Equation of State

Our Goal here is to derive the equation of state (or the mutual dependencies among local thermodynamic quantities such as \( P, T, \rho, \) and \( N_i \) — species number density), not only for the classic ideal gas, but also for photons and fermions, for which quantum effects are important. The EoS together the thermodynamic equation allows to study how the stellar material react to the heat, changing density, etc.

1 The Local Thermodynamic Equilibrium

We do this under the local thermodynamic equilibrium (LTE) assumption. The LTE means that at any position in a star, complete thermodynamic equilibrium is very nearly true: e.g., the Boltzmann populations of ion energy levels are consistent with the local kinetic temperature of electrons.

This assumption is appropriate for a star, since the mean free path of particles is generally short, compared to the variation scales of the thermodynamic quantities; e.g., \( \lambda_{ph} = (\kappa\rho)^{-1} \) is on order of 1 cm. Exception cases are stellar photo-spheres.

With such a short mean free path, how long does it take for a photon to diffuse out of a star?

**Random walk**: 1-D random walk theory.

The mean of N steps is zero, but the dispersion is not, \( \sigma^2(\sum_i x_i) = N\lambda_{ph}^2 \). The time that takes a photon to diffuse out is then \( \sim (R^2/\lambda_{ph})/c \sim 10^4 \) yrs.

The time scale to establish the LTE is also typically short enough, except for nuclear reactions, compared to the evolutionary time scale of a star with the exception of various explosions.

2 Chemical Reactions

Chemical reactions determine the species number density \( N_i \), which may have the units of number per gram of material; i.e., \( N_i = n_i/\rho \).

The thermodynamic equation with chemical reactions:

\[
dE = TdS - PdV + \sum_i \mu_i dN_i
\]  

where \( \mu_i \) is the chemical potential associated with an \( i \)th species and clearly can be defined
Stellar Astrophysics: Equation of State

as

\[ \mu_i = \left( \frac{\partial E}{\partial N_i} \right)_{S,V} \]  \hspace{1cm} (2)

The LTE requires that

\[ \sum_i \mu_i dN_i = 0 \]  \hspace{1cm} (3)

As an example,

\[ H^+ + e^- \leftrightarrow H^0 + \chi_H \]  \hspace{1cm} (4)

where \( \chi_H = 13.6 \text{ eV} \) is the ionization potential from the ground state of H.

For simplicity, we’ll assume that H has only one bound level and no other reactions that involve the above constituents and that the gas is pure hydrogen.

We will neglect the photons here since its chemical potential is zero. Consider a classic black body cavity filled with radiation in thermodynamic equilibrium with the wall. The above equation can be written as

\[ \sum_i \mu_i dN_i + \mu_\gamma dN_\gamma = 0 \]  \hspace{1cm} (5)

Since photon number is not strictly conserved, in general \( dN_\gamma \neq 0 \). While \( dN_i = 0 \) for the cavity wall (as a whole), we have \( \mu_\gamma = 0 \).

Now let us get back to ionization-recombination reaction, which can be written as

\[ 1H^+ + 1e^- \leftrightarrow 1H^0 = 0 \]  \hspace{1cm} (6)

And in general, a reaction can be written in such a symbolic form:

\[ \sum_i \nu_i C_i = 0, \]  \hspace{1cm} (7)

where \( C_i \) is the names of the participating particle (except for photons). Clearly, \( dN_i = \frac{\nu_i}{\nu_1} dN_1 \). Since \( dN_1 \) is arbitrary, we have

\[ \sum_i \mu_i \nu_i = 0 \]  \hspace{1cm} (8)

This the equation of chemical equilibrium. Here \( \mu_i \), containing the information of \( N_i \), depending on \( T \) and \( \rho \) or equivalent thermodynamic quantities as well as on a catalog of the possible reactions. When they are known, we should be able to find all \( N_i \). For a perfect (or ideal) gas, as will be assumed here, it is not difficult to establish such connection.
3 The Distribution Function

