MONTE CARLO CALCULATION OF THE TRANSLATIONAL RELAXATION OF SUPERTHERMAL H ATOMS IN THERMAL H₂ GAS

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ABSTRACT

A simple and reliable method to study the translational relaxation of “hot” H atoms following their production by chemical mechanisms is proposed. The problem is relevant to interstellar medium, shocks, photospheres, and atmospheric entry problems. It is shown that the thermalization of H atoms can be conveniently studied by the Monte Carlo method, including the thermal distribution of background molecules, and sets the basis for further investigations. The transport cross section is determined by the inversion of transport data. The collision density of H atoms in H₂ gas is also calculated and discussed in the context of simple theories. The application of the results to astrophysical problems is outlined, including numerical results for the reaction H + H₂O → H₂ + OH. An approximate analytical formula for the reaction probability during H atom thermalization is proposed.

Key words: ISM: atoms – methods: numerical – molecular processes – plasmas

1. INTRODUCTION

In many important objects, atomic hydrogen H is produced by dissociation processes from diatomic hydrogen H₂ or other hydrogen-containing molecules like H₂O, H₂S, or NH₃.

Examples are comet comas (Ip 1983), Jupiter’s atmosphere (Lodders & Fegley 2011), and photodissociation regions (Hollenbach & Tielens 1999), but the direct dissociation of H₂ by electron impact is also important in shocks as an effect of preheating electrons and, in more general terms, in all non-equilibrium plasmas produced in H₂ where the electron temperature is much higher than the gas temperature, a situation that can be produced by electric fields and is easily reproduced in discharge plasmas.

Atoms produced from dissociation reactions are often superthermal, or hot atoms, since they gain energy by sliding down a repulsive adiabatic potential to the dissociation limit. Hot atoms are also produced from symmetric charge exchange reactions, i.e., H₂⁺ + H → H₂⁺ + H⁺ of H atoms with fast ions of different origins. The average energy of these atoms is a few eV. The chemistry of such H atoms is therefore a nonthermal chemistry, since the usual assumption of a Maxwell–Boltzmann distribution of the kinetic energy of H atoms cannot be held to relate the average thermal energy and the rate coefficients of collisional processes.

The production and reactions of superthermal H atoms is a topic of great astrophysical relevance. Many chemical reactions involving H atoms and important for interstellar chemical networks have a threshold that can be overcome by the availability of extra kinetic energy. Examples are the trapping of H atoms in solid hydrogen (Miyazaki et al. 1983), the hydrogen abstraction from several molecules like H₂O, H₂S, hydrocarbons (Becker et al. 1974) and their deuterated versions (Nicholas & Vaghimani 1989; Malcolm-Lawes 1972), and the impact ionization of I group metals (Crooks et al. 1978). It is therefore important to develop practical and reliable methods to characterize the chemical reactivity of H atoms after their production including the effects due to their moderation, thermalization, loss, and reactions with other species.

This problem can be tackled by using a continuum slowing down approximation similar to the Fermi theory (Robson 2006), but a much better method is to apply a rigorous thermalization theory developed for the case of neutron kinetics in gaseous moderators (Weinberg & Wigner 1958).

While the resulting integral equations are very complex, a simpler approach to obtain rigorous numerical results is provided by the application of the Monte Carlo (MC) method, which takes into account the thermal distribution of target particles in the collision kernel and the energy dependence of the cross section.

In this paper, some calculations of the translational relaxation and chemical reactivity of superthermal H in H₂ are presented, with a cross section determined from the inversion of transport data. An accurate MC model for thermal particle transport developed in the past in our group and already validated is applied to this problem. The appropriate parameter set is individuated. Results are discussed in the light of several important astrophysical reactions.

2. METHOD OF CALCULATION

Calculations are performed using the MC method for particle transport in a thermal background described by Longo & Diemed (2009) and Panarese et al. (2011).

This method has been recently validated by comparing the calculated values of binary diffusion coefficients in different gases with calculations based on the Chapman–Enskog development extended to high orders (Panarese et al. 2011).

