Thermodynamics is a funny subject. The first time you go through it, you don't understand it at all. The second time you go through it, you think you understand it, except for one or two small points. The third time you go through it, you know you don't understand it, but by that time you are so used to it, it doesn't bother you any more.

Arnold Sommerfeld

An isotope can be characterized by the dimensionless integers

\[ Z = \text{number of protons} = \text{atomic charge} \]
\[ N = \text{number of neutrons} \]
\[ A = \text{number of nucleons} = \text{atomic number} \]

The Avogadro number, from the 2006 CODATA values of the fundamental physical constants,

\[ N_A = 6.02214179 \pm 0.00000030 \times 10^{23} \text{ 1/mol} \]

is the number of “entities” in one mole. When an individual entity has mass \( m \) in grams, the atomic mass or molar mass for a collection of the entities is

\[ W = m N_A \text{  g/mol} \]

So, the total mass of a collection of entities is the number of moles times the molar mass.
The mass of a single isotopic \( k \) is
\[
m_k = N m_n + Z m_p + Z(1 - f) m_e - \Delta m
\]
\[
= N m_n + Z m_p + Z(1 - f) m_e - \frac{B}{c^2} \quad \text{g}
\]

where \( m_n \) is the neutron rest mass, \( m_p \) is the proton rest mass, \( m_e \) is the physical electron mass, \( f \) is the ionization fraction (0 for a neutral atom, 1 for full ionization), \( \Delta m \) is the mass deficit, and \( B \) is the nuclear binding energy.

Sometimes terms of the form \([15.73 Z^{5/3} - 13.6 Z \text{ eV}]\) are added to approximate the electronic binding energy. Such terms are usually negligible and we will ignore such contributions. The molar mass of the isotope is \( W_k = n_k N_A \).

The atomic mass unit (amu) is defined as \( 1/12 \) the mass of an unbound atom of \(^{12}\text{C} \) at rest and in its ground state. We thus define the molar mass to be \( W = 12.0 \text{ g/mol} \). An amu then has a molar mass of \( W = 1 \text{ g/mol} \). Hence,
\[
1 \text{ amu} = 1/N_A = 1.660538782 \pm 0.000000083 \times 10^{-24} \quad \text{g}
\]

One can then say \( N_A \) has units of \([1/g]\) but care must be taken to apply the implicit \( \text{mol/g} \) conversion to other quantities of interest. For example, in this system of units, the molar mass \( W \) is dimensionless.

Mixing the \([1/\text{mol}]\) and \([1/g]\) systems of units can cause confusion!

Its common to set the atomic number \( A \) equal to the atomic mass \( W \). For example, for neutral \(^{16}\text{O} \) one typically sees \( A = 16 \) and \( W = 16 \text{ g/mol} \).

This approximation neglects the neutron-proton mass difference, the electron masses, and the nuclear binding energy contribution.

From our equation for the mass of an isotope, the atomic mass for neutral \(^{16}\text{O} \) is \( 15.99491 \text{ g/mol} \).

The difference between \( W \) and \( A \), the mass excess, for any given isotope is typically \( \lesssim 0.5\% \) with a maximum of about \( ~2\% \).

The number density \( n \), mass density \( \rho \), and molar abundance \( Y \) for a pure composition is
\[
n = \frac{\rho N_A}{W} \quad \text{cm}^{-3} \quad \rho = \frac{nW}{N_A} \quad \text{g cm}^{-3} \quad Y = \frac{n}{\rho N_A} = \frac{1}{W} \quad \text{mol/g}
\]

For a mixture of \( k \) isotopes, the molar abundance \( Y_i \) and mass fraction \( X_i \) of species \( i \) as
\[
Y_i = \frac{n_i}{\rho_i N_A} \quad \text{mol/g} \quad X_i = W_i Y_i = \frac{\rho_i}{\rho}
\]

where \( n_i \) is the number density and \( \rho_i \) is the mass density of species \( i \).

