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Chapter 2

Advanced gas-microphysics

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ABSTRACT

This Chapter contains the description of a miscellanea of microphysical processes incorporated in most numerical codes for studying the thermal and dynamical properties of the interstellar medium. They include the expressions of the ambipolar, Hall and Ohm resistivities of a weakly ionized gas; the formulae to compute the internal energy and adiabatic index of a Hydrogen-Helium mixture; the relations between forward and backward cross sections and rate coefficients according to the principle of detailed balance. The goal of this Chapter is to provide a collection of ready-to-use formulae for numerical evaluation.

KEYWORDS

resistivities, internal energy, detailed balance, microphysics, adiabatic index

2.1 MULTI-FLUID DESCRIPTION OF A WEAKLY IONIZED GAS

The macroscopic behavior of a conductive fluid (*plasma*) is described by the set of magnetohydrodynamic (MHD) equations, which couple the hydrodynamic equations introduced in Chap. 1 (modified by the effects of the electric and magnetic field) with Maxwell's equations. In the low-density partially-ionized ISM, the situation is complicated by the fact that the different components (neutral particles, ions, electrons, and charged dust grains) are coupled to the ambient magnetic field in different degrees, and possess different bulk velocities: magnetic fields affect the motion of the charged component of the gas, which in turn transfers the effects of the Lorentz force to the neutrals by elastic collisions. In this case, we speak of a *multi-fluid medium* (see, e.g., Wardle & Ng 1999; Desch & Mouschovias 2001; Nakano et al. 2002; Tassis & Mouschovias 2005). A multi-fluid medium is composed of an arbitrary number of species s , characterized by particle mass m_s , density ρ_s , flow velocity $\mathbf{u}_s$ and charge $Z_s e$, where e is the electron charge. Taking the zeroth- and first-order momenta of the Boltzmann equation for each species, the equations of continuity and momentum are

$$\frac{\partial \rho_s}{\partial t} + \nabla \cdot (\rho_s \mathbf{u}_s) = \sum_{s'} S_{ss'}, \quad (2.1)$$

$$\begin{aligned} \frac{\partial}{\partial t}(\rho_s \mathbf{u}_s) + \nabla \cdot (\rho_s \mathbf{u}_s \mathbf{u}_s) = & -\nabla p_s - \rho_s \nabla \mathcal{V} + e \frac{Z_s \rho_s}{m_s} \left(\mathbf{E} + \frac{\mathbf{u}_s}{c} \times \mathbf{B} \right) \\ & + \sum_{s'} \mathbf{F}_{ss'} + \sum_{s'} \mathbf{r}_{ss'}, \end{aligned} \quad (2.2)$$

where $\mathcal{V}$ is the gravitational potential, $\mathbf{E}$ is the electric field, $\mathbf{B}$ is the magnetic field, $\mathbf{F}_{ss'}$ is the friction force (per unit volume) exerted on particles of the fluid s by particles of the fluid s' by elastic collisions, $S_{ss'}$ and $\mathbf{r}_{ss'}$ are the rate of change of density and momentum, respectively, of the species s due to inelastic collisions (chemical reactions) with particles of species s' . The friction force $\mathbf{F}_{ss'}$ accounting for elastic collisions between particles with a Maxwellian is

$$\mathbf{F}_{ss'} = \gamma_{ss'} \rho_s \rho_{s'} (\mathbf{u}_{s'} - \mathbf{u}_s), \quad (2.3)$$

where $\gamma_{ss'}$ is the *collisional drag coefficient*, related to the *momentum transfer rate coefficient* $\langle \sigma v \rangle_{ss'}$ by

$$\gamma_{ss'} = \frac{\langle \sigma v \rangle_{ss'}}{m_s + m_{s'}}. \quad (2.4)$$

In general, $\langle \sigma v \rangle_{ss'}$ is a function of the temperatures T_s and $T_{s'}$ and of the relative mean velocity $|\mathbf{u}_{s'} - \mathbf{u}_s|$ of the interacting species. Thus, $\mathbf{F}_{ss'}$ is in general a non-linear function of the relative mean velocity. Accurate values of $\langle \sigma v \rangle_{ss'}$ for various colliding particles, and useful fitting formulae for a wide range of temperatures and drift velocities, are derived in [Pinto et al. \(2008\)](#).

2.1.1 Resistivities

In a multi-fluid medium, the parallel, Pedersen, and Hall conductivities are defined as

$$\sigma_{\parallel} = \frac{ec}{B} \sum_s \left(\frac{Z_s \rho_s}{m_s} \right) \beta_{sn}, \quad (2.5)$$

$$\sigma_P = \frac{ec}{B} \sum_s \left(\frac{Z_s \rho_s}{m_s} \right) \frac{\beta_{sn}}{1 + \beta_{sn}^2}, \quad (2.6)$$

$$\sigma_H = \frac{ec}{B} \sum_s \left(\frac{Z_s \rho_s}{m_s} \right) \frac{1}{1 + \beta_{sn}^2}, \quad (2.7)$$

where

$$\beta_{sn} = \frac{1}{\gamma_{sn} \rho_n} \left(\frac{Z_s e B}{m_s c} \right), \quad (2.8)$$

is the *Hall parameter*, the ratio of the cyclotron frequency of a particle s and its characteristic frequency of collision with neutral particles (see, e.g., [Nakano & Umebayashi 1980, 1986; Nakano et al. 2002](#))¹. The Hall parameter is a

