Evolution of Martian Atmosphere under Initial Atmospheric Pressure of 0.2 bar

Team 200

Problem A

Abstract

In this paper, the mechanisms of thermal escape, solar wind sputtering and photochemical reaction are studied based on Atmospheric stratification model, and the evolution of Martian atmosphere is predicted. Using Monte Carlo dynamics simulation and other calculation methods, we find that due to the strong ultraviolet radiation of the sun, the photochemical reaction in the upper atmosphere is the main reason for gas escape. At the initial atmospheric pressure of 0.2bar, after 70-90 million years, the pressure dropped to 0.1bar.

Contents

1 Nomenclature / Notations used

Main parameters		
Symbols	Description / Meaning	Numerical Value
M_p	Mass of Mars	$6.42 \times 10^{23} kg$
R_p	Radius of Mars	3389.5km
n	Solar wind particle number density	1.83×10^6

* Notations not mentioned are defined alongside.

2   Introduction

Mars, the fourth planet in the solar system, has a lot in common with our planet, and it is often called the Twin Earth. They are terrestrial planets, both have polar ice caps, and both once had active atmosphere and liquid water on their respective surfaces. In other ways, there is a big difference between them. Especially in terms of their respective atmosphere and climate, Mars can be said to be very different from Earth. The Martian atmosphere is mainly composed of carbon dioxide, followed by nitrogen and argon, as well as a small amount of oxygen and water vapor, which is less than 1% of the density of the Earth's atmosphere and the surface atmospheric pressure is 500pa.

Recently, several studies have shown that Mars probably had a dense atmosphere during the Novachian period, with a surface pressure of at least 0.5bar[1]. What caused Mars to lose its dense atmosphere? At present, the mainstream explanations include[2; 6]:

1. The heat escape caused by the thermal motion of atoms or molecules in the upper atmosphere is often called Jeans escape;

2. Solar electromagnetic radiation heats the atmosphere and causes photochemical reactions, resulting in higher energy of gas molecules and getting rid of gravitational shackles. The interaction between the high-speed charged particles carried by the solar wind (mainly including most protons, electrons and helium nuclei at a speed of 200-800km/s and the number of ions ejected per second is $1.3{\times}10^{36}$)[1] plays an important role in atmospheric erosion. There is no global magnetic field distribution similar to that of Earth on the surface of Mars, and the strong magnetic field is only within a certain range, resulting in more obvious erosion of the Martian atmosphere by the solar wind.

In addition, the Martian surface atmosphere is very active, atmospheric mobility is strong, sand and dust are frequent, which will also have an impact on the evolution of the atmosphere.[3]

With the deepening of the research, some people have put forward the idea of rebuilding the Martian atmosphere and creating a "habitable planet". Suppose we use some means to evaporate the polar ice caps and get a large amount of carbon dioxide into the atmosphere (instead of water, see the analysis in section 1), which will give Mars a thicker atmosphere and Greenhouse Effect of carbon dioxide will maintain a certain temperature on Mars. However, how long this man-made atmosphere can last in the existing Martian environment will be a key assessment criterion for such a program.

This paper studies the evolution of the atmosphere during the escape of thermal and non-thermal gases when a large amount of carbon dioxide enters the Martian atmosphere and increases its pressure to 0.2bar.

2.1   Atmosphere[4]

Planetary aeronomy problems pertain to many bodies of the Solar System that have gas envelopes. In most cases, the motion of gas in the envelope is restricted by the gravitational field of the planet or satellite, and such an envelope is referred to as an atmosphere.

The presence or absence of a gas envelope is an important indicator that reflects significant features of the origin and evolution of the planet or satellite on a geological time scale.

The chemical composition, structure, and dynamics of atmospheres highly depend on the mass and location of the celestial body in the Solar System (to which the initial composition of the atmosphere, thermal and chemical differentiation of the primordial matter, and insolation conditions are related) and on the parameters of orbital and rotational motion. Therefore, even within a small region occupied by terrestrial planets, the properties of their atmospheres are significantly different. It's as if the Martian atmosphere is mostly carbon dioxide, while the

Earth's atmosphere contains only a very small amount of carbon dioxide.

2.2 Atmospheric stratification model and definition of basic length

Relatively dense layers of the lower atmosphere (troposphere) can be treated in the gas dynamic approximation because the mean free path l is significantly smaller than the smallest microscopic length scale; Under the action of gravity field, the isothermal atmosphere obeys Boltzmann distribution, the pressure decreases with the height index. Because the mean free path increases as the number density decreases, at some altitude in the atmosphere the mean free path becomes approximately equal to the height scale, $H = (k_B T)/mg$, where k_B is the Boltzmann constant, m is the average mass of particles, g is the gravity acceleration and T is the gas temperature. This altitude is known as the exobase, and the region above the exobase is defined as the exosphere. More rigorously, the exobase of a planet or satellite with radius R_p is defined as the altitude $h_{exo} = r_{exo} - R_p$ in the atmosphere at which the probability of escape from the atmosphere without subsequent collisions for a molecule (or atom) moving upwards with a velocity exceeding the escape velocity is equal to $1/e$, as shown in figure 1.