Mass conservation of the mixture is expressed as
\[
\sum_{i=1}^{k} X_i = \sum_{i=1}^{k} W_i Y_i = \sum_{i=1}^{k} \frac{\rho_i}{\rho} = 1
\]
Quantities used as input into numerous physics modules include the averages

\[ \overline{W} = \frac{\sum n_i W_i}{\sum n_i} = \frac{1}{k} \sum_{i=1}^{k} Y_i \text{ g/mol} \]

\[ \overline{A} = \frac{\sum n_i A_i}{\sum n_i} = \overline{W} \sum_{i=1}^{k} Y_i A_i \]

\[ \overline{Z} = \frac{\sum n_i Z_i}{\sum n_i} = \overline{W} \sum_{i=1}^{k} Y_i Z_i \]

Similar to the molar abundance \( Y_i \), one defines the free electron abundance variable \( Y_e \) of a fully ionized plasma

\[ Y_e = \frac{n_e}{\rho N_A} = \frac{Z n}{\rho N_A} = \frac{Z}{\overline{W}} = \sum_{i=1}^{k} Z_i Y_i \text{ mol/g} \]

Let’s start by assuming complete ionization amongst a mixture of non-interacting photons, ions, electrons and positrons at temperature \( T \) (in K) and mass density \( \rho \) (in g cm\(^{-3}\)), but allow for arbitrary degrees of relativity and degeneracy.

Under these conditions, the mixture has a scalar pressure \( P \) (in erg cm\(^{-3}\)), specific internal energy \( E \) (in erg g\(^{-1}\)), and specific entropy \( S \) (in erg g\(^{-1}\) K\(^{-1}\)).

The Input into a typical equation of state in the temperature \( T \), density \( \rho \), average atomic mass \( W \), and average charge \( Z \).

The Output, at minimum, should consist of \( P, E, \) and \( S \) along with their first partial derivatives with respect to the input variables \( T, \rho, A, Z \).

A typical equilibrium stellar equation of state assumes

**Thermal photons:**

\[ P_{\text{rad}} = \frac{a T^4}{3} \]

\[ E_{\text{rad}} = \frac{3 P_{\text{rad}}}{\rho} \]

\[ S_{\text{rad}} = \frac{P_{\text{rad}} / \rho + E_{\text{rad}}}{T} = \frac{4 a T^3}{3} \]

where the 2006 CODATA recommended value of the radiation constant \( a \) is calculated from the measured value of the gas constant \( R \):

\[ a = \frac{4 \sigma c}{\varepsilon} = \frac{8 \pi^5 R^4}{15 h^3 c^3 N_A^3} \]
Ideal ions: 
\[ N_{ion} = \frac{N_A p}{W} \quad P_{ion} = N_{ion} kT \quad E_{ion} = \frac{3}{2} \frac{P_{ion}}{\rho} \]

where 
\[ S_{ion} = \frac{P_{ion}/\rho + E_{ion}}{T} + \eta_{ion} k_B N_{ion}/\rho \]

The entropy equation, the Sackur-Tetrode equation, is an expression for a monatomic classical ideal gas which incorporates the uncertainty principle when counting microstates for \( S = k_B \ln \Omega \).

Using
\[ \epsilon(p) = m_e c^2 \left[ \sqrt{1 + \left( \frac{p}{m_e c} \right)^2} - 1 \right] \]
\[ v(p) = \frac{\partial \epsilon}{\partial p} = \frac{p}{m_e} \left[ 1 + \left( \frac{p}{m_e c} \right)^2 \right]^{-1/2} \]
\[ \eta = \frac{\mu}{kT} \quad \beta = kT/(m_e c^2) \quad x = \frac{\epsilon}{m_e c^2} \]

where \( \eta \) is the electron degeneracy parameter and \( \beta \) is the relativity parameter, the thermodynamic integrals may be written as

Electron-Positron gas: 
the electron number density, \( P \), \( E \), and \( S \) are

\[ n_e = \int_0^\infty n_e(p) \, dp = \frac{8\pi}{h^3} \int_0^\infty \frac{p^2 dp}{\exp[\epsilon/kT - \mu_e/kT] + 1} \]
\[ P_e = \frac{1}{3} \int n_e(p) \, \textbf{p} \cdot \textbf{v} \, d^3 p = \frac{1}{3} \int_0^\infty n_e(p) \, p \, \partial \epsilon/\partial p \, dp \]
\[ = \frac{8\pi}{3h^3} \int_0^\infty \frac{p^3 \partial \epsilon/\partial p \, dp}{\exp[\epsilon/kT - \mu_e/kT] + 1} \]
\[ E_e = \frac{1}{\rho} \int_0^\infty n_e(p) \, \epsilon(p) \, dp = \frac{8\pi}{3h^3 \rho} \int_0^\infty \frac{p^3 \partial \epsilon/\partial p \, dp}{\exp[\epsilon/kT - \mu_e/kT] + 1} \]
\[ S_{ele} = \frac{1}{T} \left( P_{ele}/\rho + E_{ele} + \mu_e n_e/\rho \right) \]

where \( p \) is the momentum, \( \epsilon \) is the kinetic energy, and \( \mu_e \) is the electron chemical potential.