1. Notice that the Hall parameter is negative for negatively charged species.

measure of the coupling of the charged particles to the magnetic field: in the ISM, electrons and very small grains in general have $|\beta_{sn}| \gg 1$ and are therefore well coupled to the ambient magnetic field. Conversely, ions and large grains can decouple from the field, reducing the parallel and Pedersen conductivities. The corresponding resistivities are

$$\eta_{\text{ad}} \equiv \frac{c^2}{4\pi} \left(\frac{1}{\sigma_{\parallel}} - \frac{\sigma_{\text{P}}}{\sigma_{\text{P}}^2 + \sigma_{\text{H}}^2} \right), \quad (2.9)$$

$$\eta_{\text{H}} \equiv \frac{c^2}{4\pi} \left(\frac{\sigma_{\text{H}}}{\sigma_{\text{P}}^2 + \sigma_{\text{H}}^2} \right), \quad (2.10)$$

$$\eta_{\text{O}} \equiv \frac{c^2}{4\pi\sigma_{\parallel}}. \quad (2.11)$$

The expressions above are valid for collisions with a single neutral species. In some situations, it is necessary to account for collisions with two or more neutral species, e.g., in mixtures of H_2 , He, or H_2 , He, and H. In these cases, the formulae above can be easily generalized by writing the Hall parameter as

$$\beta_s = \frac{1}{\sum_n \gamma_{sn} \rho_n} \left(\frac{q_s B}{m_s c} \right). \quad (2.12)$$

As an example, consider the simple case of a weakly ionized plasma made of electrons and a single species of ions with charge $Z_i e$. Charge neutrality implies

$$\frac{\rho_e}{m_e} = \frac{Z_i \rho_i}{m_i}. \quad (2.13)$$

In addition, $|\beta_{en}| \gg \beta_{in}$, since $m_e \ll m_i$ while the momentum transfer rate coefficient $\langle \sigma v \rangle$ are of the same order for electron-neutral and ion-neutral collisions. Therefore

$$\eta_{\text{ad}} \approx |\beta_{en}| \beta_{in} \eta_{\text{O}}, \quad \eta_{\text{H}} \approx |\beta_{en}| \eta_{\text{O}}, \quad (2.14)$$

and

$$\eta_{\text{O}} \approx \left(\frac{m_i c B}{4\pi Z_i e \rho_i} \right) \frac{1}{|\beta_{en}|}. \quad (2.15)$$

It is important to remember that the multi-fluid approximation is valid for a weakly ionized gas, in which collisions between charged species (Coulomb interactions) can be neglected. When this is not the case, the expressions for the resistivities must be modified (see, for example [Pinto et al. 2008](#)).

Expressions for the coefficients η_{ad} , and η_{O} for a variety of astrophysical conditions can be found e.g. in [Pinto & Galli \(2008\)](#); [Pinto et al. \(2008\)](#). Tables of equilibrium abundances from a detailed chemical network relevant to the conditions of prestellar core collapse, and a code to compute them are given

by Marchand et al. (2016) and are available at the CDS via anonymous FTP². A similar task is performed by the stand-alone Fortran90 module³ NICIL, that calculates the coefficients of the non-ideal MHD terms of Ohmic resistivity, the Hall effect, and ambipolar diffusion (Wurster 2016). Applications to protoplanetary disks can be found in Umebayashi & Nakano (1990), Ilgner & Nelson (2006), and Bai & Goodman (2009).

2.2 MHD EQUATIONS

The equations of continuity, momentum, and energy for the mean fluid can be derived summing the Eqs. (2.1) and (2.2) over the species s , neglecting the rate of change of density and momentum of each species by chemical reactions ($S_{ss'} = \mathbf{r}_{ss'} = 0$). These should be compared with the equations of hydrodynamics presented in Chap. ?? . The momentum equation for the mean fluid (cf. Eq. ??) includes the Lorentz force,

$$\rho \frac{D\mathbf{u}}{Dt} = -\nabla p - \rho \nabla \mathcal{V} + \frac{\mathbf{J}}{c} \times \mathbf{B}, \quad (2.16)$$

where $\mathbf{u} = (1/\rho) \sum_s \rho_s \mathbf{u}_s$ is the *mean* fluid velocity, $\rho = \sum_s \rho_s$ and $p = \sum_s p_s$ are the total gas density and pressure, respectively, $\mathbf{J} = e \sum_s (Z_s \rho_s / m_s) \mathbf{u}_s$ is the electric current, and $D/Dt = \partial/\partial t + \mathbf{u} \cdot \nabla$ is the convective derivative. Similarly, the energy equation (cf. Eq. ??) becomes

$$\frac{\partial(\rho\epsilon)}{\partial t} + \nabla \cdot \left[\left(\rho\epsilon + p + \frac{B^2}{8\pi} \right) \mathbf{u} - \frac{(\mathbf{u} \cdot \mathbf{B})\mathbf{B}}{4\pi} \right] = \Gamma - \Lambda, \quad (2.17)$$

where the specific energy ϵ (energy per unit mass) is

$$\epsilon = \epsilon_{\text{int}} + \frac{u^2}{2} + \frac{B^2}{8\pi\rho}. \quad (2.18)$$

