Unit 12

Thermodynamics with Photons

12.1 Mixture of ideal gas and radiation: pressure effects

- It should be noted that we have been considering an ideal gas made up of particles only. When radiation is present along with the gas in thermodynamic equilibrium, the photons can cause two changes: (1) a radiation pressure; and (2) ionization effects (see Sec. 12.2). In this case, the adiabatic exponents in Eqs. (11.12-11.15) are not constant anymore, nor are they all equal.
- Considering this mixture, the total pressure is

  $$P = P_{\text{gas}} + P_{\text{rad}} = \frac{\rho k_{\mathrm{B}} T}{\mu m_{\mathrm{u}}} + \frac{1}{3} a T^4, \tag{12.1}$$

  and specific internal energy density

  $$U = \frac{3}{2} \frac{k_{\mathrm{B}} T}{\mu m_{\mathrm{u}}} + a T^4 V. \tag{12.2}$$

- Since the specific energy depends on volume and temperature $U(T, V)$, quasistatic changes to it in the first law of thermodynamics yields

  $$\mathrm{d}Q = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V + P \mathrm{d}V. \tag{12.3}$$

- Using the expression for the specific energy and pressure then gives

  $$\mathrm{d}Q = \left(4aT^3 V + \frac{3}{2} \frac{k_{\mathrm{B}}}{\mu m_{\mathrm{u}}}\right) \mathrm{d}T + \left(\frac{4}{3} a T^4 + \frac{k_{\mathrm{B}} T}{\mu m_{\mathrm{u}} V}\right) \mathrm{d}V. \tag{12.4}$$

- For an adiabatic process, this equation gives the thermodynamic response to changes in temperature and volume. It can then be nicely rewritten

  $$\left(12 P_{\text{rad}} + \frac{3}{2} P_{\text{gas}}\right) \frac{\mathrm{d}T}{T} + (4 P_{\text{rad}} + P_{\text{gas}}) \frac{\mathrm{d}V}{V} = 0. \tag{12.5}$$

- To evaluate expressions as in Equations (11.12)-(11.15), it's also useful to have a pressure differential term. Using Equation (12.1) we can write

  $$\begin{aligned} \mathrm{d}P &= \left(\frac{4}{3} a T^4 + \frac{RT}{\mu V}\right) \frac{\mathrm{d}T}{T} - \frac{R}{\mu} \frac{T}{V} \frac{\mathrm{d}V}{V}, \\ &= (4 P_{\text{rad}} + P_{\text{gas}}) \frac{\mathrm{d}T}{T} - P_{\text{gas}} \frac{\mathrm{d}V}{V}. \end{aligned} \tag{12.6}$$

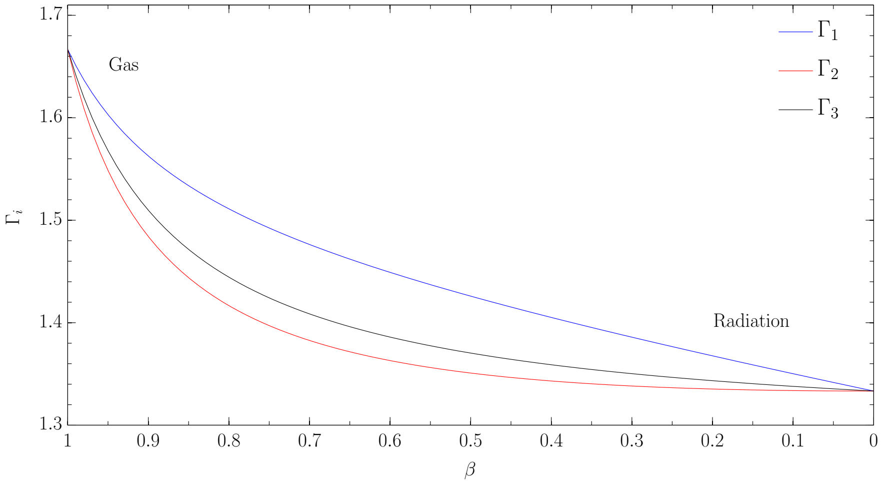

Figure 12.1: The various adiabatic exponents for different mixtures of ideal gas particles and photons.

