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

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11th Lecture

Surface transfer resistivities for a binary mixture
Integral relations

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20. Surface transfer resistivities for a binary mixture

Consider a stationary state which is perturbed from equilibrium by setting the temperature of the liquid[3] $T(x^\ell) = (1+\beta_T)T_{eq}$, the pressure of the gas $p(x^g) = (1+\beta_p)p_{eq}$ and the mole fraction of the liquid $\zeta^\ell(x^\ell) = (1+\beta_\zeta)\zeta^\ell_{eq}$

The resulting stationary state satisfies:

$$\mathrm{X}(\beta_T, \beta_p, \beta_\zeta) = \mathrm{R}(T_{eq}, \psi_{eq}) \cdot \mathrm{J}(\beta_T, \beta_p, \beta_\zeta)$$

where X and J are vectors of forces and fluxes and R a matrix of resistivities. Next we consider the following perturbations:

$$\begin{array}{rcl}
\mathrm{X}(\ \ \beta,\ \ \beta,\ \ \beta) & = & \mathrm{R}(T_{eq}, \psi_{eq}) \cdot \mathrm{J}(\ \ \beta,\ \ \beta,\ \ \beta) \\
\mathrm{X}(\ \ \beta,-\beta,\ \ \beta) & = & \mathrm{R}(T_{eq}, \psi_{eq}) \cdot \mathrm{J}(\ \ \beta,-\beta,\ \ \beta) \\
\mathrm{X}(-\beta,\ \ \beta,\ \ \beta) & = & \mathrm{R}(T_{eq}, \psi_{eq}) \cdot \mathrm{J}(-\beta,\ \ \beta,\ \ \beta) \\
\mathrm{X}(-\beta,-\beta,\ \ \beta) & = & \mathrm{R}(T_{eq}, \psi_{eq}) \cdot \mathrm{J}(-\beta,-\beta,\ \ \beta) \\
\mathrm{X}(\ \ \beta,\ \ \beta,-\beta) & = & \mathrm{R}(T_{eq}, \psi_{eq}) \cdot \mathrm{J}(\ \ \beta,\ \ \beta,-\beta) \\
\mathrm{X}(\ \ \beta,-\beta,-\beta) & = & \mathrm{R}(T_{eq}, \psi_{eq}) \cdot \mathrm{J}(\ \ \beta,-\beta,-\beta) \\
\mathrm{X}(-\beta,\ \ \beta,-\beta) & = & \mathrm{R}(T_{eq}, \psi_{eq}) \cdot \mathrm{J}(-\beta,\ \ \beta,-\beta) \\
\mathrm{X}(-\beta,-\beta,-\beta) & = & \mathrm{R}(T_{eq}, \psi_{eq}) \cdot \mathrm{J}(-\beta,-\beta,-\beta)
\end{array}$$

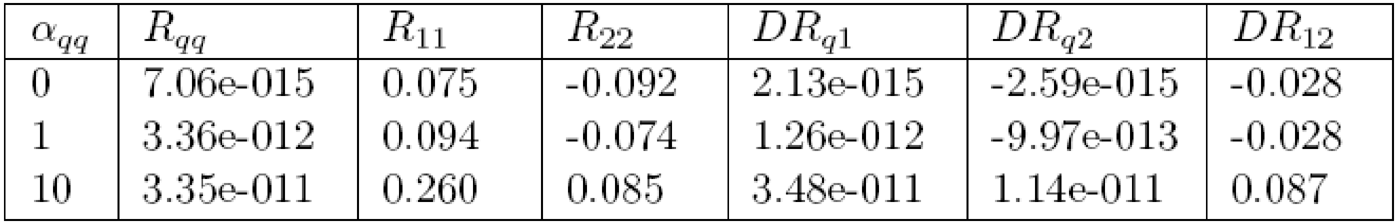
The resulting resistivity matrix is a quadratic function of beta. We find that beta=0.0002 gives an error of 0.1 permille.