Using
\[ n_e = \frac{8\pi \sqrt{2}}{h^3} m_e^3 c^3 \beta^{3/2} \int_0^\infty x^{1/2} \left( 1 + (1/2) \beta x \right)^{1/2} \left( 1 + \beta x \right) \, dx \]
\[ \eta = \frac{8\pi \sqrt{2}}{h^3} \frac{m_e^3 c^3 \beta^{3/2}}{3} \int_0^\infty x^{3/2} \left( 1 + (1/2) \beta x \right)^{3/2} \, dx \]
\[ E_e = \frac{8\pi \sqrt{2}}{h^3} m_e^3 c^3 \beta^{5/2} \int_0^\infty x^{5/2} \left( 1 + (1/2) \beta x \right)^{5/2} \left( 1 + \beta x \right) \, dx \]
\[ S_{ele} = \frac{P_{ele}/\rho + E_{ele}}{T} + \eta_e k_B n_e/\rho \]
Finally, using the Fermi-Dirac function $F_k(\eta, \beta)$

$$F_k(\eta, \beta) = \int_0^\infty \frac{x^k}{e^x - \eta + 1} \left(1 + \frac{1}{2} \beta x\right)^{1/2} dx$$

the electron and positron number densities may be written

$$N_{\text{ele}} = \frac{8\pi \sqrt{2}}{h^3} m_e^3 c^2 \beta^{3/2} \left[F_{1/2}(\eta, \beta) + \beta F_{3/2}(\eta, \beta)\right]$$

$$N_{\text{pos}} = \frac{8\pi \sqrt{2}}{h^3} m_e^3 c^2 \beta^{3/2} \left[F_{1/2}(-\eta - 2/\beta, \beta) + \beta F_{3/2}(-\eta - 2/\beta, \beta)\right]$$

The only unknown in these integrals is the normalized chemical potential $\eta$. For complete ionization, the number density of free electrons is

$$N_{\text{ele,matter}} = Z N_{\text{ion}} = \frac{Z}{A} N_A \rho$$

and self-consistency requires

$$N_{\text{ele,matter}} = N_{\text{ele}} - N_{\text{pos}}$$

which, via a root-find, determines $\eta$.

The Fermi-Dirac functions and their derivatives can be done by brute force integration, Simpson integration on nested grids in tandem with integral transformations (Cloutman 1989), or quadrature integration with an elegant choice of the ordinates and weights (Aparicio 1998).
You may download these stellar eos codes from cococubed.asu.edu:

Timmes  exact in 64-bit arithmetic, fundamental constants entered to their 2006 recommended precision, reference point for comparisons.

Iben  Eggleton, Faulkner & Flannery approximation for the Fermi-Dirac integrals, positrons not included, finite differences for some derivatives.

Weaver  Divine approximation so only Fermi integrals appear, cubic spline interpolant on tables or 3rd-order expansions, analytic derivatives.

Nadyozhin  polynomial expansions in 5 regions, transitions between regions are continuous, smooth, and consistent, analytic partial derivatives.

Arnett  hashed table lookup and bicubic interpolant for thermodynamics and derivatives or 3rd-order expansions, all integrals and root-finds off-line.

Helmholtz  hashed table lookup and thermodynamically consistent biquintic Hermite interpolant for P, E, S and derivatives, table from Timmes EOS.

Inactive: partial ionization, Coulomb interactions, and onset of ion degeneracy.

The first law of thermodynamics

\[
\frac{\partial E}{\partial T} = T \frac{\partial S}{\partial T}
\]

is an exact differential, so the three Maxwell relations

\[
\frac{\partial E}{\partial T} \bigg|_\rho = T \frac{\partial S}{\partial T} \bigg|_\rho, \quad P = \rho^2 \frac{\partial E}{\partial \rho} \bigg|_T + T \frac{\partial P}{\partial T} \bigg|_\rho, \quad -\frac{\partial S}{\partial \rho} \bigg|_T = \frac{1}{\rho^2} \frac{\partial P}{\partial T} \bigg|_\rho
\]

should be numerically satisfied if the eos is thermodynamically consistent.

Thermodynamic inconsistency appears as the unphysical buildup of S or T during simulations of what should be an adiabatic flow.

Models which are sensitive to the entropy may suffer inaccuracies if thermodynamic consistency is violated over long enough time-scales.
Interlude

Here is a live example of running eosfxt ...

