GENERAL THERMODYNAMIC RELATIONS

The first law of thermodynamics may be written as energy conservation within one gram of matter (or per baryon or per mole, i.e. in terms of specific quantities):

$$dQ = T\,dS = du + P\,dV, \tag{gt.1a}$$

where dQ is the heat input or the heat loss, T is temperature, S is entropy per gram, u is internal energy density per gram, P is pressure, and $V = 1/\rho$ is specific volume, i.e. the inverse of the density.

$$T\,dS = d\left(\frac{U}{\rho}\right) - \frac{P}{\rho^2}\,d\rho, \tag{gt.1b}$$

where U is energy density per unit volume, or

$$dS = \frac{1}{T}\,du - \frac{P}{T\rho^2}\,d\rho = \left[\frac{1}{T}\left(\frac{\partial u}{\partial T}\right)_\rho\right] dT + \left[\frac{1}{T}\left(\frac{\partial u}{\partial \rho}\right)_T - \frac{P}{T\rho^2}\right] d\rho = \tag{gt.1c}$$

$$\left(\frac{\partial S}{\partial T}\right)_\rho dT + \left(\frac{\partial S}{\partial \rho}\right)_T d\rho.$$

From the last equation it follows that

$$\left(\frac{\partial S}{\partial T}\right)_\rho = \frac{1}{T}\left(\frac{\partial u}{\partial T}\right)_\rho, \tag{gt.2a}$$

$$\left(\frac{\partial S}{\partial \rho}\right)_T = \frac{1}{T}\left(\frac{\partial u}{\partial \rho}\right)_T - \frac{P}{T\rho^2}. \tag{gt.2b}$$

Maxwell's relations come from the exactness (path-independence) of a quantity such as entropy, energy, enthalpy, Gibbs free energy, etc.

$$\left[\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial \rho}\right)_T\right]_\rho = \left[\frac{\partial}{\partial \rho}\left(\frac{\partial S}{\partial T}\right)_\rho\right]_T. \tag{gt.3}$$

$$\frac{1}{T}\frac{\partial^2 u}{\partial\rho\partial T} = -\frac{1}{T^2}\frac{\partial u}{\partial \rho} + \frac{1}{T}\frac{\partial^2 u}{\partial T\partial\rho} + \frac{P}{T^2\rho^2} - \frac{1}{T\rho^2}\frac{\partial P}{\partial T}. \tag{gt.4}$$

The term on the left hand side of (gt.4) cancels with the corresponding term on the right hand side. Rearranging the three remaining terms and using eq. (gt.2b) we obtain

$$\left(\frac{\partial u}{\partial \rho}\right)_T = \frac{P}{\rho^2} - \frac{T}{\rho^2}\left(\frac{\partial P}{\partial T}\right)_\rho = \frac{P}{\rho^2}\left[1 - \left(\frac{\partial \ln P}{\partial \ln T}\right)_\rho\right] \tag{gt.5a}$$

and

$$\left(\frac{\partial P}{\partial T}\right)_\rho = \left(\frac{\partial S}{\partial V}\right)_T = -\rho^2\left(\frac{\partial S}{\partial \rho}\right)_T. \tag{gt.5b}$$

The latter equation is much more easily derived from the exactness of the Helmholtz free energy ($F = u - TS$).

We shall need various thermodynamic functions. Among those are the adiabatic exponent γ and the adiabatic temperature gradient ∇_{ad} defined as

$$\Gamma_1 \equiv \gamma \equiv \left(\frac{\partial \ln P}{\partial \ln \rho}\right)_S , \qquad \nabla_{ad} \equiv \left(\frac{\partial \ln T}{\partial \ln P}\right)_S . \tag{gt.6a}$$

Of course, we have

$$\left(\frac{\partial \ln T}{\partial \ln \rho}\right)_S = \gamma \nabla_{ad}. \tag{gt.6b}$$