The internal energy ϵ_{int} is evaluated in Sect. 2.3 for a hydrogen-helium mixture. The quantities Γ and Λ on the right hand side of Eq. (2.17) are the total volumetric heating and cooling rates discussed in Chap. 1. In a magnetized fluid, Γ includes the contribution of the dissipation of magnetic energy (see Sect. 2.2.1). Often, the solution of Eq. (2.17) is avoided by assuming an *equation of state*, i.e. a relation between p and $\rho\epsilon$.

This set of MHD equations must be coupled to Maxwell's equations:

$$\nabla \times \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} \quad (\text{Faraday's law}), \quad (2.19)$$

$$\nabla \times \mathbf{B} = \frac{4\pi}{c} \mathbf{J} + \frac{1}{c} \frac{\partial \mathbf{E}}{\partial t} \quad (\text{Ampère's law}), \quad (2.20)$$

2. <http://cdsarc.u-strasbg.fr/http://130.79.128.5> or via <http://cdsarc.u-strasbg.fr/viz-bin/qcat?J/A+A/592/A18>.

3. Available at <https://bitbucket.org/jameswurster/nicil>.

and

$$\nabla \cdot \mathbf{B} = 0, \quad (2.21)$$

expressing the condition of no magnetic monopoles. A comparison of Faraday's law (Eq. 2.19) and Ampère's law (Eq. 2.20), shows that the time derivative of $\mathbf{E}$ (the displacement current) in Eq. (2.20) is of order of $(u/c)^2$ with respect to $c|\nabla \times \mathbf{B}|$. Thus, the displacement current can be safely neglected in all applications of Ampère's law to ISM conditions.

A relation between $\mathbf{E}$, $\mathbf{B}$ and $\mathbf{J}$ can be obtained by evaluating the term $\mathbf{E} + \mathbf{u} \times \mathbf{B}/c$ from the sum of the momentum equation for each species and using the condition of charge neutrality. Inserting this *generalized Ohm's equation* into Faraday's law, Eq. (2.19), and using Ampère's law without displacement current, an evolution equation for $\mathbf{B}$ reference system of the mean fluid can be obtained:

$$\begin{aligned} \frac{\partial \mathbf{B}}{\partial t} = & \nabla \times (\mathbf{u} \times \mathbf{B}) - \nabla \times \left\{ \frac{\eta_{\text{ad}}}{B^2} \mathbf{B} \times [(\nabla \times \mathbf{B}) \times \mathbf{B}] \right\} \\ & - \nabla \times \left[\frac{\eta_{\text{H}}}{B} (\nabla \times \mathbf{B}) \times \mathbf{B} \right] - \nabla \times (\eta_{\text{O}} \nabla \times \mathbf{B}), \end{aligned} \quad (2.22)$$

where η_{ad} , η_{H} , and η_{O} are the ambipolar diffusion, Hall, and Ohm resistivities. Their expressions are given in Sect. 2.1.1.

2.2.1 Ambipolar diffusion and Ohmic heating

In a weakly ionized fluid, the rate of energy dissipation is equal to the sum of the work done by friction forces (per unit volume) $\mathbf{F}_{sn}$ exerted by neutrals n on charged species s ,

$$\Gamma_{\text{mag}} = \sum_n \mathbf{u}_n \cdot \sum_s \mathbf{F}_{sn}, \quad (2.23)$$

(see, e.g., [Braginskii 1965](#)). Substituting in Eq. (2.23) the friction force given by Eq. (2.3) and the expressions of the drift velocities (see [Pinto & Galli 2008](#), for details), Γ_{mag} can be written in terms of the resistivities and the ambient magnetic field,

$$\Gamma_{\text{mag}} = \Gamma_{\text{ad}} + \Gamma_{\text{O}} = \frac{\eta_{\text{ad}}}{4\pi B^2} |\mathbf{B} \times (\nabla \times \mathbf{B})|^2 + \frac{\eta_{\text{O}}}{4\pi} |\nabla \times \mathbf{B}|^2, \quad (2.24)$$

where Γ_{ad} represents the dissipation of drift motions between the charged particles and the neutrals driven by the Lorentz force, whereas Γ_{O} represents the heating of the gas due to the dissipation of the electric current $\mathbf{J} = (c/4\pi)\nabla \times \mathbf{B}$. Eq. (2.24) is valid for a weakly ionized gas (i.e., one in which the collisions between charged species can be neglected with respect to collisions between charged and neutral species). The expression of Γ_{mag} valid for arbitrary ionization levels can be found in [Pinto & Galli \(2008\)](#).