For a particular species of elementary nature (ions, photons, etc.) in the LTE, the occupation number in a certain quantum state, defined by the internal energy level $j$ in the coordinate-momentum phase space is found from statistical mechanics to be

$$F(j, \mathcal{E}(p)) = \frac{1}{\exp[-\mu + \mathcal{E}_j + \mathcal{E}(p)]/kT \pm 1},$$

where $\mathcal{E}_j$ is the energy state $j$ referred to some reference energy level, $\mathcal{E}(p)$ is the kinetic energy as a function of the momentum $p$, $\mathcal{E}(p) = (p^2c^2 + m^2c^4)^{1/2} - mc^2$, and $\mu$ is the chemical potential of the species and is to be determined. A “+” or “−” is used for Fermi-Dirac or Bose-Einstein particles (fermions of half-integer spin or bosons of zero and whole integer spin), respectively. There are different ways to derive the above expression; my favorite derivation is from the maximization of entropy with Lagrange multipliers for a fixed number of particles and a fixed energy of all energy levels (read originally in Landau & Lifshitz’s Statistical Physics; but can also be found at wikipedia; e.g., under Fermi-Dirac or Bose-Einstein statistics).

The number of states in the phase space, accounting for the degeneracy of the state $g_j$, is

$$g_j \frac{d^3p d^3r}{h^3}.$$  

(10)

So the phase-space density can be defined as

$$n(p) = \frac{1}{h^3} \sum_j g_j \frac{\exp[-\mu + \mathcal{E}_j + \mathcal{E}(p)]/kT \pm 1}. $$

(11)

We can then calculate the physical space density $n$, kinetic pressure $P$, and internal energy $E$ as

$$n = \int_p n(p) 4\pi p^2 dp,$$

(12)

This gives the connection between $n$, $T$, and $\mu$.

$$P = \frac{1}{3} \int_p n(p) v p 4\pi p^2 dp,$$

(13)

where $v = \frac{\partial \mathcal{E}(p)}{\partial p}$.

$$E = \int_p n(p) \mathcal{E}(p) 4\pi p^2 dp$$

(14)
4 Black Body Radiation

What quantum mechanical effect do we expect for bosonic gas? Photons are mass-less bosons of unit spin, in particular. $\mu = 0$, as discussed earlier. Since they travel at $c$ (hence no rest frame), they have only two states (two spin orientations or polarization; the classic quantum mechanics zero spin projection is not physical here) for a given energy. Hence,

$$n_\gamma = \frac{8\pi}{h^3} \int_0^\infty \frac{p^2 dp}{\exp(pc/kT) - 1} \propto T^3.$$  \hspace{1cm} (15)

Similarly, one can easily get $P_{\text{rad}} = \frac{aT^4}{3}$ and $E_{\text{rad}} = aT^4 = 3P_{\text{rad}}$, where $a$ is the radiation constant.

The nice thing about the LTE is that all these quantities depend only on $T$.

Note that the above equation is a $\gamma$-law EoS $P = (\gamma - 1)E$ with $\gamma = 4/3$.

For later use, it is easy to define the specific energy density per unit frequency ($\nu$) as

$$u_\nu = \frac{8\pi h\nu^3}{c^3} \frac{1}{\exp(h\nu/kT) - 1} \text{erg cm}^{-3}\text{Hz}^{-1}.$$  \hspace{1cm} (16)

and the frequency-dependent Planck function

$$B_\nu(T) = \frac{c}{4\pi} u_\nu,$$  \hspace{1cm} (17)

which peaks at $h\nu = 2.8kT$.

The integrated Planck function is

$$B(t) = \int B_\nu(T) d\nu = \frac{\sigma}{\pi} T^4 \text{erg cm}^{-2}\text{s}^{-1}\text{sr}^{-1}.$$  \hspace{1cm} (18)

where $\sigma = ca/4$ is the Stefan-Boltzmann constant.