Second law consistency

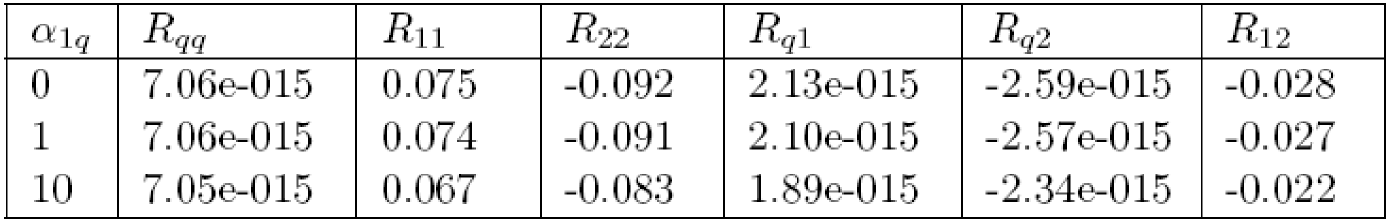
In order to assure that the excess entropy of the surface always increases, the diagonal resistivities and

$$DR_{ik} \equiv R_{ii}R_{kk} - \frac{1}{4}(R_{ik} + R_{ki})^2$$

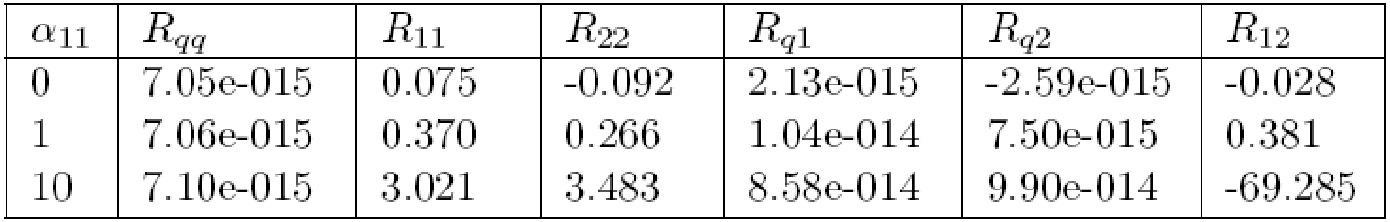
must all be positive. We find for the different alphas:



α_{qq}	R_{qq}	R_{11}	R_{22}	DR_{q1}	DR_{q2}	DR_{12}
0	7.06e-015	0.075	-0.092	2.13e-015	-2.59e-015	-0.028
1	3.36e-012	0.094	-0.074	1.26e-012	-9.97e-013	-0.028
10	3.35e-011	0.260	0.085	3.48e-011	1.14e-011	0.087



α_{1q}	R_{qq}	R_{11}	R_{22}	R_{q1}	R_{q2}	R_{12}
0	7.06e-015	0.075	-0.092	2.13e-015	-2.59e-015	-0.028
1	7.06e-015	0.074	-0.091	2.10e-015	-2.57e-015	-0.027
10	7.05e-015	0.067	-0.083	1.89e-015	-2.34e-015	-0.022



