

A Missing Thermodynamic Ingredient in Classical Nucleation Theory?

Ailo Aasen^{C, S} and Øivind Wilhelmsen
SINTEF Energy Research, Trondheim, Trøndelag, Norway
ailo.aasen@sintef.no

David Reguera
University of Barcelona, Barcelona, Spain

For over a century, Classical Nucleation Theory (CNT) has been the main tool for understanding the initial stages of phase transitions. CNT models the Gibbs energy of a nucleating embryo as the sum of a negative contribution from the bulk fluid that is proportional to the volume of the embryo, and a positive contribution that equals the surface tension times the area. The critical embryo corresponds to a maximum of the Gibbs energy, and the nucleation rate is given by an Arrhenius-type expression.

When compared to experiments, CNT yields a realistic qualitative picture of the nucleation process and has also proven to be an accurate model for the *supersaturation dependence* of nucleation rates [1]. The deviations from experiments are consistent with a temperature-dependent offset in the Gibbs energy, so that CNT underpredicts nucleation rates at low temperatures, overpredicts them at high temperature, and is essentially exact at a single temperature. The reasons for this are still not fully understood, even for pure components.

In this presentation we elucidate this issue by combining density gradient theory and molecular simulation for molecular fluids. We present a new correction to CNT depending only on bulk thermodynamic properties of the fluid and evaluate its accuracy for the Lennard-Jones fluid and water.

References:

[1]. H. Vehkamäki, *Classical Nucleation Theory in Multicomponent Systems* (Springer Verlag, Berlin, 2006).