The exobase is calculated using the formula:

$$P_{exo} = e^{- \int_{r_{exo}}^{\infty} \sigma n(h) \mathrm{d}h} \tag{1}$$

with the dimensionless parameter $Kn(h) = 1/\sigma n(h) H(h)$. Here, $h(h)$ and $T(h)$ are the number density and temperature of gas at an altitude $h = r - R_p$, σ is the elastic scattering cross section, m is the average mass of molecules and atoms, and $g(h) = (GM_p)/r^2$, where M_p is the mass of the planet and G is the gravitational constant. In the dynamics of rarefied gases, the parameter K_n is referred to as the Knudsen number, which is defined as the ratio of characteristic micro- and macroscopic gas flow scales: $Kn(h) = l(h)/H(h)$, where the characteristic microscopic scale is the free path length $l(h) = \left(\sqrt{2}\sigma n(h)\right)^{-1/2}$, and the characteristic altitude-dependent macroscopic scale is the atmospheric height scale $H(h) = k_B T(h)/(mg(h))$. In particular, the condition $K_n \ll 1$ ensures the correctness of describing the atmosphere in the gas dynamic approximation as a medium in which collisions dominate and which is considered as a continuous medium. At the exobase altitude, $K_n \approx 1$, and the relation $\sigma n_{exo} H \approx 1$ is often used for determining the exobase. In this estimate, the exobase altitude is attained for the gas concentration along the line of sight is often used for determining the exobase. Under this assumption, the escape of atoms and molecules starts directly from the physical surface of the celestial body.

2.3 Thermal escape mechanisms

The mechanism of thermal escape is that when the inherent kinetic energy of gas molecules is beyond the gravitational potential energy, the molecules escape the atmosphere. Thermal escape mainly includes two mechanisms: Jeans escape and hydrodynamic escape. The former is caused by the thermal motion of molecules, and the latter is because of macroscopic convection caused by uneven gas temperature.

Jeans escape: The thermal motion of gas molecules obeys Maxwell's law of velocity distribution. The parameters included in the distribution function are atomic mass and temperature (related to the internal energy of the gas). Since gas molecules with a smaller mass have a greater speed at the same temperature (internal energy), on planets, the main body of Jeans escape is mostly lighter elements such as H.

Hydrodynamic escape: The hydrodynamic escape means that under the action of solar radiation, the gases in the atmosphere form convection due to uneven temperature. In this process, heavier molecules are collided by lighter molecules at a higher speed and taken out of the atmosphere, which contains both heavy and light molecules.

2.4 Suprathermal particles in planetary atmospheres

In studying the atmospheric gas flow at exosphere altitudes, we should take into account possible losses and the production of atoms and molecules as a result of non-thermal processes such as ion sputtering of neutral gas, ionization and dissociation by electrons, charge exchange with the solar wind, and/or magnetospheric plasma ions. The category of suprathermal (or 'hot') particles usually includes particles whose kinetic energy is higher than $(5 - 10)k_B T$, where T is the temperature of the background atmospheric gas. The suprathermal particles are produced in various physical and chemical processes, whose products have excessive kinetic energy. If the production rate of such particles populating the range of suprathermal energies is high compared to the rate of their thermalization in elastic collisions, a stable fraction is created that can significantly perturb the locally equilibrium (Maxwell) distribution of the thermal energy of the background atmospheric gas. The principal sources of suprathermal particles in the rarefied gas of planetary atmospheres includes:

1. Charge exchange escape. Charge exchange when high-energy ions in the solar wind interact with neutral gases in the atmosphere;

2. Photochemical escape. Dissociation and dissociative ionization by UV solar radiation ;

3. Sputtering escape. Solar wind plasma sputters or hits atmospheric gases.

4. Exothermal ion-molecular and neutral chemical reactions;

The above mechanisms can change the gas molecular/atomic rate distribution in the atmosphere on a large scale or locally, and then affect the atmospheric escape rate.

3 Assumptions and Approximation

For the assumption of the problem, there are two important factors that affect the research, namely, the composition of the thicker Martian atmosphere and how the temperature of Mars changes over time. We first estimate and judge them.

The increase in the thickness of the atmosphere will reduce the thermal radiation power of Mars into space, leading to a certain increase in the temperature of Mars. The blackbody radiation formula and the greenhouse effect principle formula are now used to estimate the influence of atmospheric thickness on the temperature change of Mars.

