

Accelerating Iterative Equation of State Calculations With Superancillary Phase Boundaries

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ABSTRACT

Iterative calculations are needed to obtain the natural variables of an equation of state from the given state variables when analyzing thermal systems (machinery, systems, even simple cycle analysis). When the given state variables are entropy and enthalpy, which arise naturally in turbomachinery, this problem is particularly challenging due to the range of shapes of the phase boundary possible in these coordinates. The iterative calculation of temperature and density from entropy and enthalpy represents a computational bottleneck in many cases. In recent studies it has been shown how superancillary equations (sets of one-dimensional Chebyshev expansions) can be generated that represent the phase boundary of the equation of state to approximately numerical precision. These functions are a few hundred times faster to obtain than the full equation of state. This work shows that if the phase boundary is expressed as superancillary curves, the enthalpy-entropy calculations can be accelerated, particularly near the phase boundary, and made simultaneously more reliable than the existing approaches. The approach is applied to two pure fluids with differing phase boundary shapes.

1. INTRODUCTION

An equation of state is used to calculate thermodynamic properties for fluids with compressibility. Modern high-accuracy multiparameter equations of state are formulated in terms of the Helmholtz energy, in which the Helmholtz energy is expressed as a function of temperature and density. All other properties may be obtained from derivatives of the Helmholtz energy a . For instance pressure is obtained from $p = -(\partial a / \partial v)_T$, and entropy from $s = -(\partial a / \partial T)_v$, where a is the Helmholtz energy, T is the temperature and v the specific volume. These equations of state are implemented in libraries such as NIST REFPROP (Lemmon et al., 2018) or CoolProp (Bell et al., 2014).

2. SUPERANCILLARY CURVES

To assist the iterative calculations for phase equilibria with multiparameter equations of state (vapor-liquid equilibria is given as equal pressure and Gibbs energy in the phases for pure fluids), good guess values for densities are needed. For equations of state, these predictions can be obtained from ancillary equations, which are empirical curves fit to the vapor-liquid equilibria of the equation of state. Usually these correlations are good to less than 0.1% in density, except for in the near-vicinity of the critical point. These correlations are intended only as guess values for the iterative calculations.

Recent work (Bell and Alpert, 2021) has shown how superancillary equations may be constructed that represent the saturated liquid and vapor densities obtained from the equation of state to approximately numerical precision with the use of Chebyshev expansions. While one could in principle carry out the same process for any other property along the phase boundary, that process is relatively slow because the phase equilibrium calculations used to build the superancillary curves are carried out in extended precision and the superancillary curves add some size to the library (order of tens of kilobytes per fluid). The open-source ChebTools library (Bell et al., 2018) is used to build the superancillary curves.

For other properties like entropy and enthalpy, it is adequate to use the density superancillary curves

to get the density, and then use that temperature in the equation of state to get the other property (e.g., enthalpy or entropy). As such, in this work the `dyadic_splitting` function of ChebTools is used to build a superancillary function in the form $s'(T, \rho'_{\text{ch}}(T))$, where the $\rho'_{\text{ch}}(T)$ comes from the superancillary curve for density. The same thing is done for the vapor phase (superscript $''$). The advantage of the superancillary curves is that they are very computationally efficient. When evaluated in C++ without the C++ \leftrightarrow Python overhead, superancillary curves take approximately 40 nanoseconds to evaluate, which is on the order of 400 times faster than a phase equilibrium calculation from the full equation of state (Bell and Alpert, 2021). The power of Chebyshev expansions for numerical approximation in closed domains cannot be overstated. Figure 1 shows the deviations between the entropy and enthalpy values calculated from the equation of state and the superancillary curves. The deviations are at a level where the functions may be used without any additional fine-tuning.