Although the method is described in the above references, a self-consistent short description is provided here. The starting point is the expression of the real collision frequency for an H particle moving with velocity v, given by

\[ \nu(v) = \int d^3 w \alpha(g) f(w), \]

(1)

where f is the velocity distribution function of target particles and \( \alpha \) is the collision pair frequency defined as

\[ \alpha = \sigma n_b, \]

(2)

Here, \( \sigma \) is the total cross section, \( g = |v - w| \) is the relative speed of the collision pair, and \( n_b \) is the target particle density.
The method is based on the preliminary selection of a
maximum value for the product $g\sigma (g)$ denoted by $(g\sigma (g))_{\text{max}}$. By replacing $g\sigma (g)$ with $(g\sigma (g))_{\text{max}}$ in integral expression (1) this can be rewritten into the form $\nu (v) = \alpha_{\text{max}}$, where

$$\alpha_{\text{max}} = (g\sigma (g))_{\text{max}} \eta_b. \tag{3}$$

This replacement implies a potentially non-physical increase of the collision frequency that can be compensated by using the concept of null collision, i.e., the inclusion of artificial scattering events that accounts for the difference $\alpha_{\text{max}} - \alpha$ but has no effect on the motion of H atoms.

This solution allows an exact simple treatment of collisions in a Test Particle Monte Carlo model. This numerical method describes the motion of test particles diluted in a bulk medium of target particles.

In our case, the system is constituted by test particles of H moving in an H2 uniform bulk, in equilibrium at temperature $T_g$ and pressure $p$.

Initially, test particles are put in the origin of a three-dimensional space and are allowed to diffuse across the bulk. Test particles are initialized with the same energy and interact with bulk particles by means of binary collisions.

For each collision, the bulk particle velocity is selected according to the Maxwell–Boltzmann distribution at the temperature $T_g$, using a direct method of sampling. For this purpose, setting $v_i = r \sin \theta$ as the velocity component along the $i$-direction, a pair of values of $r$ and $\theta$ is sampled from $\theta = 2\pi \eta_1$ and $r = (-2kT_g \ln \eta_2/m_{\text{bulk}})^{1/2}$, using two random numbers $\eta_1$ and $\eta_2$ uniformly distributed between 0 and 1. Finally, the value of the $i$-component of the thermal velocity in the equilibrium bulk is sampled as $v_i = r \cos \theta$.

In order to remove the extra collision events used to equalize the collision frequency to $\alpha_{\text{max}}$, a further random number $\eta_3$ is compared to the fraction of real collisions given by $\alpha/\alpha_{\text{max}}$. If $\eta_3$ is smaller than this quantity, the collision is effective.

After an effective collision, the relative velocity vector must be rotated according to two polar angles, namely $\theta$, the scattering angle, and $\phi$, the azimuthal angle. This latter is uniformly sampled in the interval $[0, 2\pi]$, while the selection of $\theta$ depends on the interaction model.

Once the scattering angle is known, the scattering is treated taking into account the correlation with the old particle velocity using Euler angles: the relative velocity vector after the collision, $g^*$, is calculated as

$$g_x^* = g_x \cos \theta + B \sin \varphi \sin \theta, \quad g_y^* = g_y \cos \varphi + g_z \sin \varphi, \quad g_z^* = g_z \cos \theta - B^{-1} \sin \theta (g_y \cos \phi + g_z \sin \phi), \tag{4}$$

where $B = (g_x^2 + g_z^2)^{1/2}$ and $g = (g_x, g_y, g_z)$ as above is the relative velocity before the collision.

$\theta$ is determined from a quadrature of the interaction potential $\phi(r)$ based on the known value of the impact parameter $b$

$$\phi(b, E) = \pi - 2b \int_{r_m}^{\infty} \left[ 1 - \frac{b^2}{r^2} - \frac{\phi(r)}{E} \right]^{-1/2} \frac{dr}{r^2} = \pi - \chi(b, E),$$

where $r_m$ is the distance of closest approach. The value of $b$ is obtained from $b = b_{\text{max}} \sqrt{\eta_4}$, $\phi$ is simply given by $\phi = 2\pi \eta_5$. In case of isotropic elastic scattering, $\cos(\theta) = 1 - 2\eta_4$.

The motion of the colliding particle of mass $m_t$ relative to the bulk target particle of mass $m_t$ is equivalent to the motion of a particle of mass $\mu = m_m m_t/(m_t + m_m)$ relative to a center of force. The collision energy is calculated as a function of the relative speed $g$ of the interacting pair by $E_{\text{coll}} = \mu g^2/2$.

