

User guide for Matlab class thermo

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The Matlab m-files mentioned in this note are all available from GitHub:

<https://github.com/are-mj/thermodynamics>.

Several authors have used methods developed at Ruhr-Universität Bochum (Setzmann & Wagner, 1989) to design high accuracy models for the thermodynamic properties of single-component fluids. These models calculate the molar Helmholtz free energy as a function of temperature T and molar volume v , in a form that allows explicit expressions for all partial derivatives of arbitrary order. These models all have largely the same structure and can be calculated using the same Matlab function (`helmholtz.m`), but with separate parameter sets for the different fluids.

The thermo class and object

The purpose of the Matlab class thermo is to provide a flexible and efficient interface to the `helmholtz` function and to enable efficient methods for solving a range of thermodynamic problems. A Matlab class contains the code for creating one or more Matlab objects. A thermo object is created by calling the class with the name of an available fluid. Example:

```
>> th = thermo('H2O');
```

See the chapter on Parameter files near the end of the document to see which species are available.

A call to `thermo` creates a thermo object, reads the appropriate parameter file and stores the parameters as *properties* of the object. The object also contains *methods* for calculating thermodynamic variables. Note that for a single-component fluid, two independent thermodynamic variables will uniquely determine the *thermodynamic state* and thus all thermodynamic properties.

For a full list of available properties, type:

```
>> thermo.properties
```

For a list of functions available in the thermo object, type:

```
>> thermo.methods
```

Derivative order

The property `max_order` controls the maximum order of partial derivatives of the Helmholtz free energy $f(T, v)$ to be calculated. The default is 2, as nearly all thermodynamic variables may be expressed in terms of these values. However, sometimes we need derivatives of order 3, for example to find analytical Jacobians to use with Newton's method. Setting `max_order` to 3 will force these values to be calculated, at the expense of slightly longer calculation times.

Thermodynamic methods of the thermo object

Tvcalc

The basic method is Tvcalc. A call to the method Tvalc calls the helmholtz function with temperature and molar volume as arguments. The Helmholtz function returns the Helmholtz free energy and its partial derivatives up to order two or three. (Two is the default). The calculations are explicit (i.e., no iterations are needed) and fast. Tvcalc stores these values as object properties together with a number of calculated thermodynamic variables. All variables are in SI units, with the exception that kmol is used instead of mol. For a temperature of 373K and a molar volume of 30kmol/m³ we write:

```
th.Tvcalc(373,30)
```

All variables are can be accessed as needed with no extra calculations:

```
>> th.p                % Pressure (Pa)
ans =
    1.0176e+05
>> th.c                % Speed of sound (m/s)
ans =
    472.0671
```

Tpcalc

In many practical situations the temperature and pressure are known, not molar volume. Tpcalc uses repeated calls to Tvcalc to find the molar volume that gives the desired pressure:

```
>> th.Tpcalc(373,101325)
```

Let us check:

```
>> th.p
ans =
    1.0133e+05 % 101325 rounded to five significant digits
>> th.v
ans =
    30.1323
```

The Tpcalc method uses Newton's method to find the correct value of the molar volume v . By default, it starts the search at the initial molar volume for ideal gas at the given T and p . If T and p are in the vapour/gas region, Tpcalc will normally converge very fast, since the value of the derivative of p with respect to v (at constant T) is always available in the thermo object.

If T and p are in **the liquid region**, Tpcalc will need us to supply an initial guess for the molar volume as third input:

```
>> th.Tpcalc(273,101325,0.01)
>> th.v
ans =
    0.0180
>> rho = th.Mw/th.v    % Density of water is near 1000 kg/m3
rho =
    999.8327
```

phcalc and pscalc

These two methods find the temperature and molar volume that results in given values for pressure and either molar enthalpy or entropy, respectively. They are less robust than Tpcalc, but will converge fast given good initial values.

These functions are useful if we work on processes where the pressure changes at constant enthalpy (e.g., pipes) or entropy (e.g., valves).

Saturation properties

Derivative order

By default, thermo calculates derivatives up to order two. Setting the property max_order to 3 forces the calculation of third order derivatives, at the cost of a longer calculation time.

Example:

```
>> th = thermo('H2O');
>> th.Tpcalc(400,1e5);th.f_TTT
ans =
     []
>> th.max_order=3;th.Tpcalc(400,1e5);th.f_TTT
ans =
    0.2000
>> T = linspace(400,500);v = linspace(10,40);
>> tic;for i = 1:100;th.Tvcalc(T(i),v(i));end;toc
Elapsed time is 0.025994 seconds.
>> th.max_order=2;
>> tic;for i = 1:100;th.Tvcalc(T(i),v(i));end;toc
Elapsed time is 0.013975 seconds.
```

Third order derivatives are sometimes needed to calculate jacobians for solving problems involving second order derivatives.

Units

SI units are used throughout; with the exception that kmol is used instead of mol. Intrinsic variables are on a per kmol basis. Properties per kg are found by dividing by th.Mw.

thermo object vs. separate function calls

Some user may find it conceptually easier to have separate functions for each thermodynamic variable, for instance:

```
h = enthalpy(T,p,'H2')
```

rather than

```
th2 = thermo('H2');
th2.Tpcalc(T,p)
h = th2.h
```

The advantage of the latter approach is that complex calculations need not be repeated if we need more than one property at a given (T,p) pair. Without extra function calls we can get, for example, the heat capacity at constant pressure and the speed of sound:

```
>> fprintf('Heat capacity: %.0f J/K/mol\n',th.cp)
Heat capacity: 28853 J/K/mol
```

```
>> fprintf('Speed of sound: %4.0f m/s\n',th.c)
Speed of sound: 1319 m/s
```

Other thermodynamic functions

The derivatives of the helmholtz function available in the thermos object enables the efficient calculation of most thermodynamic processes. We have included a number of separate Matlab m-files demonstrating this flexibility:

`choked_flow.m`

State of choked gas flow, given upstream stagnation conditions.
Assumes isentropic process and no condensation.

