Application of Binary Tree Architecture in Fitting Helmholtz Energy Equation of State with Argon as an Example

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In this work, binary tree architecture was applied to choose the data points to be fitted and to calculate the derivatives of the Helmholtz energy with respect to temperature and density, which are the fundamental prerequisites for the development of an equation of state.

The binary tree idea was extended to a two-dimensional form for choosing data points automatically from a large experimental database during fitting. At first, one point will be chosen as the root of this two-dimensional binary tree. The root point is flexible and determined by separating and picking the experimental data to best characterize each region. The root point separates the data into four natural segments. Each segment can be subdivided by choosing a node point within the segment. The segments can be further subdivided with the use of this operation until the separation of the experimental data reaches the optimal solution. Then the so-called "leaves in the tree" are comprised of all the experimental data points to be used in fitting.

For automatic calculation needs, a method to obtain the derivatives of the Helmholtz energy with respect to any order of temperature and density, along with the virial coefficients, was derived. The binary tree will also be applied to derivative calculations to easily search for new types of terms. Based on these, we can easily analyze each term's contribution to all thermodynamic properties, especially for virial coefficients. OpenGl was applied to obtain 3D plots of each term and its derivatives.

Argon is a monoatomic molecule and is the most abundant rare gas in air. The experimental database for argon is very extensive, and it was therefore chosen to demonstrate the robustness of the method applied in this work.