We may also need specific heats, c_V and c_P , i.e. the amount of heat needed to raise a temperature of 1 gram of matter by 1 K under constant density, or under constant pressure, respectively. We have

$$c_V = T\left(\frac{\partial S}{\partial T}\right)_\rho = \left(\frac{\partial u}{\partial T}\right)_\rho , \quad \left[\mathrm{erg\ g^{-1}\ K^{-1}}\right], \tag{gt.7a}$$

$$c_P = T\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial h}{\partial T}\right)_P = \left(\frac{\partial u}{\partial T}\right)_P - \frac{P}{\rho^2}\left(\frac{\partial \rho}{\partial T}\right)_P \quad \left[\mathrm{erg\ g^{-1}K^{-1}}\right], \tag{gt.7b}$$

where $h = u + P/\rho$ is the enthalpy.

Since

$$dS = \left(\frac{\partial S}{\partial T}\right)_\rho dT + \left(\frac{\partial S}{\partial \rho}\right)_T d\rho,$$

we have

$$\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_\rho + \left(\frac{\partial S}{\partial \rho}\right)_T \left(\frac{\partial \rho}{\partial T}\right)_P .$$

From this, eqs. (gt.5b), (gt.7a) and (gt.7b), and

$$\left(\frac{\partial \rho}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_\rho \Big/ \left(\frac{\partial P}{\partial \rho}\right)_T$$

we obtain

$$c_P = c_V + \frac{T}{\rho^2}\left(\frac{\partial P}{\partial T}\right)_\rho^2 \Big/ \left(\frac{\partial P}{\partial \rho}\right)_T . \tag{gt.8}$$

Setting $dS = 0$ in equation (gt.1c) we obtain

$$\left(\frac{\partial T}{\partial \rho}\right)_S = -\left(\frac{\partial S}{\partial \rho}\right)_T \Big/ \left(\frac{\partial S}{\partial T}\right)_\rho . \tag{gt.9}$$

Combining equations (gt.5b) , (gt.6b) , and (gt.7a) we have

$$\left(\frac{\partial \ln T}{\partial \ln \rho}\right)_S = \frac{1}{\rho c_V}\left(\frac{\partial P}{\partial T}\right)_\rho = \gamma \nabla_{ad}. \tag{gt.10}$$

Using

$$\left(\frac{\partial S}{\partial P}\right)_T = -\frac{1}{\rho^2}\left(\frac{\partial P}{\partial T}\right)_\rho \Big/ \left(\frac{\partial P}{\partial \rho}\right)_T = \frac{1}{\rho^2}\left(\frac{\partial \rho}{\partial T}\right)_P , \tag{gt.11a}$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{c_P}{T}, \tag{gt.11b}$$

we find

$$\nabla_{ad} \equiv \frac{P}{T}\left(\frac{\partial T}{\partial P}\right)_S = -\frac{P}{T}\left(\frac{\partial S}{\partial P}\right)_T \Big/ \left(\frac{\partial S}{\partial T}\right)_P = \frac{P}{\rho^2 c_P}\left(\frac{\partial P}{\partial T}\right)_\rho \Big/ \left(\frac{\partial P}{\partial \rho}\right)_T . \tag{gt.12}$$

Finally, combining equations (gt.10) and (gt.12) we have

$$\gamma \equiv \left(\frac{\partial \ln P}{\partial \ln \rho}\right)_S = \frac{c_P}{c_V}\frac{\rho}{P}\left(\frac{\partial P}{\partial \rho}\right)_T = \frac{c_P}{c_V}\left(\frac{\partial \ln P}{\partial \ln \rho}\right)_T. \tag{gt.13}$$