- Plugging this into Equation (11.12) gives

$$(4P_{\rm rad} + P_{\rm gas})\frac{{\rm d}T}{T} + [\Gamma_1(P_{\rm rad} + P_{\rm gas}) - P_{\rm gas}]\frac{{\rm d}V}{V} = 0. \tag{12.7}$$

- Comparing Equation (12.5) and Equation (12.7) allows us to solve for Γ_1. It simplifies things to consider the fractional gas pressure as was done previously

$$\beta \equiv \frac{P_{\rm gas}}{P_{\rm gas} + P_{\rm rad}}. \tag{12.8}$$

- You can then show that

$$\Gamma_1 = \frac{32 - 24\beta - 3\beta^2}{24 - 21\beta}. \tag{12.9}$$

- For a gas of particles, $\beta = 1$, and therefore $\Gamma_1 = 5/3 = \gamma$, which is what we already found for an ideal gas. For a photon gas, $\beta = 0$ and $\Gamma_1 = 4/3$.

- In a similar fashion,

$$\Gamma_2 = \frac{32 - 24\beta - 3\beta^2}{24 - 18\beta - 3\beta^2}, \tag{12.10}$$

$$\Gamma_3 = \frac{32 - 27\beta}{24 - 21\beta}. \tag{12.11}$$

  See Figure 12.1 for the dependence of these on β.

- Using the equations we just developed, the specific heats can also be computed:

$$c_V = \left(\frac{{\rm d}Q}{{\rm d}T}\right)_V = c_V^0\frac{8 - 7\beta}{\beta}, \tag{12.12}$$

$$c_P = \left(\frac{{\rm d}Q}{{\rm d}T}\right)_P = c_V^0\frac{32/3 - 8\beta - \beta^2}{\beta^2}, \tag{12.13}$$

$$\tag{12.14}$$

  where $c_V^0 = \frac{3}{2}\frac{R}{\mu}$ is the ideal gas-only value.

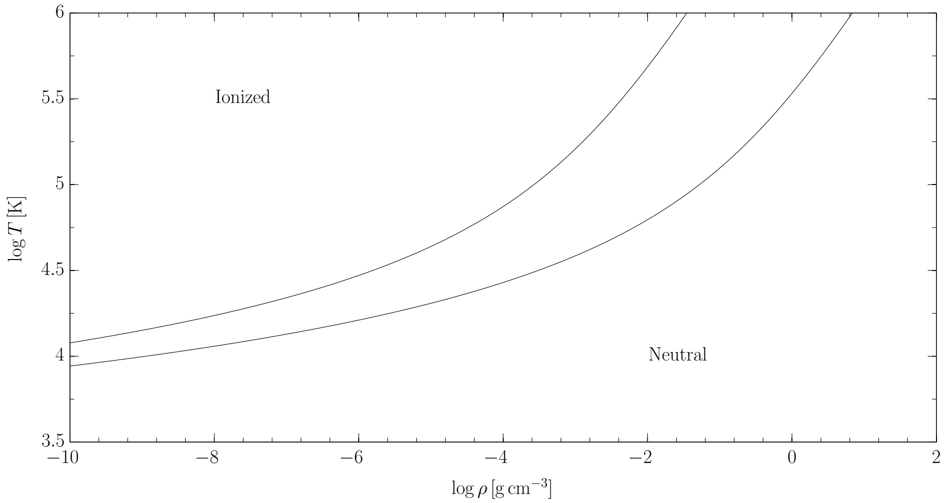

Figure 12.2: Ionization of a pure H gas using Equation (12.19). The lower line represents the state at 50% ionization, while the upper is for 99%.

- Note that the ratio of specific heats gives
$$\frac{c_P}{c_V} = \frac{\Gamma_1}{\beta}, \tag{12.15}$$
which makes sense in the appropriate limits, reducing to what we found before.
- The same procedure can be carried out for mixtures of some degenerate gas too.