As in a binary interaction, the center of mass velocity is a constant, and the velocity of the colliding particle after the collision is given by

$$v^* = \frac{m_t v + m_i w}{m_t + m_i} + \frac{m_t}{m_t + m_i} g^*. \tag{5}$$

The time difference between one collision (including null collisions) and the next one is given by the formula

$$\Delta t = -\ln \eta_b/\alpha_{\text{max}}, \tag{6}$$

where $\eta_b$ is again a random number from a uniform distribution, $0 < \eta_b < 1$. This time is inversely proportional to the gas density. An appropriate parameter to measure the degree of thermalization of an H atom in the bulk medium is therefore provided by the product $n\tau$, where $\tau$ is the average lifetime of an H atom before its chemical or diffusion loss. Calculations performed using different values of $n$ and $\tau$, but leaving the value of the product $n\tau$ unchanged, produce the same results. The finite lifetime $\tau$ is obtained in the simulation by removing the injected particles with a probability $1 - \exp(-\Delta t/\tau)$ before each collision. The removed particle is labeled in such a way that the computer simulation is not accounting for it anymore. The simulation proceeds until all particles are removed.

This procedure is exact when $\tau$ is not dependent on the atom speed and can be used when this approximation is feasible considered. In specific cases $\tau$ will be determined by the chemical network assumed. In molecular clouds, collisional loss reactions with H2 and H– and other species can be important, while in the laboratory H atoms are often lost in reactions with purposely added scavengers uncommon in space, e.g., iodine atoms. For these collisional losses $\tau = (k_L n_L)^{-1}$ where $k_L$ is the appropriate rate coefficient while $n_L$ is the number density of the corresponding reaction partner. The photoionization or the radiation ionization of H atoms is well described by a constant $\tau$ as well. Heterogeneous recombination on reactor walls in the laboratory and on dust grains in space can be treated similarly, but the formula must account for diffusion times. In case $\tau$ has a strong dependence on the H atom speed or if a loss cross section $\sigma_L$ is used instead of a loss rate coefficient, the removal process can be improved. For any collision, a candidate collision partner for any loss channel is sampled from a Maxwell distribution. The probability that a collision results in an H atom loss is $p_{\text{L}} = \sigma_{\text{L}} n_L/\alpha_{\text{max}}$ and the loss channel is selected if $\eta_7 < p_{\text{L}}$.

Collision events are sampled on a uniform grid on an axis representing the variable $u = \ln (\epsilon/\epsilon_0)$. In this way, the quantity sampled is the collision density $P(u)du$. This quantity is normalized to one atom produced per unit time.

3. RESULTS AND APPLICATIONS

The role of hot atoms in chemical reactions is well known as mentioned in the introduction. With the extra energy provided, these atoms can increase considerably, sometimes by orders of magnitudes, the rate of chemical reactions in which they are involved. There are two ways in which the non-equilibrium translational kinetics of H atoms can be described, as a result of calculations by the method described in the previous section.
One possibility is to calculate the so-called collision density or, equivalently, the energy distribution. The second one is to calculate the rate coefficients of relevant reactions with trace species present in the bulk gas (H₂).

The collision density $P(\epsilon)$ is defined in such a way that the number of collisions of each atom in the energy range $(\epsilon, \epsilon + d\epsilon)$ is given by $P(\epsilon)d\epsilon$. The knowledge of this function allows us to calculate any collisional rate once the probability $w_i(\epsilon)$ of accessing the $i$th channel is known. Alternatively, the usual kinetic distribution $f(\epsilon)$ can be calculated, if relevant, by the expression $f(\epsilon) = P(mv^2/2)mv$ where $v(\epsilon)$ is the collision frequency for test particles of speed $v$ reported at the beginning of the previous section. The collision density has been the subject of classical theoretical treatments (see also below), but in the case of slightly superthermal particles decelerated until they reach thermal energy (thermalization), which is relevant here, a full numerical approach is more appropriate. The collision density has been the subject of stochastic calculations, beginning from Rebick & Dubrin (1970). In their work the authors provide the first results for H atoms in Xe, a diluent selected in view of the high molar mass and relative chemical inertness. They neglected the effect of the target speed in some steps of the calculations, which is a quite acceptable approximation for their test case where the mass ratio is very high, but not appropriate for H in H₂. The collision frequency and dynamics is exactly accounted for using the method of this paper.