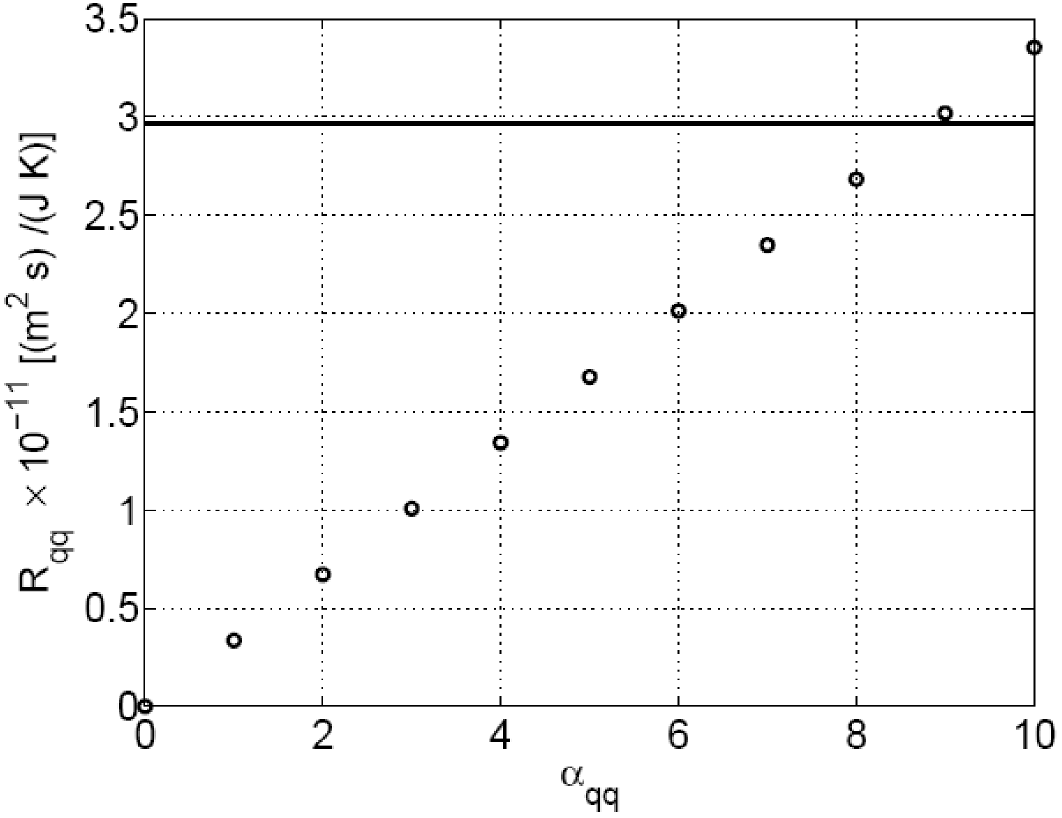
α_{11}	R_{qq}	R_{11}	R_{22}	R_{q1}	R_{q2}	R_{12}
0	7.05e-015	0.075	-0.092	2.13e-015	-2.59e-015	-0.028
1	7.06e-015	0.370	0.266	1.04e-014	7.50e-015	0.381
10	7.10e-015	3.021	3.483	8.58e-014	9.90e-014	-69.285

It is clear that α_{1q} is not relevant, while α_{qq} and α_{11} must be finite to have second law consistency.

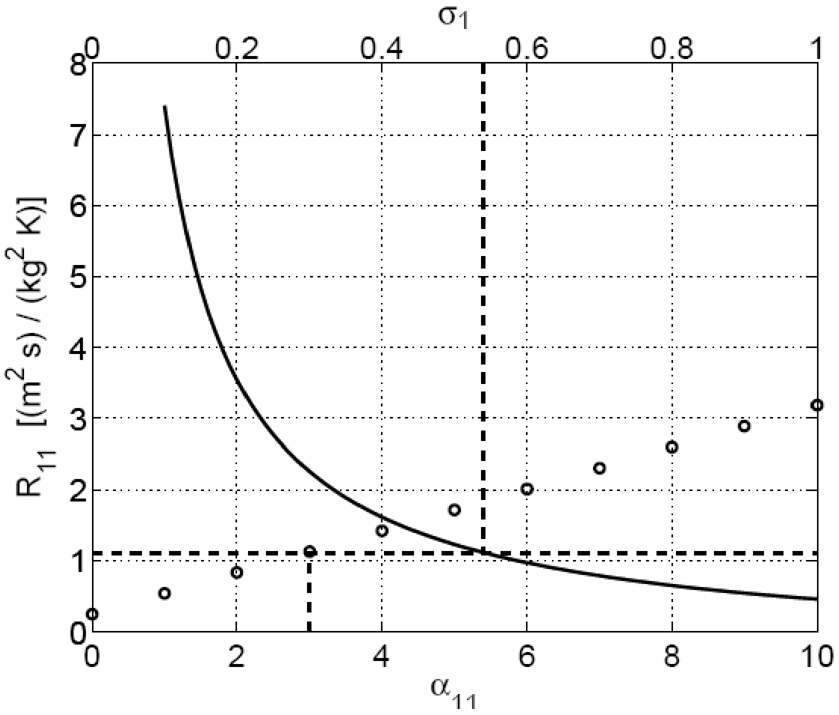
- From the tables we see that we may take α_{1q}=0.
- Furthermore we see that R_{qq} *does not depend on* α_{11}
- All resistivities depend on α_{qq}
- It follows that we should first determine α_{qq} using R_{qq} as found from kinetic theory

