On the Continuity of the Equation of State of Fluid and Solid Phases

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The pioneering work of J. D. van der Waals [1] suggested that thermophysical properties can be continuously modeled for both the gas and liquid (fluid phases) using a single mathematical function. Isotherms were shown to exhibit a loop connecting the gas and liquid regions. This apparently simple observation has been the cornerstone of equation of state (EoS) modeling of fluids throughout the 20th century. The so-called "van der Waals loop" has been shown to have a fundamental physical meaning, with the maximum and minimum defining the regions of meta-stability and the corresponding spinodal regions. Notwithstanding, a similar approach has not been popular when considering the solid-fluid equilibrium, in favor of discontinuous models where the fluid and solid are represented by independent and functionally distinct EoS. It has been suggested by J. Frenkel in 1935 [2] that the liquid-solid transition, similarly to the vapor-liquid transition, exhibits a metastable region and could be, in principle, modeled continuously. Based on this premise, we propose a single EoS framework based on artificial neural networks capable of continuously modeling fluid and solid phases (FE-ANN(s) EoS) spanning densities from the ideal gas all the way up to the crystal phase with a minimal set of parameters which define the intermolecular potential. As a proof-of-concept, the use of the FE-ANN(s) EoS is showcased for the Mie [3] force field.

The FE-ANN(s) EoS models the residual Helmholtz free energy using a single artificial neural network [4]. It is formulated without recurring to any predetermined functional form to fulfill the ideal gas law limit and Maxwell's relations analytically. The FE-ANN(s) EoS is trained using 1st and 2nd -order derivative properties of particles interacting through the Mie potential generated using high-throughput molecular dynamics simulations using LAMMPS [5]. The training data includes the compressibility, internal energy, isochoric heat capacity, isothermal compressibility, thermal pressure coefficient, thermal expansion coefficient, adiabatic index, and Joule-Thomson coefficient. The thermodynamic consistency of the trained FE-ANN(s) EoS is successfully verified against Brown's characteristics curves data [6].

The trained FE-ANN(s) EoS accurately models seen and unseen thermophysical properties. Moreover, because of its physics-informed formulation, the FE-ANN(s) EoS can predict properties for which it was not trained. Although fitted to single-phase data only, the FE-ANN(s) EoS "discovers" the unstable van der Waals loops that can predict both Vapor-Liquid Equilibria (VLE) and Solid-Liquid Equilibria (SLE). Under sensible extrapolation, the trained FE-ANN(s) EoS also predicts the triple point, in which the unstable Vapor-Liquid and Solid-Liquid regions merge. Significantly, for temperatures below the triple point, the FE-ANN(s) EoS suggests that an unstable liquid may still exist at negative pressures [7], in this case predicting a stable Solid-Vapor Equilibria (SVE).

References

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