

Verification of Onsager's Reciprocal Relations for Evaporation and Condensation Using Non-Equilibrium Molecular Dynamics

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Non-equilibrium molecular dynamic (NEMD) simulations have been used to study heat and mass transfer across a vapor-liquid interface for a one-component system using a Lennard-Jones spline potential. It was confirmed that the relation between the surface tension and the surface temperature in the non-equilibrium system was the same as in equilibrium (local equilibrium). Interfacial transfer coefficients were evaluated for the surface, which expressed the heat and mass fluxes in temperature and chemical potential differences across the interfacial region (film). In this analysis it was assumed that the Onsager reciprocal relations were valid. In this paper we extend the number of simulations such that we can calculate all four interface film transfer coefficients along the whole liquid-vapor coexistence curve. We do this analysis both for the case that we use the measurable heat flux on the vapor side and for the case where we use the measurable heat flux on the liquid side. The most important result we found is that the coupling coefficients are within the accuracy of the calculation equal. This is the first verification of the validity of the Onsager relations for transport through a surface using molecular dynamics. The interfacial film transfer coefficients are found to be a function of the surface temperature alone. New expressions are given for the kinetic theory values of these coefficients which only depend on the surface temperature. The NEMD values were found to be in good agreement with these expressions.