Non-equilibrium Thermodynamics of Interfaces with the Classical Density Functional Theory

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An interface between a vapor and a liquid phase constitutes a resistance to heat and mass transport. The coupled transport resistances can be measured [1], they can be determined from molecular simulations [2], or they can be calculated from the van der Waals square gradient model [3]. We here express transport resistances of the interface with integral relations [4] and evaluate these relations with the classical density functional theory (DFT). The DFT formalism allows for a description of thermodynamic properties across an interface with good quantitative agreement to molecular simulations; and for appropriate expressions of the Helmholtz energy also with good agreement to experimental data. The integral relations express the interfacial resistances to heat transport, to mass transport and the coupling coefficients of heat and mass transport. Required is thereby only the local heat transport resistance $r_{qq}(z)$ and the local enthalpy (of an equilibrium interface). The integral relations are derived assuming the local validity of the Gibbs-Helmholtz relation across the interface. The validity of the integral relations has been verified from molecular simulation results [5]. The enthalpy is taken from the DFT formalism. The local heat transport resistance $r_{qq}(z)$ is correlated with two parameters. These two parameters turn out to be temperature-independent and all interfacial resistivities can be consistently described with good accuracy.

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