

HOW TO DESCRIBE TRANSPORT ACROSS THE WATER INTERFACE

This note gives a short background and explanation for the coefficients tabulated. Transport of heat and mass across interfaces can be described consistently with NET. In a single-component system, the formulation is [1]:

$$\frac{1}{T^o} - \frac{1}{T^i} = R_{qq} J_q^o + R_{q\mu}^o J, \quad (1)$$

$$-\left(\frac{\mu^o}{T^o} - \frac{\mu^i}{T^i}\right) + h^o \left(\frac{1}{T^o} - \frac{1}{T^i}\right) = R_{\mu q}^o J_q^o + R_{\mu\mu}^o J, \quad (2)$$

where the superscripts i and o indicate the values just inside or outside the interface respectively. Furthermore, J_q^o is the measurable heat flux, J is the mass flux, μ is the chemical potential, h is the specific enthalpy, and R_{ij} are the *overall* interface transfer coefficients, known as interface resistivities [1, 2]. Following Onsager, the matrix of coefficients is symmetric, $R_{q\mu} = R_{\mu q}$. This equality, which has been verified by simulations [2], means that there are only 3 independent resistivities for heat and mass transfer across the interface. The Kapitza resistance, which frequently is reported from simulations and experiments, is given by $R_K = R_{qq}(T^s)^2$, where T^s is the surface temperature [1]. These coefficients can be expanded in the total curvature, $H = \kappa_1 + \kappa_2$ and the Gaussian curvature, $K = \kappa_1\kappa_2$ [3]:

$$R_{ij} = R_{ij,0} [1 + d_{ij}H + \nu_{ij}(d_{ij}H)^2 + \bar{\nu}_{ij}d_{ij}^2K], \quad (3)$$

where κ_1 and κ_2 are the principal curvatures and subscript 0 refers to the planar interface. The length, d_{ij} , gives the typical size of a droplet where curvature corrections become important, while ν_{ij} and $\bar{\nu}_{ij}$ are scalars which decide the importance of the second order corrections. Alternatively, one can describe the fluxes as functions of the thermodynamic forces:

$$L_{qq} \left(\frac{1}{T^o} - \frac{1}{T^i}\right) + L_{q\mu} \left[-\left(\frac{\mu^o}{T^o} - \frac{\mu^i}{T^i}\right) + h^o \left(\frac{1}{T^o} - \frac{1}{T^i}\right)\right] = J_q^o, \quad (4)$$

$$L_{\mu q} \left(\frac{1}{T^o} - \frac{1}{T^i}\right) + L_{\mu\mu} \left[-\left(\frac{\mu^o}{T^o} - \frac{\mu^i}{T^i}\right) + h^o \left(\frac{1}{T^o} - \frac{1}{T^i}\right)\right] = J, \quad (5)$$

where L denotes conductivities, where $L_{\mu q} = L_{q\mu}$. The advantage of using Eqs. 1-2 is that the interface transfer coefficients of the interface, R , and the resistances of adjacent systems can be added, using the principle of “resistances in series”, in analogy with electrical circuits [4]. This is not possible for the conductivities. However, often it is more practical to use the conductivities, they can be calculated as:

$$L_{qq} = \frac{R_{\mu\mu}}{R_{\mu\mu}R_{qq} - R_{q\mu}^2} \quad (6)$$

$$L_{q\mu} = -\frac{R_{q\mu}}{R_{\mu\mu}R_{qq} - R_{q\mu}^2} \quad (7)$$

$$L_{\mu\mu} = \frac{R_{qq}}{R_{\mu\mu}R_{qq} - R_{q\mu}^2} \quad (8)$$

For a single-component system, the coefficients from NET depend only on the interface temperature, T^s . The concept of interface temperature, assumes that the interface can be described as a separate thermodynamic system which is autonomous, i.e. in local equilibrium. Local equilibrium in this context means that interfacial properties, such as the surface tension, the interface transfer coefficients and other thermodynamic excess variables in a system which is globally at *nonequilibrium*, have the same values as in a system at *equilibrium* at the temperature T^s . The assumption of local equilibrium of the interface has been verified several times, with both theory and simulations [5, 6]. For water in the interval where the coefficients have been tabulated, we find that $T^s \simeq T^l$. The chemical potential and enthalpy in Eqs. 1-5 can be calculated with a suitable equation of state.

- [1] S. Kjelstrup and D. Bedeaux, *Non-Equilibrium Thermodynamics of Heterogeneous Systems* (World Scientific, Singapore, 2008).
- [2] J. Xu, S. Kjelstrup, D. Bedeaux, A. Røsørde, and L. Rekvig, *J. Colloid Interface Sci.* **299**, 452 (2006).
- [3] Ø. Wilhelmsen, T. T. Trinh, S. Kjelstrup, T. S. van Erp, and D. Bedeaux, *Phys. Rev. Lett.* **114**, 065901 (2015).
- [4] Y. A. Cengel, *Heat and Mass Transfer - A Practical Approach* (McGraw-Hill, New York, 2006).
- [5] E. Johannessen and D. Bedeaux, *Physica A* **330**, 354 (2003).
- [6] I. Inzoli, S. Kjelstrup, D. Bedeaux, and J. M. Simon, *Chem. Eng. Sci.* **66**, 4533 (2011).