5 Fermi-Dirac EoS

Elections, protons, and neutrons are fermions. They all have spin one half. Hence $g = 2$. We choose an energy reference level of $E_0 = mc^2$ (no internal energy level; alternative choices would only lead to an additive constant in the definition of $\mu$). The occupation number is

$$F(E) = \frac{1}{\exp ((E(p) - (\mu - mc^2))/kT) + 1},$$  \hspace{1cm} (19)

where, in general, $E(p) = mc^2 \left[ 1 + \left( \frac{p}{mc} \right)^2 \right]^{1/2}$ and $v(p) = \frac{p}{m} \left[ 1 + \left( \frac{p}{mc} \right)^2 \right]^{-1/2}$. 
5.1 The Complete Degenerate Gas

Now let us examine the behavior of the above integral when \( T \to 0 \). The exponential tends to be either zero or infinity, depending on whether the kinetic energy \( \mathcal{E}(p) < (\mu - mc^2) \) or \( \mathcal{E}(p) > (\mu - mc^2) \). We call this critical kinetic energy, \( \mathcal{E}_F = (\mu - mc^2) \), as the “Fermi energy”, though we are yet to determine \( \mu \). Fermions fill the energy range, \( 0 \leq \mathcal{E} \leq \mathcal{E}_F \) — “filled Fermi sea”, which is capped by \( \mathcal{E}_F \). Correspondingly, we have \( p_F \), as defined by

\[
\mathcal{E}_F = mc^2 \left[ (1 + x_F^2)^{1/2} - 1 \right],
\]

where \( x_F = \left( \frac{p_F}{mc} \right) \) is the dimensionless momentum.

The number density can be calculated as

\[
n = \frac{8\pi}{h^3} \int_0^{p_F} p^2 dp = \frac{8\pi}{3} \left( \frac{h}{mc} \right)^{-3} x_F^3,
\]

where \( \left( \frac{h}{mc} \right) \) is the Compton wavelength and is \( 2.4 \times 10^{-10} \) cm for electrons and about \( 1.8 \times 10^3 \) smaller for neutrons (due to the mass difference). For the complete degenerate electron gas, we then have

\[
\frac{\rho}{\mu_e} = Bx_F^3,
\]

where \( B = \frac{8\pi m_e}{3} \left( \frac{h}{m_e c} \right)^{-3} = 9.7 \times 10^5 \) g cm\(^{-3}\) and \( \mu_e \) is electron mean molecular weight. Therefore, once \( \frac{\rho}{\mu_e} \) is known, we can derive \( x_F \), and hence \( p_F \) and \( \mathcal{E}_F \).

The demarcation between non-relativistic and relativistic mechanics occurs when \( p_F \sim m_e c \) or \( x_F \sim 1 \). The corresponding density is \( \sim 10^6 \) g cm\(^{-3}\), which, incidentally, is a typical central density of white dwarfs.

For typical densities in a neutron star (comparable to the nuclear densities of \( \rho \approx 2.7 \times 10^{14} \) g cm\(^{-3}\)), it is easy to show \( x_F \approx 0.35 \). Thus neutron stars are non-relativistic.

The pressure and internal energy density can be calculated as

\[
P = \frac{8\pi m_e^4 c^5}{3} \int_0^{x_F} \frac{x^4}{(1 + x^2)^{1/2}} dx,
\]

and

\[
E = 8\pi \left( \frac{h}{mc} \right)^{-3} mc^2 \int_0^{x_F} x^2[(1 + x^2)^{1/2} - 1] dx,
\]

which have limiting forms of \( P \propto E \propto x_F^5 \propto \rho^{5/3} \) for \( x_F \ll 1 \) and \( P \propto E \propto x_F^4 \propto \rho^{4/3} \) for \( x_F \gg 1 \).

It is easy to show \( E/P = 3/2 \) (hence \( \gamma = 5/3 \), assuming a \( \gamma \)-law EoS, \( P = (\gamma - 1)E \)) for \( x_F \ll 1 \) and \( E/P = 3 (\gamma = 4/3) \) for \( x_F \gg 1 \). Thus, the completely degenerate gas in a non-relativistic limit acts like a monatomic ideal gas whereas, in the extreme relativistic limit, it behaves like a photon gas.
5.2 Application to White Dwarfs

The above \( P(x(\rho)) \) relation together with the hydrostatic equation forms a second-order differential equation (e.g., \( \rho \) vs. \( M_r \)). Its solution would give the structure of a WD.

But here, we will only show the \( M - R \) scaling via the virial theorem in the hydrostatic form \( 3(\gamma - 1)U = -\Omega \) (remember \( 2K = 3P \)), assuming a white dwarf with constant density and composition throughout. Of course, the constant density (hence constant pressure) assumption does not satisfy the hydrostatic equation. But this does not change the above scaling, qualitatively.