`compressor.m`

Outlet conditions from gas compressor

`twophase_tank_rhs.m`

Right-hand side for ODE system solving mass and energy balance and phase equilibrium for a two-phase tank being filled or emptied.

`shocktube.m`

`shocktube_ig.m`

See also: `demo_shocktube.m`

Pressures and temperatures in idealised shock tube for real and ideal gas

`shock_from_mach.m`

`shock_from_pressure.m`

`shock_from_velocity.m`

Calculate shock for real gases with various input variables

Demo files

`demo_gas_tank_system.m`

Simple simulation of filling a gas tank from another tank

`twophase_region.m`

Plot phase envelope and isotherms in a p-v plot

`demo_shocktube.m`

Calculate shock tube temperatures and pressures for a range of initial pressures

`phase_diagram.m`

Plots phase boundaries for the gas, liquid and solid regions in a T-p diagram. Currently available only for H₂O and CO₂.

Parameter files

Parameters for selected species

`parameters_Air.m`

Air treated as a single species. Single-phase only. (Lemmon, Jacobsen, Penoncello, & Friend, 2000)

parameters_Ar.m

Argon. Single-phase only. (Tegeler, Span, & Wagner, 1999)

parameters_CO2.m

Carbon dioxide. Gas and liquid. (Span & Wagner, 1996) and (Giordano et al., 2006).

parameters_H2O.m

Water and steam. (Wagner & Pruss, 2002) and (Wagner et al., 2011)

parameters_O2.m

Oxygen. Single-phase only. (Lemmon, Jacobsen, Penoncello, & Friend, 2000)

parameters_N2.m

Nitrogen. Single-phase only. (Lemmon, Jacobsen, Penoncello, & Friend, 2000)

parameters_H2.m

parameters_paraH2.m

parameters_orthoH2.m

Hydrogen. Gas and liquid. (Leachman, Jacobsen, Penoncello, & Lemmon, 2009)

Parahydrogen and orthohydrogen are “spin isomers”. These are relevant for liquid and low temperature gas. The first file is for normal H₂, which is the equilibrium combination at room temperature and higher: 75% orthohydrogen and 25% parahydrogen. See [Wikipedia](#) and (Leachman J. , 2015)

Utility functions

newton.m

Solver for nonlinear equation systems using Newton’s method.

References

- Giordano, V. M., Datchi, F., & Dewaele, A. (2006). Melting curve and fluid equation of state of carbon dioxide at high pressure and high temperature. *The Journal of chemical physics*, 125(5), 054504. <https://arxiv.org/pdf/cond-mat/0607785.pdf>
- Leachman, J. (2015, July 15). *Why equilibrium hydrogen doesn't exist*. Retrieved from <https://hydrogen.wsu.edu/2015/06/22/why-equilibrium-hydrogen-doesnt-exist/>
- Leachman, J., Jacobsen, R., Penoncello, S., & Lemmon, E. (2009). Fundamental Equations of State for Parahydrogen, Normal Hydrogen, and Orthohydrogen. *Journal of Physical and Chemical Reference Data A*, 721-784. Retrieved from https://www.researchgate.net/profile/Steve-Penoncello/publication/228339083_Fundamental_Equations_of_State_for_Parahydrogen_Normal_Hydrogen_and_Orthohydrogen/links/571a82e508ae7f552a47330e/Fundamental-Equations-of-State-for-Parahydrogen-Normal-Hydrogen-and-Orthohydrogen.pdf
- Lemmon, E., Jacobsen, R., Penoncello, S., & Friend, D. (2000). Thermodynamic properties of air and mixtures of nitrogen, argon, and oxygen from 60 to 2000 K at pressures to 2000 MPa. *J. Phys. Chem. Ref. Data.*, 331-385. http://thermophysics.ru/pdf_doc/refer331.pdf
- Setzmann, U., & Wagner, W. (1989). A New Method for Optimizing the Structure of Thermodynamic Correlation Equations. *International Journal of Thermophysics*, 1103–1126. Retrieved from <https://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.471.8839&rep=rep1&type=pdf>
- Span, R., & Wagner, W. (1996). A New Equation of State for Carbon Dioxide ... *Journal of Physical and Chemical Reference Data*, 25, 1509-1596. Retrieved from <https://pdfs.semanticscholar.org/990f/7d99a7bfa2b851711a8f2add054728ee6922.pdf>
- Tegeler, C., Span, R., & Wagner, W. (1999). A new equation of state for argon covering the fluid region for temperatures from the melting line to 700 K at pressures up to 1000 MPa. *Journal of Physical and Chemical Reference Data*, 779-850. <https://www.nist.gov/system/files/documents/srd/jpcrd561.pdf>
- Wagner, W., & Pruss, A. (2002). The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water. *Journal of Physical and Chemical Reference Data*, 387-535. Retrieved from <http://www.personal.psu.edu/mrh318/Wagner-Pruss-JPCRD-2002.pdf>
- Wagner, W. et al. (2011). New Equations for the Sublimation Pressure and Melting Pressure of H₂O Ice Ih. *Journal of Physical and Chemical Reference Data* 40.4: 043103. https://tsapps.nist.gov/publication/get_pdf.cfm?pub_id=909228