The Helmholtz EOS

The Helmholtz free energy $F$, which has $(T, \rho)$ as the natural variables, is

$$F = E - TS$$

$$dF = -SdT + \frac{P}{\rho^2} d\rho$$

With mixed partials commuting and the pressure and entropy defined as

$$P = \rho^2 \frac{\partial F}{\partial \rho} \bigg|_T$$

$$S = -\frac{\partial F}{\partial T} \bigg|_\rho$$

$$\frac{\partial^2 F}{\partial T \partial \rho} = \frac{\partial^3 F}{\partial \rho \partial T}$$

The thermodynamic consistency relations are satisfied.
Thermodynamic consistency is guaranteed for the interpolant if the thermodynamics are evaluated in this order: P first, S second, and E third.

This procedure is almost too robust! The interpolated values may be horribly inaccurate, but they will be thermodynamically consistent.

Consider any interpolating function for F whose mixed partials commute. The function and its derivative values determine the coefficients a, b, c, and d in terms of the C_i. The two polynomials multiplying the resultant C_i are the cubic Hermite basis functions

\[
\psi_0(z) = 2z^3 - 3z^2 + 1 \\
\psi_1(z) = z^3 - 2z^2 + z
\]

where

\[
z = \frac{x - x_i}{x_{i+1} - x_i}
\]

and the interpolating cubic Hermite polynomial is

\[
H_3(z) = f_i \psi_0(z) + f_{i+1} \psi_0(1 - z) + \left. \left( x_{i+1} - x_i \right) \frac{\partial f}{\partial x} \right|_i \psi_1(z) - \left. \left( x_{i+1} - x_i \right) \frac{\partial f}{\partial x} \right|_{i+1} \psi_1(1 - z)
\]

The derivative of the cubic Hermite polynomial is given by the derivative of the basis functions.

Suppose one wants to define a function on the interval \([x_i, x_{i+1}]\) that has the following properties:

\[
\begin{align*}
f(x_i) &= C_1 \\
f(x_{i+1}) &= C_2 \\
f'(x_i) &= C_3 \\
f'(x_{i+1}) &= C_4
\end{align*}
\]

where the C_i are arbitrary constants. The lowest order polynomial that could satisfy these four conditions is a cubic

\[
f(x) = a + bx + cx^2 + dx^3
\]
Imposing second derivative constraints on the interval \([x_i, x_{i+1}]\)

\[
\begin{align*}
  f(x_i) &= C_1 \\ 
  f(x_{i+1}) &= C_2 \\ 
  f'(x_i) &= C_3 \\ 
  f'(x_{i+1}) &= C_4 \\ 
  f''(x_i) &= C_5 \\ 
  f''(x_{i+1}) &= C_6
\end{align*}
\]

and applying the the same procedure as above to the quintic polynomial

yields the three quintic Hermite basis functions:

\[
\begin{align*}
  \psi_0(z) &= -6z^5 + 15z^4 - 10z^3 + 1 \\
  \psi_1(z) &= -3z^5 + 8z^4 - 6z^3 + z \\
  \psi_2(z) &= \frac{1}{2} (-z^5 + 3z^4 - 3z^3 + z^2)
\end{align*}
\]

The resulting biquintic interpolation function for rectangle bounded by \(\rho_i \leq \rho < \rho_{i+1}\) and \(T_i \leq T < T_{i+1}\) is given by

\[
H_5(\rho, T) = \sum_{l,k} F_{l,k}^{T} \psi_l^T \psi_k^T
\]

where

\[
\begin{align*}
  x &= \frac{\rho - \rho_i}{\rho_{i+1} - \rho_i} \\
  y &= \frac{T - T_i}{T_{i+1} - T_i}
\end{align*}
\]

\[
F_{T}^{l,k} = \frac{\partial F}{\partial T} \bigg|_{l,k} (T_{j+1} - T_j)
\]

\[
F_{TT}^{l,k} = \frac{\partial^2 F}{\partial T^2} \bigg|_{l,k} (T_{j+1} - T_j)^2
\]

... and so on for the rest of the terms.

The one dimensional quintic polynomial is extended to two dimensions by interpolating each of the basis functions in the second dimension.

This bicubic Hermite interpolant forms the heart of the Helmholtz EOS.

To use it, one must tabulate the Helmholtz free energy \(F\) and 8 of its partial derivatives as a function of density and temperature.

In return for this investment, the values of the function, first partial, and second partial derivatives are reproduced exactly on grid points and change continuously as the interpolating point moves from cell to cell.