According to the single-layer greenhouse gas model[5](shown in figure Figure.2)

$$T_0 = \sqrt[4]{\frac{\eta S_0 (1 - \alpha)}{4\sigma}} \tag{2}$$

where S_0 is the solar radiation power density, α is the Surface reflection coefficient of Mars, σ is the Boltzmann constant, and η is the coefficient, which characterizes Greenhouse Effect of the atmosphere.
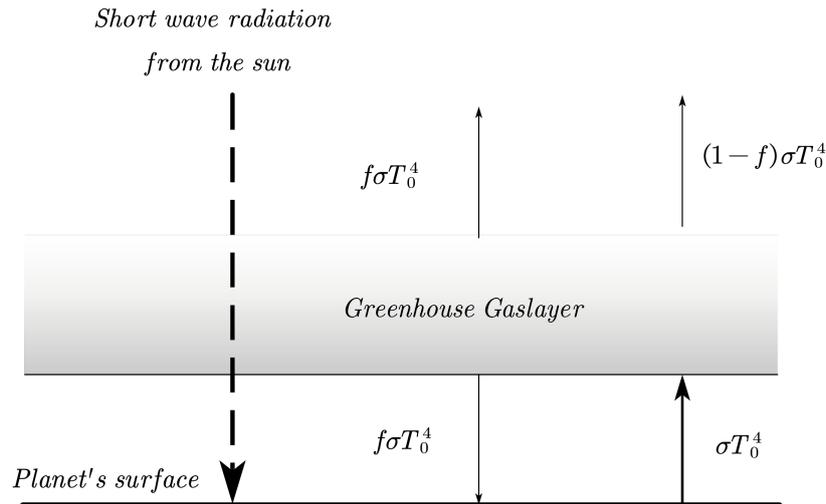
Figure 1

According to observations, Mars currently has an atmosphere with a pressure of 600Pa and an average temperature of 210K.If the pressure on the surface of Mars P is raised to 0.2bar, so the surface temperature of Mars $T = \sqrt[4]{\frac{\eta}{\eta_0}} = 257.6K$.

Now consider the composition of the Martian atmosphere. It should be noted that the saturated vapor pressure of water is about 191.5Pa at the temperature of 257.6K, that is, the maximum partial pressure that water vapor can provide at this time is 191.5Pa, and the partial pressure of CO_2 is not less than 19.8kPa. Therefore, for the assumption of the problem, we approximate It is believed that the Martian atmosphere at a pressure of 0.2 bar is composed of CO_2.

In addition, because the average temperature on the surface of Mars is now about 210K, this is not much different from 257.K. In other words, the thicker Martian atmosphere will not have a major impact on the temperature of Mars. Therefore, we ignore the changes in the temperature of Mars over time.

Also, based on the basic information about the facts, we make the following assumptions:

1. Assuming that the temperature distribution of Mars does not change with space, and because the pressure of 0.2 bar is not too large, the Martian atmosphere can be considered as an ideal gas, so in this article we use an isothermal atmosphere model.

2. Because the time scale of the evolution of the Martian atmosphere is much longer than the cycle of solar activity (about 11 years), the time required for significant changes in solar activity is very long (billions of years), so the influence of solar activity can be ignored It is believed that the particle flux density and radiant energy flux density received by Mars remain unchanged.

3. Similarly, because the Martian rotation period is much smaller than the time scale of atmospheric evolution, it is not necessary to discuss the conditions of the day and night hemispheres separately.

4. Because the eccentricity of the orbit of Mars is small (about 0.09), the orbit of Mars is regarded as a circle. Because the equatorial radius (3396.2 km) of Mars is not much different from the polar radius (3376.2 km), Mars is regarded as an ideal sphere.

5. Because the Martian gas is rare, the high-speed airflow in the middle and lower layers has limited influence on the upper atmosphere, so the influence of atmospheric macroscopic flow is ignored.

4 Theoretical analysis

The planetary atmosphere density decreases as altitude grows; starting with the exosphere altitude particles can run planet-size distances with a very low probability of collisions. At such altitudes, the atoms and molecules whose energy is higher than their gravitational energy and whose radial velocity is directed upward, can escape into open space. At the exobase altitude he, a transition occurs from the continuous-medium regime to the rarefied-gas regime, and individual collisions are to be considered using kinetic and/or stochastic methods.