In Eq. (2.24), the heating term Γ_{ad} can also arise from the dissipation of MHD waves by ion-neutral friction. In this case, a time average of the fluctuating

component of the magnetic field must be taken. The result is (Pinto et al. 2012)

$$\Gamma_{\text{ad}}(k) = \frac{B_0^2 k^2 \delta B^2(k)}{32\pi^2 \gamma_{\text{in}} \rho_i \rho_n}, \quad (2.25)$$

where k is the wavenumber, B_0 the mean field and $\delta B(k)$ the wave amplitude. Equation (2.25) need to be properly averaged over the spectrum of wave energy $\delta B^2(k)$.

2.2.2 Minimal chemical model

The evaluation of the resistivity coefficients listed in Sect. 2.1.1 requires the knowledge of the ionization fraction of the gas and the composition of the plasma component in terms of the ion, electron and charged dust grain fractions. Chemical models for this purpose often involve hundreds of species and thousands of reactions, and their inclusion in 2D and 3D numerical codes is not straightforward (see Chap. ??). For a first assessment of the resistive properties of an interstellar cloud or a protostellar disk, one can resort to the simplified treatment used by Oppenheimer & Dalgarno (1974). In this approach, only a small set of generic species is considered, e.g., molecular ions like HCO^+ and H_3^+ , heavy (“metal”) atomic ions like Na^+ and Mg^+ , and charged dust grains. This formulation still allows for the proper treatment of the destruction of molecular ions by including charge transfer to heavy atoms as well as dissociative recombination with electrons, with the subsequent destruction of the heavy atomic ions by recombination on charged grains. Examples and applications to collapse models of this minimal chemical model can be found in Glassgold et al. (2012) and Padovani et al. (2014).

2.3 INTERNAL ENERGY OF A HYDROGEN-HELIUM MIXTURE

Consider a gas with mass fractions X of hydrogen and Y of helium, neglecting contributions of heavy elements. Following Black & Bodenheimer (1975), and D’Angelo & Bodenheimer (2013), define $y = \rho_{\text{H}}/(\rho_{\text{H}_2} + \rho_{\text{H}})$ the degree of dissociation of H_2 , $x = \rho_{\text{H}^+}/(\rho_{\text{H}^+} + \rho_{\text{H}})$ the degree of ionization of H, $z_1 = \rho_{\text{He}^+}/(\rho_{\text{He}^+} + \rho_{\text{He}})$ the degree of single ionization of He, and $z_2 = \rho_{\text{He}^{++}}/(\rho_{\text{He}^{++}} + \rho_{\text{He}^+})$ the degree of double ionization of He, respectively. The total specific internal energy is

$$\epsilon_{\text{int}} = \epsilon_{\text{H}_2} + \epsilon_{\text{H}} + \epsilon_{\text{H}^+} + \epsilon_{\text{HH}} + \epsilon_{\text{He}} + \epsilon_{\text{He}^+} + \epsilon_{\text{He}^{++}}, \quad (2.26)$$

where

$$\epsilon_{\text{H}} = \frac{3}{2} \left(\frac{k_{\text{B}} T}{m_{\text{H}}} \right) X(1+x)y \quad (2.27)$$

is the translational energy of H,

$$\epsilon_{\text{H}^+} = \left(\frac{I_{\text{H}}}{m_{\text{H}}} \right) Xxy \quad (2.28)$$

is the ionization energy of H,

$$\epsilon_{\text{HH}} = \left(\frac{E_{\text{H}_2}}{m_{\text{H}_2}} \right) X y \quad (2.29)$$

is the dissociation energy of H_2 ,

$$\epsilon_{\text{He}} = \frac{3}{2} \left(\frac{k_{\text{B}} T}{m_{\text{He}}} \right) Y (1 + z_1 + z_1 z_2) \quad (2.30)$$

is the translational energy of He,

$$\epsilon_{\text{He}^+} = \left(\frac{I_{\text{He}}}{m_{\text{He}}} \right) Y z_1 (1 - z_2) \quad (2.31)$$

is the ionization energy of He, and

$$\epsilon_{\text{He}^{++}} = \left(\frac{I_{\text{He}^+}}{m_{\text{He}}} \right) Y z_1 z_2 \quad (2.32)$$

is the ionization energy of He^+ . In these expressions, $I_{\text{H}} = 13.60$ eV, $I_{\text{He}} = 24.59$ eV, and $I_{\text{He}^+} = 54.42$ eV are the ionization energies of H, He, and He^+ , respectively, and $E_{\text{H}_2} = 4.48$ eV is the dissociation energy of H_2 . The quantities y , x , z_1 and z_2 are computed from standard Saha equations (see their expressions in [D'Angelo & Bodenheimer 2013](#)). The expression for the specific energy of H_2 must take into account also the energy stored in the internal degrees of freedom of the molecule, expressed by the *partition function* $Z(T)$,

$$\epsilon_{\text{H}_2} = \left(\frac{3}{2} + \frac{\text{d} \ln Z}{\text{d} \ln T} \right) \left(\frac{k_{\text{B}} T}{m_{\text{H}_2}} \right) X (1 - y). \quad (2.33)$$

