Homework 3: Rate Coefficients

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Background & Motivation. *Two particle interactions lie at the core of the physics of interstellar gas. Collisions of atoms and ions lead to line emission and thence loss of energy from the gas. In ionized plasma, there is continual "recombination" (e.g.* $p^+ + e^- \rightarrow H^0$*) which is balanced by photo-ionization or ionization by collisions with electrons. The formation of molecules – cosmochemistry – starts with interactions usually between simple ions and atoms. This homework provides the foundation to reaction kinetics.*

Due February 2, 2023

Each problem (1ab, 2–5) carries 10 points.

[1a] **Center of Mass (CM) Frame**. Consider two particles, $i = 1, 2$, of mass m_i and velocity[1] $\vec{v}_i$, as measured in the lab frame. We apply a Galilean transformation, $\vec{V}$ in which case the velocities of the particles are $\vec{u}_i = \vec{v}_i - \vec{V}$. Show that the choice of

$$\vec{V} = \frac{m_1\vec{v}_1 + m_2\vec{v}_2}{M}$$

not only minimizes the total kinetic energy of the system but also the (absolute) linear momentum of the system; here, $M = m_1 + m_2$. The former property explains why the CM frame should be used for considering reactions (as opposed to the lab frame). The latter property simplifies calculations of velocities following a reaction. [5 pt]

[1b] **Velocity Distribution.** We now assume that the both species are in thermal equilibrium with temperature, T. The velocity density distribution for $\vec{v}_i = (v_{xi}, v_{yi}, v_{zi})$ is given by the Maxwell-Boltzmann (M-B) function:

$$f_i(\vec{v}_i)d^3v_i = \left(\frac{\beta m_i}{2\pi}\right)^{3/2} \mathrm{e}^{-1/2\beta m_1 v_1^2} d^3v_i$$

where $\beta = 1/k_BT$. Note that the M-B velocity distribution is isotropic. Thus, $d^3v = dv_xdv_ydv_y = 4\pi v^2 dv$ where $v^2 = v_x^2 + v_y^2 + v_z^2$. Verify that $\int f_i(\vec{v}_i)d^3v_i = 1$. [5 pt]

[1] We use the convention $\vec{v}$ for the 3-D velocity vector while v is the speed of the particle, $v = \sqrt{\vec{v}\cdot\vec{v}}$.

Incidentally, I prefer to remember the velocity distribution as

$$f_v(v) = \frac{4}{\sqrt{\pi}} x^2 \mathrm{e}^{-x^2} dx$$

where $x = v/v_p$ with $v_p = \sqrt{2k_B T/m}$ (the most probable velocity). The normalization, if forgotten, can be computed readily.

[2] **Distribution of the relative and CM velocities.** Since the particles of the two species are independently the joint probability of velocity distribution is given by the product of the probability functions:

$$f_{1,2}(\vec{v}_1, \vec{v}_2) d^3v_1 d^3v_2 = f_1(\vec{v}_1) d^3v_1 f_2(\vec{v}_2) d^3v_2$$

Consider the transformation, $(\vec{v}_1, \vec{v}_2) \rightarrow (\vec{u}, \vec{V})$ where $\vec{V}$ is the CM velocity and $\vec{u} = \vec{v}_1 - \vec{v}_2$ is the relative velocity. Show that the

$$f_{1,2}(\vec{v_1}, \vec{v}_2) d^3v_1 d^3v_2 = f_u(\vec{u}) d^3v f_V(\vec{V}) d^3V \tag{1}$$

where

$$\begin{aligned} f_u(\vec{u}) &= \left(\frac{\mu\beta}{2\pi}\right)^{3/2} \exp\left(-1/2\beta\mu u^2\right), \\ f_V(\vec{V}) &= \left(\frac{M\beta}{2\pi}\right)^{3/2} \exp\left(-1/2\beta M V^2\right). \end{aligned}$$

where $\mu = m_1 m_2/M$ is the so-called reduced mass. Note that $\vec{v}$ and $\vec{V}$ are independently distributed, since the RHS of Equation 1 is product of of the probability distributions for $\vec{u}$ and $\vec{V}$.

