Extrapolation into the Meta and Unstable Regions of the Phase Diagram of Fluids

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Knowledge about the fluid behavior in the metastable and unstable region is of great interest for many applications. In the field of atmospheric science, understanding the nucleation of water droplets is vital for comprehending cloud formation. Metastable atmospheric conditions, where air is supersaturated with water vapor, can lead to the spontaneous nucleation of tiny droplets. This process is fundamental to the initiation of cloud particles, influencing weather patterns and precipitation. In nanotechnology and materials science, the behavior of fluids in nano-sized pores becomes a critical aspect of designing and understanding nanomaterials. Confined spaces at the nanoscale can lead to unique fluid behaviors, including capillary condensation and the formation of metastable states. These phenomena are vital in applications such as nanoporous materials for gas storage, separation processes, and catalysis.

In this work, we show how to extrapolate from stable fluid states into the metastable and unstable regions to predict thermodynamic properties. We demonstrate how a suitable extrapolation can be used to construct a "proxy equation of state (EoS)" for the metastable and unstable regions of the phase diagram. The proxy EoS exhibits a single Maxwell loop for all fluids tested and allows prediction of surface properties such as the surface tension when combined with density gradient theory, even in the case where the original EoS prohibits such calculations due to unphysical artefacts.

Comparison between the extrapolated states and simulation results for molecular fluids reveals excellent agreement in the metastable regions of the phase diagram. Combining square gradient theory with a proxy EoS based on very accurate multiparameter EoSs give excellent agreement between surface tension calculations and experimental results. The surface tension is calculated using the density gradient theory method with a constant influence parameter for the tested fluids. One example with good results is the extrapolation of the IAPWS 1995 EoS for water [1].

The presented extrapolation and methodology to develop a proxy EoS reveals a path to obtain reliable thermodynamic properties within the metstable and unstable parts of the phase diagrams of fluids.

References

1. W. Wagner, A. Pruß. The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use. J. Phys. Chem. Ref. Data 31, 387–535 (2002) https://doi.org/10.1063/1.1461829