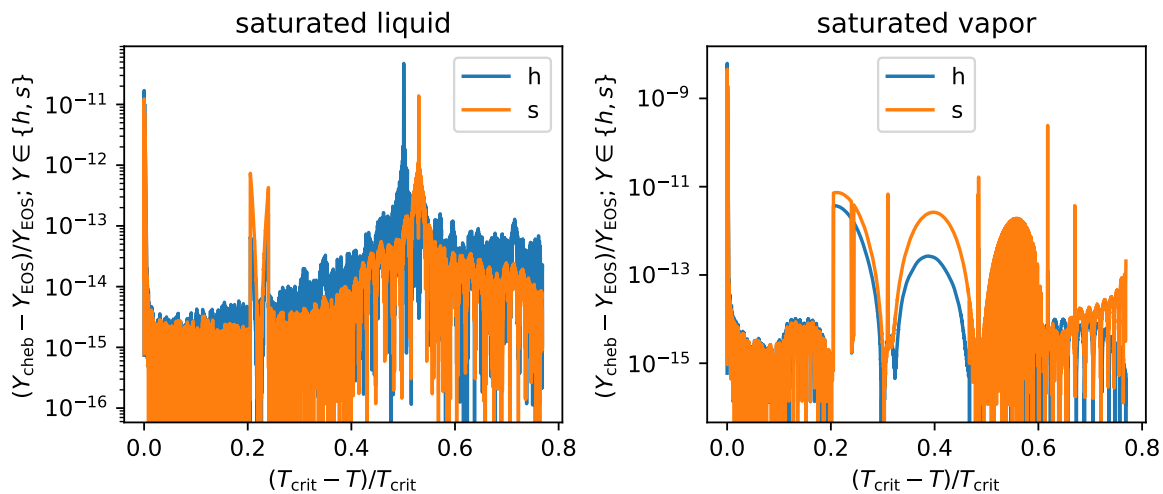


Figure 1: Deviations in enthalpy and entropy for the saturated liquid and vapor curves for propane as compared with the equation of state (Lemmon et al., 2009). Iterative VLE calculations from CoolProp, and superancillary density curves from Bell and Alpert (2021).

While the temperature dependence of each of ρ' and ρ'' is monotonic, this may not be the case for the saturated entropy. Györke et al. (2019) shows the plethora of different sorts of extrema in entropy (with the temperature as independent variable) that may be present along the saturated vapor curve. A further advantage of Chebyshev expansions is that they can be used to straightforwardly identify their extrema, from identifying the values of x where dy/dx is equal to zero. While rootfinding of Chebyshev expansions is somewhat slow (order of tens of microseconds), the identification of extrema can be carried out at the time of expansion construction.

3. ENTHALPY-ENTROPY CALCULATIONS

The equations of state have as independent variables temperature and density. If other thermodynamic properties are provided (e.g., enthalpy and entropy), one- or two-dimensional rootfinding must be applied to obtain the temperature and density that matches the given state variables. Enthalpy and entropy are one of the most challenging and computationally expensive iterative calculations commonly required for thermal systems (Vitale et al., 2015; Li et al., 2021). This represents close to a worst-case. When developing CoolProp, significant effort was expended in making a generalized H-S solver for pure fluids, but ultimately those efforts were abandoned. The approach in this work represents a way to resolve the H-S problem. Mapping between an h - s input and T - ρ is complicated because:

- Neither given variable is an independent variable of the equation of state
- Neither h nor s gives a straightforward means of determining if an input state point is supercritical

or subcritical (for all inputs with temperature or pressure specified, one need only compare with the pressure at the critical point, for instance)

- The phase boundary can demonstrate a variety of different qualitative behaviors (Györke et al., 2019). Different behaviors can be seen in Fig. 2 for propane and MD₄M (tetradecamethylhexasiloxane), a siloxane. Propane has no extremum in entropy, while MD₄M does, a consequence of molecular structure. One remarkable feature is how smoothly the functions are able to resolve the extrema at the “top” of the phase equilibrium bubble for MD₄M