The partition function of H_2 can be factorized into its rotational, vibrational, and electronic contributions,

$$Z = Z_{\text{rot}} Z_{\text{vib}} Z_{\text{el}}. \quad (2.34)$$

The rotational partition function of ortho/para- H_2 , approximated as a rigid quantum rotor, is

$$Z_{\text{p,o}} = \sum_J (2J + 1) e^{-J(J+1)\Theta_{\text{rot}}/T}, \quad (2.35)$$

where $\Theta_{\text{rot}} = 85.5$ K and the sum is performed over even (odd) values of J for para- (ortho-) H_2 . The vibrational partition function of H_2 , approximated as a quantum harmonic oscillator, is

$$Z_{\text{vib}} = (1 - e^{-\Theta_{\text{vib}}/T})^{-1}, \quad (2.36)$$

with $\Theta_{\text{vib}} = 6140$ K. The electronic partition function of H_2 is simply equal to the degeneracy of the lowest electronic level,

$$Z_{\text{el}} = 2I + 1, \quad (2.37)$$

where $I = 0$ ($I = 1$) for para- (ortho-) H_2 .

The partition function of a mixture of para/ortho H_2 , when the two species are in equilibrium, is the sum of the corresponding partition functions Z_p and Z_o . However, if no efficient mechanism for converting between the two species is available, the H_2 ortho/para ratio can be considered “frozen”. This leads to

$$Z_{\text{rot}} = Z_p^{f_p} (Z_o e^{2\Theta_{\text{rot}}/T})^{f_o}. \quad (2.38)$$

where f_p and f_o are the fractional abundances of para- and ortho- H_2 (with $f_p + f_o = 1$), and the additional exponential is required in the ortho- H_2 to ensure that $Z_o e^{2\Theta_{\text{rot}}/T} \rightarrow 1$ when $T \rightarrow 0$ (Boley et al. 2007b). For an in-depth discussion, see, e.g., Pathria & Beale (2011). Fig. 2.1 shows the specific energy e of a gas with $X = 0.71$ and $Y = 0.27$, density $\rho = 10^{-12} \text{ g cm}^{-3}$, and ortho/para H_2 ratio 3:1 computed according to Eq. (2.26).

2.3.1 Equation of state and adiabatic index

The *adiabatic exponents* characterize the behavior of a thermodynamic system undergoing infinitesimal adiabatic changes. The *first adiabatic exponent*, defined as

$$\Gamma_1 = \left(\frac{\partial \ln p}{\partial \ln T} \right)_S \quad (2.39)$$

at constant entropy S , describes how pressure responds to compression, and is relevant for dynamical processes like collapse, pulsation, wave propagation, etc. It enters in the definition of the *adiabatic sound speed* c_s , a quantity needed to evaluate the stability condition of a numerical scheme, defined as the square root of the derivative of the pressure p with respect to the density ρ at constant entropy S . Other adiabatic exponents are Γ_2 , that describes how temperature responds to changes in the pressure (relevant for determining whether convection takes place), and Γ_3 , which describes how temperature responds to compression. The *equation of state* of an ideal gas is

$$p = \frac{k_B}{\mu m_H} \rho T, \quad (2.40)$$

where k_B is the Boltzmann constant, μ is the *mean molecular weight*, and m_H the mass of a hydrogen atom. Using Eq. (2.39), the adiabatic sound speed is

$$c_s = \left(\frac{\partial p}{\partial \rho} \right)_S^{1/2} = \sqrt{\frac{\Gamma_1 p}{\rho}}. \quad (2.41)$$

The mean molecular weight is⁴

$$\mu^{-1} = \frac{1}{4} [2X(1 + y + 2xy) + Y(1 + z_1 + z_1 z_2)]. \quad (2.42)$$

4. It is assumed that dissociation of H_2 has been completed before ionization of H begins, and that the first stage of ionization of He has been completed before the second begins.