12.2 Mixture of ideal gas and radiation: ionization effects

- As mentioned at the beginning of this section, the other consideration is the ionization of the gas that radiation produces, which has profound effects on the thermodynamic state of the gas.
- Let's just consider a hydrogen gas for simplicity in what follows.
- In general radiation causes ionization and subsequent recombination:
$$\mathrm{H}^+ + \mathrm{e}^- \longleftrightarrow \mathrm{H}^0 + \chi_\mathrm{H}, \tag{12.16}$$
where $\chi_\mathrm{H} = 13.6\,\mathrm{eV}$ is the energy needed to ionize hydrogen. We will only consider the ground state.
- To measure the number densities of electrons (n_e), ions (n^+), and neutral H (n^0) in thermodynamic equilibrium, we employ the tools we used in Sec. 6.1 using a Boltzmann distribution.
- After taking into account the appropriate degeneracy factors and energy levels and chemical potentials, we can form the ratio $n^+ n_e/n^0$ using Equation (6.12) and obtain the *Saha equation* for a pure hydrogen gas
$$\frac{n^+ n_e}{n^0} = \left(\frac{2\pi m_e k_\mathrm{B}}{h^2}\right)^{3/2} T^{3/2} \mathrm{e}^{-\chi_\mathrm{H}/kT}. \tag{12.17}$$
- We constrain the system to have charge neutrality, $n_e = n^+$ and nucleon number density $n^+ + n^0 = n$. Then we define the fraction of ionization
$$y = \frac{n_e}{n} = \frac{n^+}{n}, \tag{12.18}$$
as we did in Equation (5.16).

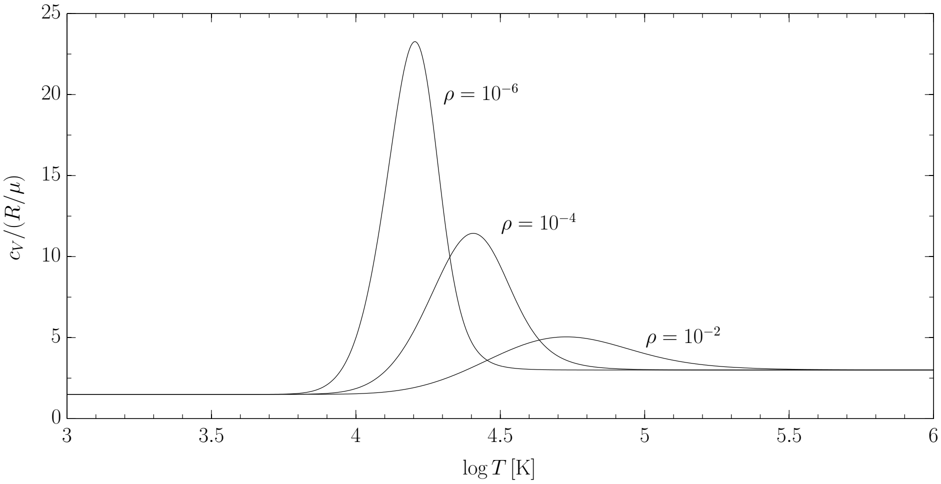

Figure 12.3: The specific heat at constant volume for H at different densities (in $\mathrm{g\,cm^{-3}}$). The familiar value of 3/2 is found for lower temperatures before ionization takes place. Full ionization occurs at the highest temperatures where the value reaches 3, which is twice the value of neutral gas because the number of particles per gram is twice as large.

- Then the Saha equation is

$$\frac{y^2}{1-y} = \frac{1}{n}\left(\frac{2\pi m_e k_\mathrm{B}}{h^2}\right)^{3/2} T^{3/2}\mathrm{e}^{-\chi_\mathrm{H}/kT}. \tag{12.19}$$

- We already see that at high temperatures we expect either collisions or a strong radiation field to ionize the gas $y \to 1$.
- We recognize for a pure hydrogen gas that $n = \rho/\mu m_\mathrm{u}$ with $\mu = 1$, so Equation (12.19) can be solved for a given ionization fraction in terms of temperature and mass density.
- Figure 12.2 shows the necessary conditions for 50% and 99% ionization.
- Note that at about 10^4 K is the half ionization point for hydrogen, only weakly dependent on density.
- A good rule of thumb is that a temperature for half ionization is $\chi/kT \sim 10$ to within a factor of a few depending on density.
- Recall that $1eV \sim 10^4$ K. So , for example, the first ionization potential of He is 24.6 eV. Thus at about 3×10^4 we'd expect ionization to take place, and about double that temperature for removing the 2nd He electron.
- Given the number densities, we can compute the pressure and internal energy as in previous cases and then the full thermodynamic set of quantities.
- Recognize that the pressure

$$P = (n_e + n^+ + n^0)k_\mathrm{B}T = (1+y)N\rho k_\mathrm{B}T, \tag{12.20}$$

since $N\rho = n = n^+ + n^0$. N is the total nucleon number (ions plus neutrals) per unit mass, and is independent of density, thus constant.