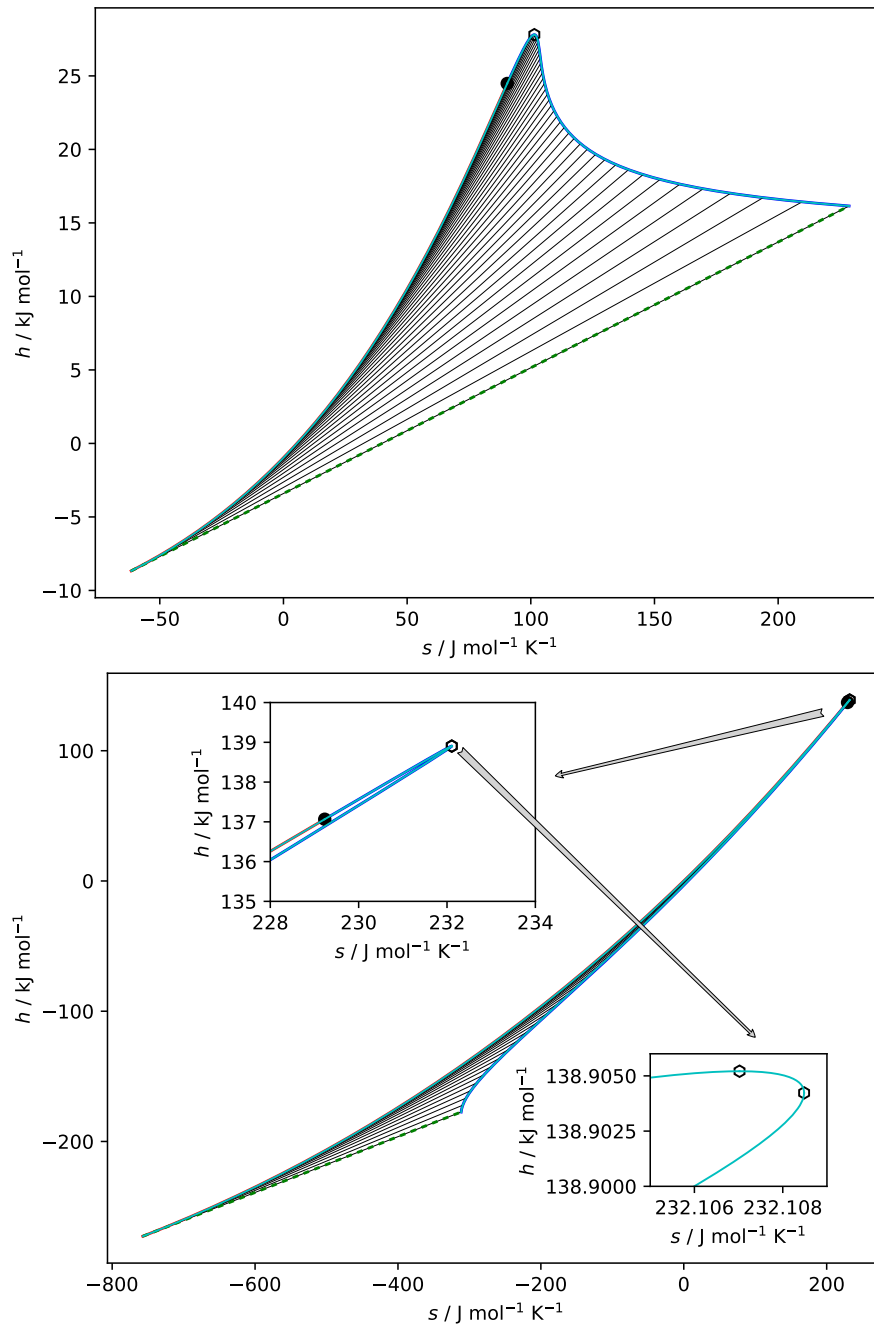


Figure 2: H-S plots for propane (Lemmon et al., 2009) (top) and MD₄M (Thol et al., 2019) (bottom). For MD₄M two insets are shown, zooming in towards the extremum in entropy. Saturated liquid is red, saturated vapor is blue, and the superancillary is overlaid in cyan. The thin straight lines are the isotherms, and the critical point is a filled circle and the extrema open hexagons.