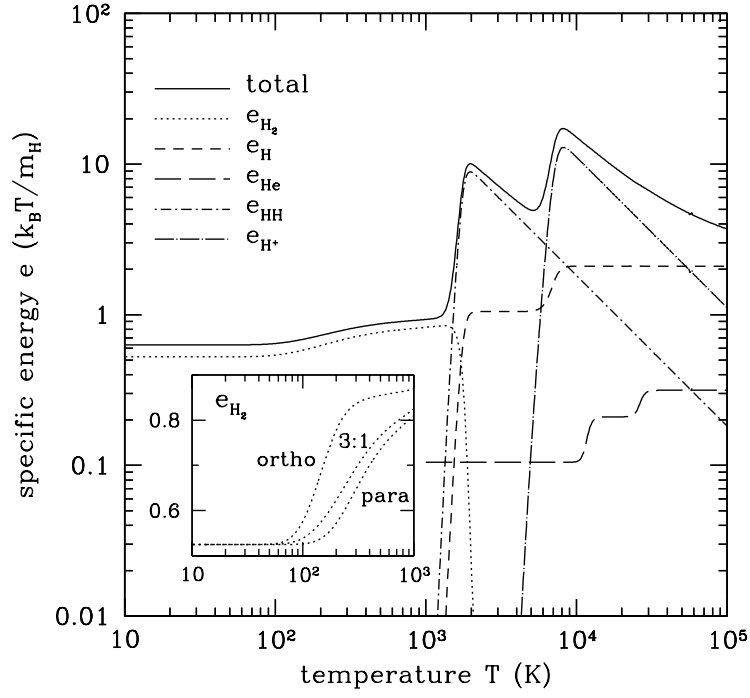


FIGURE 2.1 Specific energy e of a gas with $X = 0.71$ and $Y = 0.27$, density $\rho = 10^{-12} \text{ g cm}^{-3}$, and ortho/para H_2 ratio 3:1 in LTE. The inset shows e_{H_2} for ortho- H_2 , para- H_2 , and a 3:1 ortho/para mixture.

The first adiabatic exponent can also be written as

$$\Gamma_1 = \chi_\rho + \frac{1}{c_V} \left(\frac{k_B}{\mu m_H} \right) \chi_T^2, \quad (2.43)$$

where c_V is the *specific heat at constant volume*,

$$c_V = \frac{d\epsilon_{\text{int}}}{dT}, \quad (2.44)$$

and the so-called density and temperature exponents are

$$\chi_\rho = \left(\frac{\partial \ln p}{\partial \ln \rho} \right)_T = 1 - \frac{\partial \ln \mu}{\partial \ln \rho}, \quad (2.45)$$

$$\chi_T = \left(\frac{\partial \ln p}{\partial \ln T} \right)_\rho = 1 - \frac{\partial \ln \mu}{\partial \ln T}. \quad (2.46)$$

In the special case when chemical reactions can be ignored, and the composition of the gas is fixed, μ takes a constant value, $\chi_\rho = \chi_T = 1$, and Γ_1 takes the usual form

$$\Gamma_1 = \gamma = \frac{c_p}{c_V}, \quad (2.47)$$

where γ is the adiabatic index, and c_p is the *specific heat at constant pressure*,

$$c_p = c_V + \frac{k_B}{\mu m_H}, \quad (2.48)$$

(Meyer's relation). In this case, from the definition of c_V (Eq. 2.44), the expressions of the specific energies, Eqs. (2.27)–(2.32), and the definition of the mean molecular weight (Eq. 2.42), one obtains

$$c_V = \frac{3}{2} \frac{k_B}{\mu m_H} + x_{\text{H}_2} \frac{k_B}{m_{\text{H}_2}} \frac{d}{dT} \left(T \frac{d \ln Z}{d \ln T} \right), \quad (2.49)$$

where $x_{\text{H}_2} = X(1 - y)$ is the mass fraction of H_2 . The first term in Eq. (2.49) represents the contribution to c_V of the translational degrees of freedom of all species (equivalent to a single species with mass μm_H), while the second term represents the contribution of internal degrees of freedom of H_2 . Substituting in Eq. (2.49) the partition function of H_2 (Eq. 2.34) for a given combination of ortho and para states, and using Meyer's relation (Eq. 2.48), one can easily compute the adiabatic index γ as function of T for a hydrogen-helium mixture with arbitrary fractional abundance of H_2 (see, e.g., [Sharda et al. 2019](#)).

In general, however, the chemical composition of the gas changes with temperature and density owing to chemical reactions. In this case, the calculation of the adiabatic index requires the evaluation of derivatives of the molecular weight μ with respect to density and temperature, Eqs. (2.45) and (2.46) (see, e.g., Appendix A of [Tomida et al. 2013](#)). The calculation is easily done in the case of *local thermodynamic equilibrium*, as detailed in the next section.

2.3.2 Local thermodynamic equilibrium

Under the assumption of local thermodynamic equilibrium (LTE), the dissociation and ionization degrees y , x , z_1 , and z_2 can be obtained as functions of ρ and T from the Saha equation (see their expressions, for example, in D'Angelo & Bodenheimer 2013). Fig. 2.2 shows the mean molecular weight from Eq. (2.42) in LTE as function of T for various values of ρ for a gas with $X = 0.71$ and $Y = 0.27$. The values of μ are bounded between the upper value $\mu = 4/(2X + Y) = 2.37$ corresponding to a fully molecular gas at low temperature, and a lower value $\mu = 4/(8X + 3Y) = 0.61$ at high temperatures representing a fully dissociated and ionized medium. Results for e , c_V , and Γ_1 for a mixture of H, H₂, and He in LTE as a function of T are shown in Decampli et al. (1978), Boley et al. (2007b), Boley et al. (2007a), D'Angelo & Bodenheimer (2013), and Tomida et al. (2013). Fig. 2.3 shows the change in adiabatic index γ for a 1 M_⊙ cloud undergoing gravitational collapse.