Because \( \Omega \sim GM^2/R \) and \( U = VE \propto R^3(M/R^3)^{5/3} \) (in the non-relativistic limit), \( M \propto R^{-3} \).

This scaling shows the remarkable property that as mass increases, the radius decreases and is quit unlike the homology result for MS stars.

Similar dimensional analysis gives \( M \propto R^0 \) in the extreme relativistic limit. An exact analysis yields

\[
\frac{M}{M_\odot} = \frac{M_\infty}{M_\odot} = 1.456 \left( \frac{2}{\mu_e} \right)^2,
\]

where \( M_\infty \) is the Chandrasekhar limiting mass. A full virial analysis shows that \( \frac{1}{2} \frac{d^2I}{dt^2} = 3(\gamma - 1)U + \Omega \) becomes negative if the star mass exceeds \( M_\infty \). The interpretation is that an electron degenerate object (of fixed \( \mu_e \)) cannot have the mass exceeding the Chandrasekhar limit. The EoS is too soft! Increasing density and pressure cannot halt the collapse because the relativistic limit (related to the limit of the speed of light) has already been reached. So a star needs either to start with a low mass or to rid itself of enough mass to eventually leave a WD with \( M < M_\infty \).

A similar limit (\( \sim 3M_\odot \)) can be found for a neutron star mass.

5.3 Temperature Effects

Now let us see what we really mean by stating \( T \to 0 \). Suppose the temperature is low — on some scale yet to be determined — but not zero. Fermions deep in the Fermi sea, at energies much less than \( \mathcal{E}_F \), need roughly an additional \( \mathcal{E}_F \) energy units to move around in energy. If this energy input, as measured by \( kT \), is much smaller than \( \mathcal{E}_F \), the low-energy particles are excluded from promotion to already occupied upper energy levels. But Fermions near the surface of the sea, within a depth of \( \sim kT \), may find themselves elevated into energies greater an \( \mathcal{E}_F \). The net effect is that the occupation distribution smooths out to higher energies. Apparently, the criterion for the transition between degeneracy and near- or degeneracy is \( \mathcal{E}_F \sim kT \). (The figure in the textbook shows the distribution for \( \mathcal{E}_F \sim 20kT \).)

The criterion gives a \( \rho/\mu_e - T \) relation that roughly separates the two regimes, as shown in Fig. 3.7. For a non-relativistic electron gas \( (\mathcal{E}_F = m_e c^2 x^2 / 2) \),

\[
\frac{\rho}{\mu_e} = 6.0 \times 10^{-9} T^{3/2} \text{ g cm}^{-3}.
\]

\[\text{(25)}\]
For a relativistic electron gas ($\mathcal{E}_F = m_e c^2 x$),

$$\frac{\rho}{\mu_e} = 4.6 \times 10^{-24} T^3 \text{ g cm}^{-3}. \quad (26)$$

The center of the present sun is non-degenerate, but close enough to the transition line that good solar model needs to include the effects of Fermi-Dirac statistics.

## 6 Ideal Gas

The Boltzmann distribution for an ideal gas is characterized by $\mu/kT \ll -1$, i.e., the occupation number is very low. For simplicity, we assume that the gas particles are non-relativistic with $\mathcal{E} = p^2 / 2m$, $v = p/m$, and they have only one energy state $\mathcal{E}_j = \mathcal{E}_0$. The number density of the gas is then

$$n = 4\pi \frac{\hbar^3}{g} \int_0^{p=\infty} e^{(\mu - \mathcal{E}_0 - p^2 / 2m)/kT} p^2 dp. \quad (27)$$

Taking logarithmic differentials of the above equation on both sides yields the distribution function for a Maxwell-Boltzmann ideal gas:

$$\frac{dn(p)}{n} = \frac{4\pi}{(2\pi mkT)^{3/2}} e^{-p^2 / 2mkT} p^2 dp. \quad (28)$$

From this equation, it is easy to get the pressure $P$ and to prove $P = nkT$, which is true even if the particles are relativistic.