The setup for the approach proposed in this work requires a few steps:

- Identify all extrema of the saturation entropy, temperatures where $ds''/dT = 0$.
- For the portions of the curves between these extrema, build Chebyshev expansion sets in the form $T(s'')$ with the `dyadic_splitting` function of `ChebTools` (yielding a monotonic portion of the phase boundary)

Then, for a given value of h,s , the algorithm proceeds as follows:

1. Determine which portions of the phase boundary have entropy bounds which bracket the given value of entropy. If the minimum and maximum values of the entropy for this portion bracket the entropy, the portion could be valid.
2. If there is one potentially valid chunk, then if $h > h_{\text{ch}}(T_{\text{ch}}(s))$, the input is homogeneous. The subscript `ch` indicates the evaluation of a Chebyshev expansion for this portion.
3. If there are more than one potentially valid portions, if a ray starting at infinite enthalpy to the given enthalpy at constant entropy crosses the phase boundary an even number of times, the input enthalpy is homogeneous (or solid).

A key point is that the entire phase determination routine never invokes a full phase equilibrium calculation. It only uses sets of Chebyshev expansions. Thus, the phase equilibrium portion of the calculation takes significantly less than a microsecond in C++. The single-phase portion of the solver is the same as usual, where guess values can (at least in theory) be provided by the phase equilibria.

The two-phase solver for a given h,s pair is relatively straightforward. The residual function to be driven to zero is that the vapor quality calculated from the enthalpy is the same as the vapor quality calculated from the entropy. Mathematically, that is

$$r_{2\phi}(T) = \frac{h - h'_{\text{ch}}(T)}{h''_{\text{ch}}(T) - h'_{\text{ch}}(T)} - \frac{s - s'_{\text{ch}}(T)}{s''_{\text{ch}}(T) - s'_{\text{ch}}(T)} \quad (1)$$

where again, the sets of Chebyshev expansions are used in place of the full phase equilibrium calculation. Here, in order to ensure reliability, Brent's method (1973) is used, which is a bounded one-dimensional solver with quadratic updates.

4. RESULTS

In this work, a preliminary analysis of computational efficiency and reliability is carried out with propane. A more complete analysis will be the subject of an archival publication. Here only two-phase inputs are considered, as they straightforwardly demonstrate the potential for improvement. A grid in temperature and vapor quality covering the limits of the EOS was generated. The critical temperature is not a valid point for the solver (because the entropy and enthalpy differences go to zero, resulting in an invalid residual), and neither are either are vapor qualities of 0 or 1 for similar reasons. Therefore the vapor qualities were moved just inside $(10^{-6}, 1 - 10^{-6})$. The bounds for the iterative calculation can be set as the triple point and the temperature that causes the vapor quality to be zero or one. This corresponds to the saturation temperature where the entropy is the same as the given entropy (what was calculated above in the phase determination routine). For more complicated phase boundaries, more thought needs to be given to the range of valid temperatures.

Timing-wise, the speedup is significant. Admittedly, the two-phase calculation is the best case for Chebyshev acceleration. Nevertheless, the median time for calculations with the accelerated Chebyshev phase equilibrium calculations is on the order of $40 \mu\text{s}/\text{call}$, whereas that of `CoolProp` is on the order of $1500 \mu\text{s}/\text{call}$, which represents a speedup on the order of $35\times$. The calls in `CoolProp` are so much slower because they use the full equation of state to get the saturated phase enthalpies and entropies. A histogram is shown in Figure 3. The current speedup is conservative because the iterative calculations were

implemented in Python, for ease of prototyping. The timing calculations should be done in a compiled low-level language like C++, for which a further speedup of a factor of at least $100\times$ would not be surprising. *Probably* the Chebyshev method is more than $3000\times$ faster than the iterative routines in CoolProp. NIST REFPROP does not support two-phase h,s inputs, so it is not possible to compare against the speed or accuracy of REFPROP.

In order to assess the accuracy of this approach, deviations between the temperatures obtained from the iterative calculation T_{iter} and the original temperature T_{init} are plotted in Fig. 3. When temperature deviations were below the denormal limit in double precision (rounded to zero, yielding $\log_{10}(0) = -\infty$), they were entered as 10^{-16} . Most deviations, except for one outlier, are less than 10^{-8} K.