- The specific internal energy is

$$U = \frac{3}{2}(1+y)\frac{n}{\rho}k_\mathrm{B}T + y\frac{n}{\rho}\chi_\mathrm{H} = \frac{3}{2}(1+y)Nk_\mathrm{B}T + yN\chi_\mathrm{H}, \tag{12.21}$$

This can be understood since, to completely ionize the gas, we need to add $N\chi_\mathrm{H}$ to strip off the electrons, and another $3/2NkT$ to bring the ions up to the ambient temperature.

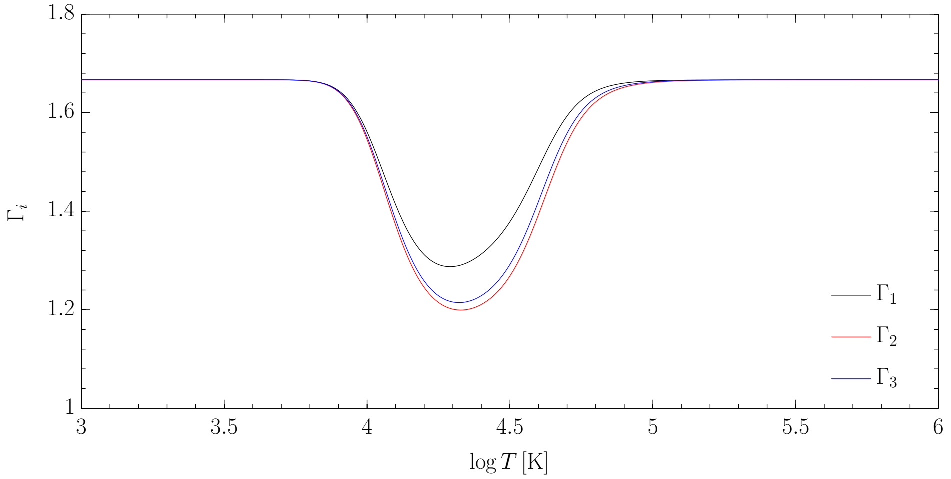

Figure 12.4: Adiabatic exponents for ionized H at a density of $10^{-4}\,\mathrm{g\,cm^{-3}}$.

- From these expressions the specific heats can be computed from the appropriate differentials. Since $U = U(T, y)$, and $c_V = \mathrm{d}U/\mathrm{d}T$, we get extra terms.

- It works out to be

$$c_V = \frac{3}{2} N k_\mathrm{B} (1+y) \left[1 + \frac{2}{3} D(y) \left(\frac{3}{2} + \frac{\chi_\mathrm{H}}{k_\mathrm{B} T} \right)^2 \right], \tag{12.22}$$

where

$$D(y) = \frac{y(1-y)}{(2-y)(1+y)}. \tag{12.23}$$

- Note that $D(0) = D(1) = 0$, so the specific heat only changes by $1 + y$ as the gas goes from neutral to fully ionized. But D is finite for intermediate values of y, thus bringing in contributions from the other terms.

- A few examples of c_V are shown in Figure 12.3 for several densities.

- Finally, the adiabatic exponents can be computed in similar ways using the prior results and Eqs. (11.12)-(11.15).

- Their values for a density of 10^{-4} across the ionization fraction range is shown in Figure 12.4.

- The Γ_i all take their ideal gas values for full ionization and for complete neutrality.

- Where ionization occurs, the values decrease quickly, and then increase again as ionization completes.

- To understand this, consider adiabatic compression of the gas, and let's focus on Γ_3, which, according to Equation (11.15), relates the temperature and volume.

- Before ionization, we see the value of 5/3 for the neutral gas, which simply means it is heating up under compression as $T \sim \rho^{2/3} \sim V^{-2/3}$.

- When ionization starts to occur, the value decreases, and the temperature sensitivity on volume is weaker. The energy is used to ionize the gas, instead of heating it up as quickly.

12.3 Useful ideal gas equations

Let's collect many of the useful relationships:

$$\begin{aligned}
P &= \frac{\rho R T}{\mu} = \frac{\rho k_{\mathrm{B}} T}{\overline{m}} && (12.24)\\
P\rho^{-\gamma} &= \mathrm{const} && (12.25)\\
c_s &= \sqrt{\frac{\gamma R T}{M}} = \sqrt{\frac{\gamma P}{\rho}} && (12.26)\\
C_P - C_V &= R/\mu && (12.27)\\
C_V &= \frac{3}{2}\frac{R}{\mu} && (12.28)\\
C_P &= \frac{5}{2}\frac{R}{\mu} && (12.29)\\
U &= \int_0^M C_V T \,\mathrm{d}m' && (12.30)
\end{aligned}$$