Furthermore, the integral in Eq. 27 yields $\mu$ in terms of the number density:

$$e^{\mu/kT} = \frac{nh^3}{g(2\pi mkT)^{3/2}} e^{\mathcal{E}_0/kT}. \quad (29)$$

If the particles (e.g., ions) have multiple energy levels, which are populated or depopulated by photon absorption or emission, for example. Because the photon chemical potential is zero, $\mu_1 = \mu_2$ for any two levels. From the similar equations as the above, it is easy to show

$$\frac{n_1}{n_2} = \frac{g_1}{g_2} e^{-(\mathcal{E}_1 - \mathcal{E}_2)/kT}, \quad (30)$$

which is the Boltzmann population distribution.

## 7 “Almost Perfect” EoS

The quantum mechanics effect on fermions (Pauli exclusion) or bosons (Bose-Einstein condensate) affect the occupation distribution in the phase (or energy) space, but does not alter
the energy of individual particles. In real gas, interactions need to be accounted for that modify the “perfect” results as discussed so far.

In addition, a stellar EoS might consist of many components with radiation, Maxwell-Boltzmann, and degenerate gases competing in importance. Fig. 3.9 summarizes some of the effects for a hypothetical gas composed of pure hydrogen.

At high temperature and/or low density, radiation pressure becomes important. The demarcation between the radiation and ideal gas pressures \( aT^4/3 = \rho kT/\mu m_A \) for completely ionized hydrogen gas is

\[
\rho = 1.5 \times 10^{-23} T^3 \text{ g cm}^{-3}.
\]  

At \( \rho \sim 1 \text{ g cm}^{-3} \), such gas can also get pressure-ionized because the Wigner-Seitz radius \( a \sim [3/(4\pi n_I)]^{1/3} \) is comparable to the first Bohr orbit.

A measure of the interaction energy between ions is the Coulomb potential. The ratio

\[
\Gamma_C \equiv \frac{Z^2 e^2}{a kT}
\]

characterizes the importance of the Coulomb effects relative to the thermal agitation. When \( \Gamma_C \) is much greater than 1, the gas settles down into a crystal.

### 8 The Saha Equation

Often the number densities of some species cannot be set \textit{a priori}. This will affect the mean molecular weight, as discussed earlier, and other parameters (e.g., various derivatives), as will be discussed later. If the system is in thermodynamic equilibrium, however, then the chemical potentials of the reacting constituents depend on one another and this additional constraint is sufficient to determine the number densities.

Again consider the ionization-recombination reaction:

\[
H^+ + e^- \leftrightarrow H^0 + \chi_H
\]

and assume that no other reactions are taking place that involve the above constituents and that the gas is ideal and purely hydrogen with only one state. We establish the reference energy levels for all species by taking the zero energy as the just-ionized to be the \( H^+ + e^- \) state. Thus \( \mathcal{E}_0 \) is zero for both electrons and protons, whereas \( = -\chi_H \) for neutral hydrogen. To avoid the double counting, we may choose \( g^- = 2 \) and \( g^+ = 1 \) (or vice versa) as well as \( g^0 = 2 \). Then it is easy to show

\[
n_e = \frac{2[2\pi m_e kT]^{3/2}}{h^3} e^{\mu^-/kT} \tag{34}
\]

\[
n^+ = \frac{[2\pi m_p kT]^{3/2}}{h^3} e^{\mu^+/kT} \tag{35}
\]
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\[ n^0 = \frac{2[2\pi(m_e + m_p)kT]^{3/2}}{h^3} e^{\mu^0/kT} e^{\chi_H/kT}. \]  

(36)

Notice that for the LTE, \( \mu^- + \mu^+ - \mu^0 = 0 \) and \( [m_e m_p/(m_e + m_p)] \approx m_e \), we have the Saha equation:

\[ \frac{n^+ n_e}{n^0} = \left( \frac{2\pi m_e kT}{h^2} \right)^{3/2} e^{-\chi_H/kT}. \]  

(37)

The electrical neutrality gives \( n_e = n^+ \). Using \( y \) to parameterize the fraction of all hydrogen that is ionized, i.e., \( y = \frac{n^+}{n} \) (where \( n = n^0 + n^+ \)), the equation then becomes

\[ \frac{y^2}{(1-y)} = \frac{1}{n} \left( \frac{2\pi m_e kT}{h^2} \right)^{3/2} e^{-\chi_H/kT}. \]  

(38)

The dominant factor here is the exponential, while the dependence on the density is weak. The characteristic temperature for ionization-recombination is \( \sim 1.6 \times 10^4 \) K, or roughly \( y \approx 1/2 \) when \( \chi/kT \sim 10 \).