In order to calculate the frequency of H–H₂ collisions, a reliable momentum transfer cross section is necessary. This cross section can be evaluated by fitting the binary diffusion coefficient $D$ of H atoms in H₂ gas at different temperatures. This is calculated using the collision integrals reported by Stallcop et al. (1996) and based on an accurate interaction potential. The MC method described in the work by Panarese et al. (2011) is used to obtain $D$ as a function of $T_g$ from a guessed cross section of the form $\sigma(\epsilon_0/v_0)^p$ with $v_0 = 3.75$ km s⁻¹. The best fit (Figure 1) is obtained for $\sigma_0 = 17.5$ Å² and $p = 0.9$. These values are used in the subsequent calculations of H thermalization.

Figure 1 is cut at $T_g = 2 \times 10^3$ K, since above this temperature the equilibrium dissociation of H₂ at 1 atm cannot be neglected. However, a comparison of the two values of the formal quantity $D(T_g)$ at a higher $T_g$ is still meaningful as a check of our simplified cross section at a high energy. These two values are also very close at $T_g \approx 10^4$ K.

The relevant numerical parameters that specify the thermalization regime in our problems are the initial H energy $\epsilon_0$, the gas temperature $T_g$, the gas density $n$, and the average lifetime of H atoms in the gas, $\tau$. This last parameter describes the effect of processes that remove H atoms from the gas. This process can be, e.g., the photoionization of H atoms. In this and similar cases, $\tau$ is defined as usual through the photochemical expression $\tau = n_H/R$ where $R$ is the chemical loss rate of H atoms.

In order to reduce the number of parameters, in this study $\epsilon_0$ is fixed to 2.4 eV. This value is compatible with direct dissociation from the $^1\Sigma_g$ ground state to the triplet state correlated to H(1s) + H(1s) and provides an important example. This choice of a delta function for the energy distribution of the source can be extended to more complex cases by simple statistical sampling of the more involved source function.

The collision density in the case of H atoms that originated with a single energy is characterized by a singular contribution corresponding to the first collision of H with H₂, with an H energy that is by necessity equal to $\epsilon_0$. A finite amplitude for $P(\epsilon)$ could be obtained by selecting the initial energy from a Gaussian, as in the work by Prisant et al. (1978). Following the custom for $P(\epsilon)$ plots in nuclear applications (Weinberg & Wigner 1958) this contribution has not been represented.

Results for $P(\epsilon)$ are better discussed in light of the semi-analytical theory of Placzek (1946), based on an iterative solution of a simplified integral equation, which is obtained for $P(\epsilon)$ in the limit of zero gas temperature and for rigid sphere elastic scattering. It is important to note that stochastic approaches allow us to remove both limitations of the Placzek equation. Nevertheless, the solution of this equation allows us to establish three important general features that are approximately valid also for $T_g > 0$.

1. In the so-called asymptotic region far below $\epsilon_0$ but above the bulk thermal energy, $P(\epsilon) = 1/\xi$ where $\xi$ is the average logarithmic energy loss for a single collision. For H in H₂, this means $P(\epsilon) = 1.4$.
2. Very close to the source energy $\epsilon_0$, $P(\epsilon)$ is here given by a simple expression as a function of the mass ratio $A = m_{H_2}/m_H = 2$, i.e., $P(\epsilon) = (A + 1)^2/4A = 1.125$.
3. A discontinuity is present in the function at $\epsilon = \epsilon_0(A - 1)/(A + 1)^2 = 0.11\epsilon_0$, associated with the lowest energy value of the initial redistribution by the first collision. In fact, the maximum loss for the H energy corresponds to a head-on collision with an H₂ at rest: in this case the final H speed is equal to $(A - 1)/(A + 1) = 1/3$ the initial H speed.

Such features are confirmed by our calculations for different values of $T_g$, as shown in Figure 2. In this case the particles were removed when moderated below 0.024 eV in order to avoid any interference in the moderation kinetics. This choice produces a non-exponential loss of the particles during moderation.

In Figure 3, the collision density corresponding to $T_g = 100$ K and different $\tau$ is reported. The equilibrium result is also reported for reference. The plots illustrate the role and effects of the two fundamental parameters $\tau/T_0$ and $T_g$ on the calculated collision density. $T_0 = (\sigma_0 v_0)^{-1}$ is the characteristic collision time. An estimate of $T_0$ for a typical interstellar medium (ISM) density of $10^7$ cm⁻³ leads to $T_0 \approx 1.5 \times 10^6$ s.