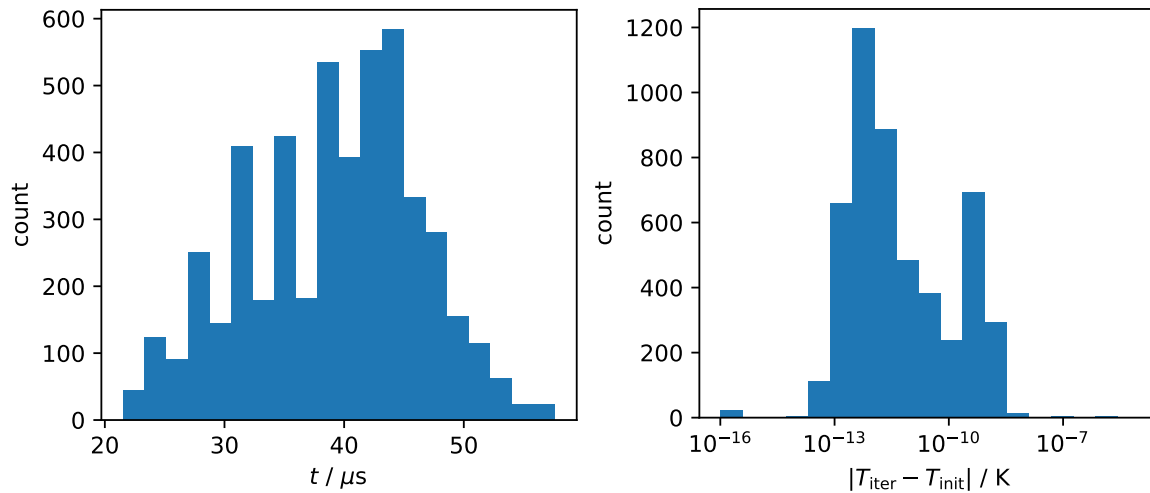


Figure 3: Histograms of the elapsed time per call and absolute error in saturation temperature.

5. CONCLUSIONS

This study continues the analysis of superancillary equations (Bell and Alpert, 2021; Bell, 2021; Bell and Deiters, 2021). For two-phase inputs, the speedup is at least $35\times$, and likely more than $3000\times$ compared with the routines implemented in CoolProp version 6.4.1. The next step is to extend the analysis to single-phase inputs and more complicated fluids to yield a universally applicable approach for pure fluids. The single-phase problem is challenging due to the presence of points in the phase diagram where the specific heat goes to infinity, which may divert the solver, slow it down, or cause it to fail. The specific heat appears in the entries in the Jacobian when solving for temperature and density for given enthalpy and entropy. Obtaining robust single-phase routines is therefore much more challenging than two-phase inputs, but no less important for practical applications.

Other state inputs, for instance internal energy and density (arising from the conservation of mass and energy) can be attacked in the same way as h,s . The case of u,ρ inputs is even more straightforward than h,s because the density is one of the inputs, and thus it is “only” necessary to determine the temperature for the given internal energy. The same general approach of constructing monotonic Chebyshev portions of the phase boundary for the phase determination may be applied.

NOMENCLATURE

Variables

a	Helmholtz energy	(J mol ⁻¹)
s	entropy	(J mol ⁻¹ K ⁻¹)
T	temperature	(K)
h	enthalpy	(J mol ⁻¹)
u	internal energy	(J mol ⁻¹)
v	specific volume	(m ³ mol ⁻¹)
Y	independent variable	
ρ	density	(mol m ⁻³)

Subscript

ch	Chebyshev
iter	Iterative solution
init	Initial value

Superscript

"	Saturated vapor
'	Saturated liquid

SUPPORTING INFORMATION

The supporting information, available at <https://doi.org/10.18434/mds2-2397>, includes:

- The Python script used to build the phase boundaries and generate the figures in this paper.

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