Neglecting any radiation contribution, the thermal pressure can be expressed as

\[ P = (n_e + n^+ + n^0)kT = (1 + y)N\rho kT, \]  

(39)

where \( N \) is the total ion plus neutral atom number density per unit mass and is a constant, independent of density.

The specific internal energy to be used later is

\[ E = (1 + y)N \frac{3kT}{2} + yN\chi_H \text{ erg g}^{-1}, \]  

(40)

in which the ionization energy is accounted for. With the Saha equation, it is clear that \( P \) and \( E \) involve only the temperature and density.

For real calculation, of course, all species, energy levels, and reactions must be considered. For example, one also has the ionization-recombination for Helium at high temperatures (24.6 eV and 54.4 eV for the first and second electrons).

The presence of such zones of ionization has profound consequences for the structure of a star.

Later we will further use similar Saha equations for some fast nuclear reactions under certain states where the thermodynamic equilibrium can be assumed.

Knowing the thermal energy and pressure, we can derive other useful parameters. As an example, we consider the specific heat, \( c_\rho = \left( \frac{\partial E}{\partial T} \right)_\rho = \left( \frac{\partial E}{\partial y} \right)_T \left( \frac{\partial y}{\partial T} \right)_\rho \) for the above pure hydrogen gas (Eq. 40):

\[ \left( \frac{\partial E}{\partial T} \right)_\rho = \& \left( \frac{\partial E}{\partial T} \right)_y + \left( \frac{\partial E}{\partial y} \right)_T \left( \frac{\partial y}{\partial T} \right)_\rho = \&(1+y)N \frac{3kT}{2} \left[ \frac{1}{T} + \frac{2}{3} \left( \frac{3 + \chi_H}{kT} \right) \right] \frac{1}{(1+y)\frac{\partial y}{\partial T}}. \]  

(41)
Take a log of the Saha equation and then take the partial derivative of $T$,

$$\left(\frac{2}{y} + \frac{1}{1-y}\right) \frac{\partial y}{\partial T} = \left(\frac{3}{2} + \frac{\chi}{kT}\right) \frac{1}{T}. \quad (42)$$

Define $D(y) = \frac{y(1-y)}{(2-y)(1+y)}$,

$$\frac{1}{(1+y) \partial y} = D(y) \left(\frac{3}{2} + \frac{\chi}{kT}\right) \frac{1}{T}. \quad (43)$$

Therefore,

$$c_\rho = (1 + y) N \frac{3k}{2} \left[1 + D(y) \frac{2}{3} \left(\frac{3}{2} + \frac{\chi}{kT}\right)^2\right] \text{erg g}^{-1} \text{K}^{-1}. \quad (44)$$

where the second term arises from the consideration of the ionization-recombination reaction. Note that $D(1) = D(0) = 0$ and, for general $0 \leq y \leq 1$, $D(y) \geq 0$. Thus the term is greater than zero, meaning that an increase of the temperature, keeping the density fixed, requires more energy when the reaction occurs than when it does not.

\section{Adiabatic Exponents and Other Derivatives}

Having the EoS, we can in principle construct a simplified stellar model. But to construct realistic ones and to evolve them, we need several thermodynamic derivatives. We need them, for example, to study the stability of a model and to determine weather or not the convection needs to be considered. Such derivatives include the specific heats ($c_\rho$ and $c_p$), power-law exponents of the EoS $[\chi_T = \left(\frac{\partial \ln P}{\partial \ln T}\right)_\rho$ and $\chi_\rho = \left(\frac{\partial \ln P}{\partial \ln \rho}\right)_T$], and adiabatic exponents $[\Gamma_1 = \left(\frac{\partial \ln P}{\partial \ln \rho}\right)_{ad}]$, etc.. In realistic situation, the calculations need to be done numerically.

Thus it is desirable to express the derivatives as a function of selected common independent variables. Among the five variables in the first law of thermodynamics ($E$, $S$, $P$, $T$, and $V$), only two are independent. The law can be expressed in various forms by replacing $E$ with $H = E + PV$ (enthalpy), $F = E - TS$ (free energy), or $\Phi = E + PV - TS$ (the Gibbs free energy) and using $s$ and $V$, $s$ and $P$, $T$ and $V$, or $T$ and $P$ as independent variables.