2.3.3 Non-equilibrium conditions

The assumption of LTE is valid in stellar and planetary interiors, and in the latest phases of collapsing clouds, but is not applicable in general in the ISM, where the dissociation fraction of H₂ and the ionization fraction of H and He can differ dramatically from their LTE values as given by the Saha equation. They must be obtained instead by solving the rate equations (see Chap. ??, including the effects of the non-equilibrium radiation field (see Chap. ?? and ??). As a consequence, the thermodynamic properties of the gas cannot in general be expressed as only functions of local state variables like ρ and T . Moreover, the gas responds differently when the energy input is radiative or thermal, and adiabatic indexes cannot be properly defined. The rate of energy loss of the gas by radiation Λ (*radiative cooling*, see Chap. 1) must be included, and the internal energy of the gas must be modified accordingly: processes involving emission of photons, like H₂ dissociation, H and He ionization, should not be included in the expression of e in Eq. (2.26), but properly accounted for in the radiative cooling rate Λ .

2.4 REACTION EQUILIBRIA AND DETAILED BALANCE

Processes that produce a transition from one state to another (either non-reactive processes involving a redistribution of internal energy, or reactive processes leading to the formation/destruction of a chemical bond) can be classified into two broad categories: collisional and radiative. Collisional processes are characterized by two cross sections, one for the forward and one for the backward direction, whereas radiative processes require the knowledge of three rate coefficients: one for true absorption, one for spontaneous emission, and one for stimulated emission. In fact, the methods of statistical mechanics allow to es-

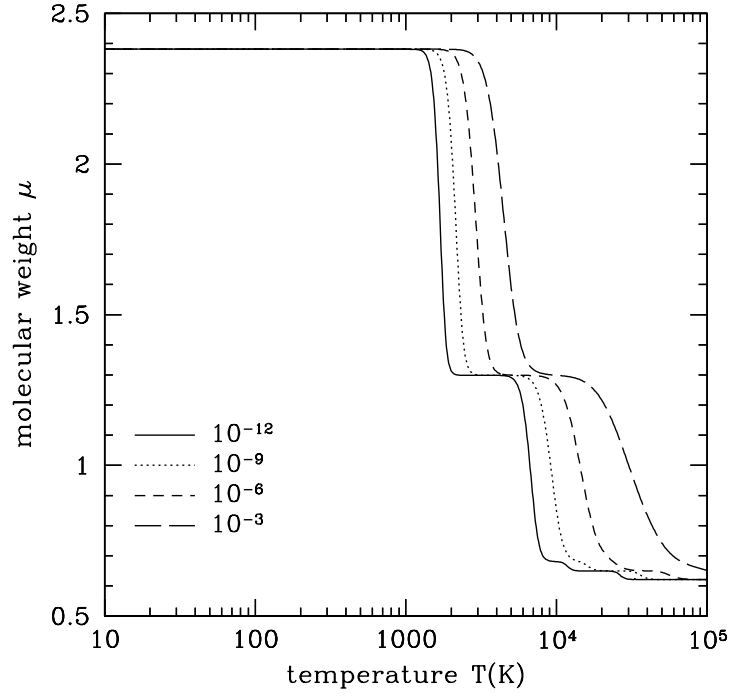


FIGURE 2.2 Mean molecular weight in a gas in LTE with $X = 0.71$ and $Y = 0.27$ for a range of temperature from $T = 10$ K to $T = 10^5$ K for various values of the density ρ , in g cm^{-3} in the labels.

establish relations between these quantities, which reduce the requirements for a complete description of the system to the independent determination of only one cross section (or rate coefficient) each for collisional and radiative processes.

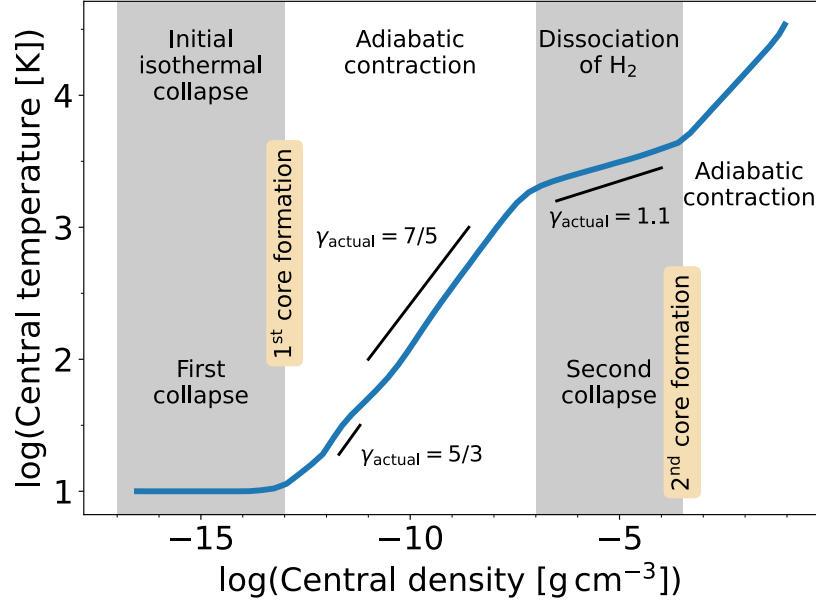


FIGURE 2.3 Evolution of the central temperature T_c as a function of the central density ρ_c for a $1 M_\odot$ cloud undergoing gravitational collapses, showing the change in adiabatic index γ .