A superthermal tail is associated with the slowing down of freshly produced H atoms, whose distribution shape is affected...
by $T_s$ and the shape of $\sigma_s$ but essentially corresponds to the Placzek solution for $A = 2$. The low energy component of $P(u)$ is essentially determined by the equilibrium contribution, the relative importance of the two being controlled by the parameter $c_0/T_s$. Even at energies much higher than those corresponding to the Maxwellian bulk, in the tail region, the thermal distribution of molecules cannot be neglected. This has the effect of smearing the Placzek peak of Figure 2, which no longer appears as a salient feature at temperatures higher than a few 10 K even for rigid sphere scattering. Only detailed calculations can then accurately establish the tail shape.

The presence of the superthermal tail is expected to limit the validity of the traditional chemical kinetics of astrophysical objects and phenomena in several ways. For example, the rate coefficients of a reactive process involving H atoms will not be given by the equilibrium formula based on the Maxwell–Boltzmann distribution, but a superthermal contribution to the rate coefficients will need to be accounted for, i.e., $K_{\text{eq}} = K_{\text{eq}}(T_s) + K_{\text{neq}}$ (Ip 1983; Crooks et al. 1978). This last contribution $K_{\text{neq}}$ can be determined in specific cases by running an MC simulation based on the prescriptions provided in this paper.

Details differ depending on the gas temperature and the threshold of the reaction. For reactions with no threshold (where effects are still possible due to the cross section shape or resonances) or a threshold comparable to the thermal energy, the rate coefficient can be corrected by the modification of the translational distribution which is not described by a Maxwell–Boltzmann law. The expression of the rate coefficient $K_p$ for a process $p$, whose related cross section is $\sigma_p$, is a function of the H translational distribution:

$$K_p = \sqrt{\frac{2}{\mu}} \int_0^{\infty} \sigma_p(\epsilon) \epsilon^{1/2} f_{\text{cm}}(\epsilon) d\epsilon,$$

where $f_{\text{cm}}(\epsilon)$ is the distribution of impact energy in the cm frame. In the equilibrium case, $f_{\text{cm}}(\epsilon)$ is a Maxwellian distribution with $m$ replaced by $\mu$ and $K_p$ is a function of $T_s$. When a superthermal component is present, this equation is still valid but $K_p$ cannot be written as a function of the gas temperature. Examples of such reactions may be reconsidered in this light are the radiative association reactions of H with C+ (Barinovs & van Hemert 2006) and H+ (Stancil et al. 1993), which are of importance for the ISM and for the early universe chemistry, respectively.

Superthermal atoms can also affect the cooling function of the gas due to the strong energy dependence of the collisional de-excitation coefficients, i.e., the rate constants of the reactions $H^+H_2(v, j) \rightarrow H^+(v', j')$ (Capitelli et al. 2006). The complex thermalization of H atoms will also affect preheating in strong shocks in hydrogen and the cooling function, e.g., for early universe models (Coppola et al. 2012). The atomic component is more mobile than the bulk gas because of the much higher diffusion coefficient, and can contribute to affect the shock profile. A similar effect has been studied in the past by Bruno et al. for nitrogen shocks by a Direct Simulation Monte Carlo model (Bruno et al. 2002).

A much more important and complete nonthermal effect is expected in cases where the reaction threshold is much higher than the average thermal energy: the thermal rate of such processes is essentially zero, and calculations based on the method described in this paper can be used to define a specific rate $Q$ that enters in an expression as

$$\text{Reaction rate} = Q \chi_s dn_H/\text{dt},$$

where $\chi_s$ is the mole fraction of the trace partner $s$ and $dn_H/\text{dt}$ is the production rate of high energy atoms per unit volume and time.

$Q$ is therefore the number of reactive collisions of H atoms with a reactive trace species during their moderation, normalized to a unit fraction of the trace (but in practice the fraction is $\ll 1$, with $s$ being a trace).