[3] **Rate Coefficients.** Let n_i be the number density of species i. Let $\sigma(u)$ be the cross-section for an interaction between species 1 and 2 to occur; here, as above, u is the relative speed of particle 1 and particle 2. The "reaction" volume covered by, say, one particle of species 1, in time dt is $u\sigma(u)dt$. Thus the probability that a reaction will occur within this volume is $n_2 u\sigma(u)dt$. Since there are n_1 particles of species 1 in a unit volume, the number of reactions per unit volume is $n_1 n_2 u\sigma(u)dt$. Thus, the rate of reactions per unit volume is $\mathcal{R} = n_1 n_2 u\sigma(u)$. It is traditional to quote the "rate coefficient", $k \equiv \mathcal{R}/(n_1 n_2) = u\sigma(u)$.

Now we generalize this to the case where the two species are in thermal equilibrium with temperature T. The relative velocity distribution, $f_u(u)$ is given by Equation 2. The rate coefficient for a thermal plasma is then

$$k = \langle u\sigma(u)\rangle = \int u\sigma(u) f_u(u) d^3u$$

where the angular bracket indicate averaging over the M-B velocity distribution. Assume a simple "power law" model[2], $\sigma(u) = \sigma_0(u/u_0)^{-n}$. Develop an analytical expression for k.

[4] **Recombination energy loss.** Consider the reaction, $p^+ + e^- \rightarrow \mathrm{H}^0$ ("recombination"). In the CM frame, the total kinetic energy prior to the reaction is $E = {}^1\!/\!_2\mu u^2$. Following the reaction, this energy along with the ionization potential energy is radiated away via the a "free-bound" photon. The recombination cross-section can be approximated as $\sigma(u) \propto u^{-n}$ with $n \approx 2.6$. Compute the average kinetic energy of the recombining electron. Comment on the fact that $\langle E \rangle$ is less than ${}^3\!/\!_2 k_B T$. Does this mean that a recombining plasma heats up as it recombines? Next, what is the velocity distribution of the H atom?

[5] **Collisional Ionization.** In hot gas, energetic electrons collide with atoms or ions and eject an electron. The collisional ionization cross-section can be approximated by the following simple model:

$$\sigma_{\rm ci}(E) = C\left(1 - \frac{I}{E}\right)$$

where E is the energy of the colliding electron and I is the ionization energy. Develop an expression for the collisional ionization rate coefficient, $k_{\rm ci}$ and compute the mean energy of the *ejected electron*.

[6] **C$^+$ Fine Structure Line.** The ground state of C$^+$ (1s^{2}2s^{2}2p) is split by spin-orbit interaction. The wavelength of this fine structure line (FSL) is 157.77 μm. The A-coefficient is $2.4 \times 10^{-6}\,\mathrm{s^{-1}}$. The collisional de-excitation rate coefficients due to collisions with electrons and H atoms are as follows:

$$\begin{aligned} k_{10}(e^-) &= 4.5 \times 10^{-10} T_2^{-1/2}\,\mathrm{cm^3\,s^{-1}} \\ k_{10}(\mathrm{H}) &= 7.6 \times 10^{-10} T_2^{0.1281+0.0087\ln T_2}\,\mathrm{cm^3\,s^{-1}} \end{aligned}$$

Explain the temperature dependency. Next, compute the critical density for each process. The cooling timescale is defined as $t_{\rm cool} = {}^3\!/\!_2 n k_B T/\Lambda$ where n is the total particle density and Λ is the cooling rate per unit volume due to C$^+$ FSL cooling. Compute the cooling timescale for the CNM [$n_{\rm H} = 30\,\mathrm{cm^{-3}}$, $x_e = n_e/n_{\rm H} = 3 \times 10^{-4}$ and $T = 100\,\mathrm{K}$] and the WNM [$n_{\rm H} = 0.6\,\mathrm{cm^{-3}}$, $x_e = 0.02$ and $T = 5{,}000\,\mathrm{K}$].

[2] The use of power-law approximation is common in astronomy. The power law model need only hold over the range of temperature of interest. $n = 0$ corresponds to "hard spheres", $n \approx 1$ corresponds to ion-neutral collisions and also electron-positron collisions, $n \approx 2$ corresponds to ion-electron collision, while $n \approx 2.6$ corresponds to the recombination of protons with electrons to form H atoms.