The e−e Helmholtz free energy table is constructed with the Timmes EOS, which was designed for maximum accuracy and consistency.

The Helmholtz free energy table is constructed with \(A=1\) and \(Z=1\) (pure hydrogen) so that \(Y_e=1\), but is valid for any composition because simple scaling relations exist for \(Y_e\) under the assumption of complete ionization.
All the necessary pieces for a table driven equation of state are now in place; 1) a method which assures thermodynamic consistency, 2) a suitable interpolating polynomial, and 3) an electron-positron equation of state table with precise entries.

How accurate, how thermodynamically consistent, and how fast is the Helmholtz equation of state?

Thermodynamic consistency is, as expected, at the floating point limit for any choice of the grid density.

Three different density-temperature grids were considered in order to assess the accuracy as a function of the table size. The "nominal grid" consists of 10 points per decade in both the density and temperature.

<table>
<thead>
<tr>
<th>Type of Temperature and Density Sweep</th>
<th>EOS Ordered</th>
<th>Random</th>
<th>Entropy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Timmes</td>
<td>106</td>
<td>106</td>
<td>106</td>
</tr>
<tr>
<td>Helmholtz</td>
<td>0.8</td>
<td>0.9</td>
<td>0.8</td>
</tr>
<tr>
<td>Arnett</td>
<td>1.0</td>
<td>1.1</td>
<td>1.1</td>
</tr>
</tbody>
</table>

*CPU time per call for each EOS operating in serial mode on the nominal grid. All values have been normalized to the Arnett EOS for ordered sweeps in serial mode (see Timmes & Arnett 1999 for a discussion of the tabular Arnett EOS). The table entries are generally independent of the machine architecture and compiler options used.

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<td>106</td>
</tr>
<tr>
<td>Helmholtz</td>
<td>0.4</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Arnett</td>
<td>0.4</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

*CPU time per call for each EOS operating in pipeline mode, with a pipe size of 104, on the nominal grid. All values have been normalized to the Arnett EOS for ordered sweeps in serial mode (see Timmes & Arnett 1999 for a discussion of the tabular Arnett EOS). The table entries are generally independent of the machine architecture and compiler options used.
Interlude

Here is a live example of running helmeos ...

The Helmholtz equation of state has a maximum error of $10^{-6}$ in any quantity, displays thermodynamic consistency at the floating point limit, and executes faster than any known stellar equation of state. It is the stellar EOS of choice in many hydrodynamic and stellar evolution codes.

Stars are a fundamental building block of astronomy and astrophysics. The breadth of the demand for a new research and education tool in computational stellar astrophysics led to our construction of the general, modern stellar evolution library MESA (Modules for Experiments in Stellar Astrophysics) that combines the following advantages:

1. **Openness**: should be open to any researcher, both to advance the pace of scientific discovery, but also to share the load of updating physics, fine-tuning, and further development.

2. **Modularity**: should provide independent, reusable modules.

3. **Wide applicability**: should be capable of calculating the evolution of stars in a wide range of environments, including low and massive stars, binaries, accreting, mass-losing stars, early and advanced phases of evolution etc. This will enable multi-problem physics validation.

4. **Modern techniques**: should employ modern numerical approaches, including high-order interpolation schemes, advanced AMR, simultaneous operator solution; should support well-defined interfaces for related applications, e.g., atmospheres, wind simulations, nucleosynthesis simulations, and hydrodynamics.

5. **Microphysics**: should allow for up-to-date, wide-ranging, flexible, and modular micro-physics.

6. **Performance**: should parallelize on present and future shared-memory, multi-core/thread and possibly hybrid architectures so that performance continues to grow within the new computational paradigm.
The MESA equation of state combines (for the first time) several efforts that offer the current best physics in their regimes of applicability.

**HIPACC Stellar EOS Projects**

- Run the executable eosfxt/eosfxt.exe and examine the output. Open the source code for eosfxt.f90 and find the physics we discussed. Change eosfxt.f90 source to different conditions, compile, link, and run.

- Run the eoshelm/helmholtz.exe test case and examine the output. Open the helmholtz.f90 source code and find the interpolation we discussed.

- Open the eoshelm/drive_helmholtz.exe source and examine what it does. Run the executable and use the provide gnuplot file pressure_contour.gplt to visualize the results.

- Modify drive_helmholtz.f90 and pressure_contour.gplt to plot the adiabatic index $\Gamma_1$ in the $T-\rho$ plane; does it ever drop below 4/3, what does that mean?