Examples of such reactions are the reaction of hydrogen with $H^+$ leading to detachment in the so-called non associative channel:

$$H^+ + H \rightarrow 2H + e.$$

This process has a threshold of about 0.7 eV and its cross section increases by an order of magnitude in the energy range 1–10 eV (Janev et al. 2003). This reaction can be of relevance for chemical networks connected with radiation transport in astrophysical systems in view of the great importance of $H^+$ ions as radiation absorbers.
Another example is the abstraction of H atoms from water, e.g., the reaction

$$\text{H} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{OH}. \quad (10)$$

This is potentially an important reaction in astrophysical systems, since it represents a source of OH radicals in rovibrationally excited states. In spite of this, the above reaction is usually not included in chemical networks in view of its relative high threshold, about 1 eV. This situation, however, can change in the presence of superthermal atoms, and for future reference a calculation of its rate coefficient is provided as a function of the initial energy of hydrogen.

The rate constant $Q(\epsilon_0, T_g)$ can be evaluated by calculating, in an MC simulation, the sum

$$Q(\epsilon_0, T_g) = N^{-1} \sum \frac{g_{\text{H}_2\text{O}} \sigma_{\text{abs}}(g_{\text{H}_2\text{O}})}{g_{\text{H}_2}} \sigma_{\text{el}}(g_{\text{H}_2}), \quad (11)$$

where $\sigma_{\text{abs}}$ is the abstraction cross section and $\sigma_{\text{el}}$ is the cross section of the elastic process, $N$ is the number of H atoms in the simulation, and the sum includes all H/H$_2$ elastic collisions.

The cross section $\sigma_{\text{abs}}(\epsilon)$ is reported as a full line in Figure 4 in the paper by Brouard et al. (2004).

The results in Figure 4 show that hot H atoms can be an effective source of OH radicals in the presence of traces of water diluted in H$_2$. The slight increase observed for the highest value of $T_g$ ($2 \times 10^3$ K) is due to the effect of the relative speed in H/H$_2$ collisions on the energy distribution of H atoms and confirms the necessity of calculating accurately the effects of the relative speed under some circumstances.

The use of the MC method described here produces an exact evaluation of the quantity $Q$. An approximate analytical estimate can be provided under the hypotheses that

1. the Placzek equation applies;
2. the reactive cross section in the energy range $(0, \epsilon_0)$ is larger for $\epsilon$ close to $\epsilon_0$; and
3. the mass of the H atom is much smaller than that of the reaction partner.

The last hypothesis allows us to neglect the difference between the energy of the atom and the energy available for the collision. An analytical solution of the Placzek equation in the energy range $(\alpha \epsilon_0, \epsilon_0)$, where $\alpha = ((1 - A)/(1 + A))^2$, is given by the expression (Glasstone & Edlung 1952)

$$P(\epsilon) = \delta(\epsilon - \epsilon_0) + \epsilon_0^{\alpha/(1 - \alpha)} \frac{1}{1 - \alpha} \frac{\epsilon}{\epsilon^{1/(1 - \alpha)}}. \quad (12)$$

Having defined the function

$$q(\epsilon) = \frac{\sigma(\epsilon)}{\sigma_0(\epsilon)}, \quad (13)$$

$Q$ can be written as the result of the integration in the range $(0, \epsilon_0)$ of the product $q P$, i.e.,

$$Q = q(\epsilon_0) + \epsilon_0^{\alpha/(1 - \alpha)} \frac{1}{1 - \alpha} \int_{K_T}^{\epsilon_0} q(\epsilon) \frac{d\epsilon}{\epsilon^{1/(1 - \alpha)}}, \quad (14)$$

where the lower integration limit is a reasonable cutoff (see Figure 3), since at such low energies the collision density is thermal.

In Figure 4, results of Equation (14) for several values of $\epsilon_0$ are reported for the reaction of H abstraction from water. In this case the agreement is very good, since this reaction meets requirements 2 and 3 above. Of course, the results at the highest value of $T_g$ are not matched since at high $T_g$ the Placzek equation is not exact anymore. Equation (14) can be used as an alternative to MC calculations for fast, approximate calculations in other cases.

4. CONCLUSIONS

In this paper, it was shown that the problem of the thermalization of hot H atoms produced by photochemical, electron, or ion impact processes in hydrogen-based plasmas of astrophysical relevance can be conveniently addressed by a simple MC procedure recently developed, which, while being very simple, allows for a rigorous treatment of the thermal distributions of background species. The relevant physical parameters are identified and the importance of superthermal H tails for the chemical network and thermal balance in different systems is discussed. As an example, the abstraction probability of H atoms with water molecules is evaluated as a function of the initial H energy $\epsilon_0$ and $T_g$. A simple formula is proposed to estimate the nonthermal contribution to a reaction rate.

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