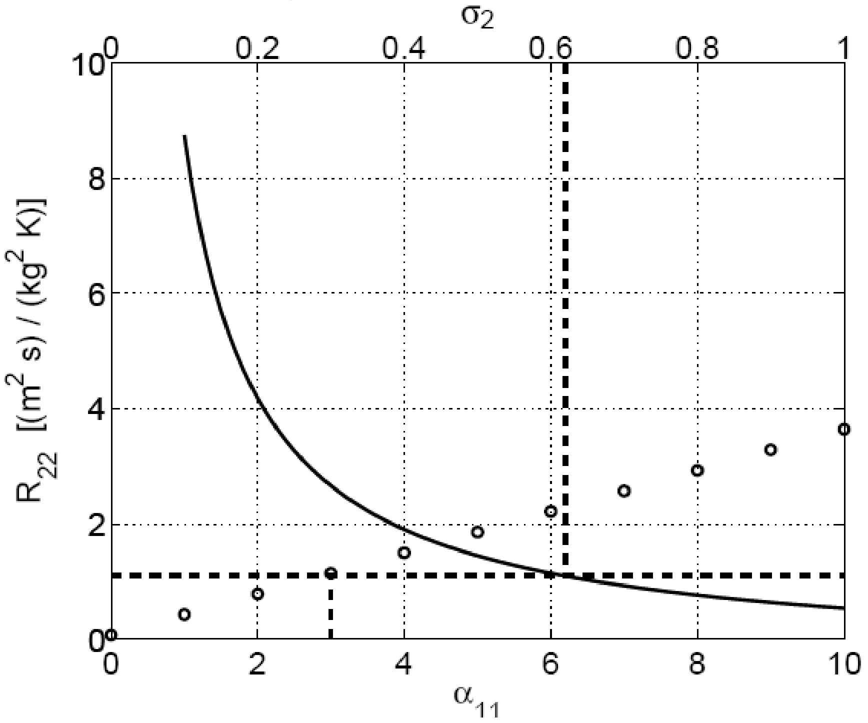
It follows that

$$\alpha_{qq} \approx 9$$



In kinetic theory the resistivities R_{11} and R_{22} depend on the condensation coefficients. As cyclohexane and n-hexane are rather similar molecules the condensation coefficients should be rather similar in size. The calculations give





parameters	R_{qq}	R_{11}	R_{22}	R_{q1}	R_{q2}	R_{12}
$\sigma_1 = 0.54$ $\sigma_2 = 0.62$	2.97e-011	1.11	1.09	3.83e-007	4.41e-007	0.013
$\alpha_{qq} = 9$ $\alpha_{1q} = 0$ $\alpha_{11} = 3$	3.02e-011	1.12	1.14	2.31e-006	2.27e-006	-0.817

The results are given in the table

Conclusions

- By a proper choice of the alphas one obtains the same diagonal resistivities as kinetic theory
- The of diagonal coefficients found from kinetic theory are up to an order of magnetude to smal
- This confirms earlier results from MD simulations
- We did the above analysis for $T_{eq} = 330 \; and \; \psi_{eq} = 700$
- For each temperature and chemical potential difference the analysis should be done again which is rather time consuming
- The integral relation method helps

