The Role of Temperature in Nucleation Processes

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Nucleation is the start of a phase transformation where nuclei of the new phase form from a supersaturated old phase. It can be described as a particle flux along the cluster size coordinate. Nucleation is a highly non-linear process with respect to the chemical potential difference between old and new phase. Classical Nucleation Theory is the state-of-the-art theory to describe nucleation processes. The theory has also been given within the framework of mesoscopic non-equilibrium thermodynamics. However, in many cases nucleation rates from experiments and simulations are orders of magnitude different from the predicted values. Recently, in Molecular Dynamics simulations of a nucleating cluster in a supersaturated old phase, it was observed that the cluster temperature is different from that of the surrounding old phase. It is our objective to theoretically describe such a non-isothermal nucleation process in order to investigate whether this effect might be responsible for the difference in prediction and experiment. We give a sound theoretical description of the non-isothermal nucleation process also using mesoscopic non-equilibrium thermodynamics by including a thermal driving force in the entropy production for cluster formation. This results in a correction term for the isothermal nucleation rate from Classical Nucleation Theory. This correction term includes the diffusion coefficient along the cluster size coordinate, the thermal conductivity and the heat of transfer. The correction term enables us to account for the temperature difference in simulations and experiments. Case studies of a number of nucleation processes among which the condensation of liquid water from water vapour shall be reported. We discuss the effect of temperature on this process and determine the temperature of the differently sized clusters.