Phys. Fluids*, Vol. 14, pp. 306-312.