Many other thermodynamic quantities can be calculated using the equations derived above and now rewritten here together:

$$\left(\frac{\partial u}{\partial \rho}\right)_T = \frac{P}{\rho^2}\left[1 - \left(\frac{\partial \ln P}{\partial \ln T}\right)_\rho\right], \tag{gt.14a}$$

$$c_V = \left(\frac{\partial u}{\partial T}\right)_\rho, \quad \left[\mathrm{erg\,g^{-1}K^{-1}}\right], \tag{gt.14b}$$

$$c_P = c_V + \frac{T}{\rho^2}\left(\frac{\partial P}{\partial T}\right)_\rho^2 \Big/ \left(\frac{\partial P}{\partial \rho}\right)_T, \tag{gt.14c}$$

$$\nabla_{ad} \equiv \frac{P}{T}\left(\frac{\partial T}{\partial P}\right)_S = \frac{P}{\rho^2 c_P}\left(\frac{\partial P}{\partial T}\right)_\rho \Big/ \left(\frac{\partial P}{\partial \rho}\right)_T = \frac{c_P - c_V}{c_P}\left(\frac{\partial \ln T}{\partial \ln P}\right)_\rho, \tag{gt.14d}$$

$$\gamma \equiv \left(\frac{\partial \ln P}{\partial \ln \rho}\right)_S = \frac{c_P}{c_V}\left(\frac{\partial \ln P}{\partial \ln \rho}\right)_T, \tag{gt.14e}$$

$$\left(\frac{\partial \ln T}{\partial \ln \rho}\right)_S = \frac{1}{\rho c_V}\left(\frac{\partial P}{\partial T}\right)_\rho = \gamma \nabla_{ad}. \tag{gt.14f}$$

We shall consider now two limiting cases, gas that is non-relativistic (N-R) , and gas that is ultra-relativistic (U-R) , and in both cases the gas energy density is equal to its kinetic energy density. Let us assume that we have $U = 1.5P$, and $U = 3P$, in the two limiting cases, respectively. Combining these two relations with the energy conservation equation in the form given by the equation (gt.1b) at the beginning of this chapter, and taking $dS = 0$, we find the following adiabatic relation for a non-relativistic gas:

$$0 = d\left(\frac{U}{\rho}\right) - \frac{P}{\rho^2}\,d\rho = 1.5\,d\left(\frac{P}{\rho}\right) - \frac{P}{\rho^2}\,d\rho = \frac{1.5}{\rho}\,dP - \frac{2.5P}{\rho^2}\,d\rho, \tag{gt.15}$$

and therefore

$$\gamma \equiv \left(\frac{\partial \ln P}{\partial \ln \rho}\right)_S = \frac{5}{3}, \qquad \text{(non-relativistic)}, \tag{gt.16}$$

and the following adiabatic relation for an ultra-relativistic gas:

$$0 = d\left(\frac{U}{\rho}\right) - \frac{P}{\rho^2}\,d\rho = 3d\left(\frac{P}{\rho}\right) - \frac{P}{\rho^2}\,d\rho = \frac{3}{\rho}\,dP - \frac{4P}{\rho^2}\,d\rho, \tag{gt.17}$$

and therefore

$$\gamma \equiv \left(\frac{\partial \ln P}{\partial \ln \rho}\right)_S = \frac{4}{3}, \qquad \text{(ultra-relativistic)}. \tag{gt.18}$$

These formulae for the adiabatic exponent γ hold for any gas which has pressure and energy density dominated by particles with either $p \ll mc$ (N-R) , or $p \gg mc$ (U-R) , no matter what are the details of their distribution functions. Therefore, stars that have adiabatic structure, for example stars that are fully convective, have a power law relation between pressure and density, $P \sim \rho^\gamma$, with $\gamma = 5/3$ if gas is non-relativistic, or $\gamma = 4/3$ if gas is ultra-relativistic. Such power law equation of state is called **polytropic**, and self-gravitating spheres with such equation of state are called **polytropes**. Many different types of stars are, to a very high precision, polytropes. These include very massive, and very low mass main sequence and pre-main sequence stars, very low mass and very large mass white dwarfs. In addition, convective cores or convective envelopes of stars can also be described as partial polytropes. Historically, polytropes were very important in the development of a theory of stellar structure. A very detailed account of that is given by S. Chandrasekhar in his book: *An Introduction to the Study of Stellar Structure.*