These relations are most easily established under conditions of thermodynamic equilibrium, where the *principle of detailed balance* states that *every elementary process is statistically balanced by its reverse*. However, they are generally valid, as long as the individual interacting particles (nuclei, atoms, or molecules) can be considered isolated except at the moment of interaction.

In the case of collisionally induced transitions between a bound state i and a bound state j of a given species, with energy E_i and $E_j > E_i$ and statistical weights g_i and g_j , respectively, the relation between the cross sections for the forward (excitation) and backward (de-excitation) processes is

$$g_i \sigma_{ij}(\epsilon) \epsilon = g_j \sigma_{ji}(\epsilon') \epsilon', \quad (2.50)$$

where ϵ is the collision energy in the center of mass, $\epsilon' = \epsilon - E_{ji}$, and $E_{ji} = E_j - E_i$. Clearly, $\sigma_{ij}(\epsilon)$ is defined only for energies ϵ larger than E_{ji} , the *energy threshold* of the transition. Impacting particles with kinetic energy greater than E_{ji} may excite the species from i to j , while collisions with particles of any energy may de-excite the species from j to i . In such a collisional de-excitation, the impacting particle carries away the energy E_{ji} .

The collisional excitation rate $\gamma_{ij}(T)$ (in $\text{cm}^3 \text{s}^{-1}$) is defined as the integral of $v \sigma_{ij}$ over $4\pi v^2 f(v) dv$, where $f(v)$ is the distribution of collision velocities v , measured in the center of mass. Assuming a Maxwellian velocity distribution

with temperature T and defining the collision energy $\epsilon = \mu v^2/2$, where μ is the reduced mass of the interacting particles, the collisional excitation rate is

$$\gamma_{ij}(T) = \left[\frac{8}{\pi \mu (k_B T)^3} \right]^{1/2} \int_{E_{ji}}^{\infty} \sigma_{ij}(\epsilon) \epsilon e^{-\epsilon/k_B T} d\epsilon. \quad (2.51)$$

Substituting Eq. (2.50) one obtains

$$\gamma_{ij}(T) = \frac{g_j}{g_i} e^{-E_{ji}/k_B T} \gamma_{ji}(T), \quad (2.52)$$

a relation often adopted in astrochemical models.

The principle of detailed balance can also be applied to processes involving transitions to and from a free state (continuum), like e.g., radiative association/photodissociation and recombination/photoionization. As an example, consider the general radiative association reaction



where n indicates the energy level of the species AB. The rate of radiative association to $AB(n)$ (in $\text{cm}^3 \text{s}^{-1}$) is

$$k_{\text{ra},n}(T) = 4\pi \int_0^{\infty} Q \sigma_{\text{ra},n}(v) v f(v) v^2 dv, \quad (2.54)$$

where

$$Q = 1 + \frac{c^2}{2h\nu^3} J_\nu \quad (2.55)$$

is the correction factor for stimulated radiative association, J_ν is the mean specific intensity of the radiation field, and $f(v)$ is the particle velocity distribution. The photodissociation rate from level n (in s^{-1}) is

$$R_{\text{ph},n} = 4\pi \int_{\nu_n}^{\infty} \frac{\sigma_{\text{ph},n}(\nu)}{h\nu} J_\nu d\nu, \quad (2.56)$$

where $\nu_n = (E_n - D_0)/h$ is the threshold frequency from level n and D_0 the dissociation energy (measured from the ground state). The cross sections of radiative association and photodissociation are related by Milne's relation

$$\sigma_{\text{ra},n}(v) = \frac{2g_n}{g_A g_B} \left(\frac{h\nu}{\mu c v} \right)^2 \sigma_{\text{ph},n}(\nu), \quad (2.57)$$

where g_A , g_B and g_n are the statistical weights, μ is the reduced mass of A and B, and the relation between v and ν is

$$h\nu = \frac{1}{2} \mu v^2 + E_n - D_0. \quad (2.58)$$

Milne's relation, Eq. (2.57), is useful to compute either of the two cross sections when the other is known. Moreover, it makes possible to derive a relation between the radiative association and reaction rates. Assuming thermodynamic equilibrium, $f(v)$ is Maxwellian, and J_ν is a black body, both characterized by the same temperature T . With these assumptions, substituting Eq. (2.57) in Eq. (2.54) one finds

$$k_{\text{ra},n} = \left(\frac{h^2}{2\pi\mu k_B T} \right)^{3/2} \frac{g_n e^{-E_n/k_B T}}{g_A g_B} e^{D_0/k_B T} R_{\text{ph},n}^*, \quad (2.59)$$

where the * indicates that the photodissociation rate is computed for a black-body radiation field⁵. Thus, the rate of radiative association of A and B (including stimulated radiative association) in a gas with Maxwellian velocity distribution with temperature T (a condition generally verified in the ISM) can be obtained directly from the photodissociation rate of AB in a black-body radiation field with the same temperature T .

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5. The first factor on the right-hand side of Eq. (2.59) is the cube of the thermal de Broglie wavelength $\lambda_T = h/(2\pi\mu k_B T)^{1/2}$.

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