\subsection{Maxwell’s relations}

Using the above expressions and such mathematical relations as

$$\frac{\partial^2 \Phi}{\partial P \partial T} = \frac{\partial^2 \Phi}{\partial T \partial P}, \quad (45)$$

one can easily drive the Maxwell’s relations (giving it a try!):
\[
\left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial P}{\partial S} \right)_V \quad (46)
\]
\[
\left( \frac{\partial T}{\partial P} \right)_S = \left( \frac{\partial V}{\partial S} \right)_P \quad (47)
\]
\[
\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V \quad (48)
\]
\[
\left( \frac{\partial S}{\partial P} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_P \quad (49)
\]

These relations are very useful to express the derivatives in certain forms and to know their relationships.

### 9.2 Other relations

Such partial derivatives can be expressed in different forms, using the Jacobian transformation, e.g.,

\[
\left( \frac{\partial V}{\partial T} \right)_P = \frac{\frac{\partial(V,P)}{\partial(V,T)}}{\frac{\partial(V,P)}{\partial(V,T)}} = - \left( \frac{\partial P}{\partial T} \right)_V \quad (50)
\]

This relation can also be derived from

\[
dV = \left( \frac{\partial V}{\partial T} \right)_P dT + \left( \frac{\partial V}{\partial P} \right)_T dP \quad (51)
\]

by holding \( V \) constant, \( dV = 0 \).

The relation will be used shortly.

### 9.3 Application example

The above relations and transformations are often needed to ride the final expressions of the so-called secondary variables, \( E, H, F, \Phi \), and the entropy variable.

Consider the relation between \( c_P \) and \( c_\rho \) or \( c_{V_\rho} \). Start by letting \( T \) and \( P \) be independent and write the specific heat content as

\[
dq = TdS = T \left[ \left( \frac{\partial S}{\partial T} \right)_P dT + \left( \frac{\partial S}{\partial P} \right)_T dP \right]. \quad (52)
\]

and

\[
dP = \left( \frac{\partial P}{\partial T} \right)_V dT + \left( \frac{\partial P}{\partial V} \right)_T dV. \quad (53)
\]
This gives
\[ dq = T \left( \frac{\partial S}{\partial T} \right)_p dT + T \left( \frac{\partial S}{\partial P} \right)_T \left[ \left( \frac{\partial P}{\partial T} \right)_V dT + \left( \frac{\partial P}{\partial V} \right)_T dV \right]. \] (54)

While holding \( V \) constant,
\[ \left( \frac{\partial q}{\partial T} \right)_V = T \left( \frac{\partial S}{\partial T} \right)_P + T \left( \frac{\partial S}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_V. \] (55)

\[ c_p - c_V = -T \left( \frac{\partial S}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_V. \] (56)

Using one of the Maxwell’s relations
\[ \left( \frac{\partial S}{\partial P} \right)_T = -\left( \frac{\partial V}{\partial T} \right)_P \] (57)

and then the relation we have just derived:
\[ \left( \frac{\partial V}{\partial T} \right)_P = \frac{\left( \frac{\partial P}{\partial T} \right)_V}{\left( \frac{\partial P}{\partial V} \right)_T} \] (58)

we have
\[ c_p - c_V = -T \left( \frac{\partial P}{\partial V} \right)_T^{-1} \left( \frac{\partial P}{\partial T} \right)_V^2. \] (59)

### 10 Review

Key Concepts: local thermodynamic equilibrium, random walk, chemical potential \( \mu \), chemical equilibrium, Fermi energy, Chandrasekhar limiting mass

What is an equation of state?

Why should the chemical potential of photon gas be equal to zero?

How to derive such quantities as density, pressure, and thermal energy for photon, ideal (Maxwell-Boltzmann), and completely degenerate gases, starting from the basic occupation distribution (with different \( \mu \) limits)?

What is the degenerate pressure?

What is the Saha equation? Under which circumstance can the equation be used?

In reality, what may be various interactions that may make an EoS imperfect?

Get familiar with derivations of various adiabatic exponents and other derivatives.