21. Integral relations

The excess entropy production could be written as

$$\hat{\sigma}_s = J_q^{\prime,g}\left(\frac{1}{T^\ell}-\frac{1}{T^g}\right)-\sum_{i=1}^{n}J_{\xi_i}\left[\left(\frac{\tilde{\mu}_i^\ell}{T^\ell}-\frac{\tilde{\mu}_i^g}{T^g}\right)-\tilde{h}_i^g\left(\frac{1}{T^\ell}-\frac{1}{T^g}\right)\right]$$

The resulting linear force-flux relations are

$$\begin{aligned}\frac{1}{T^\ell}-\frac{1}{T^g} &= R_{qq}^{\prime g}\,J_q^{\prime,g}-\sum_{i=1}^{n}R_{qi}^{\prime g}\,J_{\xi_i}\\ \left(\frac{\tilde{\mu}_i^\ell}{T^\ell}-\frac{\tilde{\mu}_i^g}{T^g}\right)-\tilde{h}_i^g\left(\frac{1}{T^\ell}-\frac{1}{T^g}\right) &= R_{jq}^{\prime g}\,J_q^{\prime,g}-\sum_{i=1}^{n}R_{ji}^{\prime g}\,J_{\xi_i}\end{aligned}$$

Ignore the primes in the above and the following equations when you compare with the copy of the thesis!

The derivation of the integral relations is straightforward. See the text in the thesis. I just give the result for a binary mixture.

$$
\begin{aligned}
R'^{g}_{qq} &= \ \mathfrak{E}_r \left\{ r_{qq} \right\} \\
R'^{g}_{q1} &= \ \mathfrak{E}_r \left\{ r_{qq}(h - h^g_1) + r_{q1}\,\xi_2 \right\} \\
R'^{g}_{q2} &= \ \mathfrak{E}_r \left\{ r_{qq}(h - h^g_2) - r_{q1}\,\xi_1 \right\} \\
R'^{g}_{11} &= \ \mathfrak{E}_r \left\{ r_{qq}(h - h^g_1)^2 + 2r_{q1}\,\xi_2\,(h - h^g_1) + r_{11}\,\xi_2^2 \right\} \\
R'^{g}_{12} &= \ \mathfrak{E}_r \left\{ r_{qq}(h - h^g_1)(h - h^g_2) + r_{q1}(\xi_2\,(h - h^g_2) - \xi_1\,(h - h^g_1)) - r_{11}\,\xi_1\,\xi_2 \right\} \\
R'^{g}_{22} &= \ \mathfrak{E}_r \left\{ r_{qq}(h - h^g_2)^2 - 2r_{q1}\,\xi_1\,(h - h^g_2) + r_{11}\,\xi_1^2 \right\}
\end{aligned}
$$

The excesses are calculated in the standard way. The continuous resistivities were given by

$$
\begin{aligned}
r_{qq}(x) &= r^g_{qq} + (r^\ell_{qq} - r^g_{qq})\,q_0(x) + \alpha_{qq}(r^\ell_{qq} + r^g_{qq})\,q_1(x) \\
r_{q1}(x) &= r^g_{q1} + (r^\ell_{q1} - r^g_{q1})\,q_0(x) + \alpha_{q1}(r^\ell_{q1} + r^g_{q1})\,q_1(x) \\
r_{11}(x) &= r^g_{11} + (r^\ell_{11} - r^g_{11})\,q_0(x) + \alpha_{11}(r^\ell_{11} + r^g_{11})\,q_1(x)
\end{aligned}
$$

The modulatory curves were discussed earlier.

Remarks

- If one uses the integral relations it is sufficient to calculate the equilibrium enthalpy and density profiles
- Together with the continuous resistivities one obtains the resistivities for the discrete description
- This is a great simplification

Overall conclusions

- There is still a lot to be done.
- MD simulations would be very helpful but they have almost only be done for one component systems. We have been doing these mostly for one but recently also for a two component system.
- Experiments would be great. Some but not many have been done. There are many coefficients to determine.
- It would be important to come to some common understanding on how to describe transport into and through a surface.
- It is very important to obtain the excess entropy production, in order to give a solid base for transport phenomena into and through a surface.