4.1 Thermal escape.

4.1.1 Jeans escape

In this model, the velocity of gas molecules obeys Maxwell's velocity distribution law[4]:

$$f(v) = 4\pi(\frac{m}{2\pi kT})^{\frac{3}{2}}\exp(\frac{mv^2}{2kT})v^2 \tag{3}$$

$$f(v_x) = (\frac{m}{2\pi kT})^{\frac{1}{2}}\exp(\frac{mv^2}{2kT}) \tag{4}$$

From this, the particle flow density can be calculated(7):

$$F_{Jeans} = \int_{v_{esc}}^{\infty} f_{MB}(v)\mathrm{d}v \int_0^{\pi/2} 2\pi\sin\theta\cos\theta\mathrm{d}\theta \tag{5}$$

where v is the velocity magnitude, f_{MB} is the Maxwellian-Boltzmann velocity distribution function, θ the angle between the velocity direction and the zenith direction and Vesc the escape velocity. The integration provides the usual Jeans formula for the escape flux:

$$F_{esc}(r_{exo}) = \frac{n(r_{exo})U}{2\sqrt{\pi}}((\frac{v}{U})^2 + 1)e^{-(\frac{v}{U})^2} \tag{6}$$

Where U is the average velocity of gas molecules and v is the escape velocity of the planet. Use λ to express the ratio between these two speeds, as the ratio of the potential energy of the particle in the gravitational field of the planet to the thermal kinetic energy:

$$\lambda(r_{exo}) = \frac{v_{esc}^2}{U^2} = \frac{GM_pm}{k_BTr_{exo}} = \frac{r_{exo}}{H} \tag{7}$$

It follows that as λ → 0, the atmosphere loses its gravitational bond to the planet and atmospheric outflow occurs in a continuous medium regime owing to the excessive kinetic energy of thermal motion, while in the limit of large values of λ, the atmosphere remains fully gravitationally bound, and the thermal escape is vanishingly small. Celestial bodies with small values of λ close to the exobase have the most extended atmospheres.

The limit λ → 0 is known as the Jeans limit, which characterizes the maximum possible velocity of thermal escape:

$$\lim_{\lambda\to 0} F_{esc}(r_{exo}) = \frac{n(r_{exo})U}{2\sqrt{\pi}} = \frac{1}{4}n(r_{exo})v_{th} \tag{8}$$

4.1.2 Hydrodynamic escape

The radiation reflected by the surface heating the atmosphere and the temperature difference between day and night are two main ways to generate convection. The former forms vertical

flow, while the latter forms horizontal flow, but both of them are localized in the troposphere near the surface. Compared with the direct effect of electromagnetic radiation, its influence on the escape layer atmosphere can be neglected.

In this part we only consider the factors of Jeans escape.

4.2 Non-thermal escape

4.2.1 Sputtering escape

The main component of the solar wind is positively charged high-speed H+ ions. The solar wind's effects on the molecules in the atmosphere mainly include photochemistry and sputtering. Sputtering is a phenomenon in which particles in the solar wind collide with atmospheric molecules at a high speed to change the velocity distribution of atmospheric molecules. The process of sputtering does not involve the transfer of charges or the change of chemical bonds, and can be regarded as a mechanical process. Because the speed of particles in the solar wind is very large, it has a positive effect on the escape of the atmosphere. Because the magnetic field of Mars is very small, it is difficult to deflect the charged solar wind, so the impact of the solar wind on Mars is more significant than that of the earth.

4.2.2 Photochemical escape

In the upper atmosphere, high energy ultraviolet photons can react more readily with molecules. Photodissociation can break a molecule into smaller components and provide enough energy for those components to escape. Photoionization produces ions, which can get trapped in the planet's magnetosphere or undergo dissociative recombination . In the first case, these ions may undergo Sputtering escape. In the second case, the ion recombines with an electron, releases energy, and can escape.(8) Because we ignore the magnetosphere of Mars itself, we only need to consider the latter case described above. That is, ions and electrons recombine into atoms and then escape. We believe that the photochemical process caused by ultraviolet rays mainly occurs in the exosphere of Mars. The reaction may generate various ions and atoms in various states. We consider the following main reactions:

$$CO_2 + h\nu \longrightarrow CO_2^+ + e \tag{9}$$

$$CO_2^+ + e \longrightarrow CO + O \tag{10}$$

$$CO + h\nu \longrightarrow CO^+ + e \tag{11}$$

$$CO^+ + e \longrightarrow C + O \tag{12}$$

As mentioned before, we only consider the escape after recombination of ions and electrons into atoms. The above reaction equations can be combined into(9):

$$CO_2 + h\nu \longrightarrow CO + O \tag{13}$$

$$CO + h\nu \longrightarrow C + O \tag{14}$$

That is, the photolysis reaction of two molecules. According to existing studies, for this type of reaction, The altitude dependent production rate P(r) for photodissociation of a molecular neutral n can be obtained by the relation:

$$P(r) = an_n(r) \int_\lambda \sigma_n^{pd}(\lambda) F(r, \lambda) d\lambda \tag{15}$$

where $n_n(r)$ is the altitude dependent neutral density, For $F(r, \lambda)$ the solar flux at the altitude r(Take the radiant energy flux when the sun zenith angle is 60° as the average) and $\sigma_n^{pd}(\lambda)$ the

photodissociation cross section for the neutral at wavelength λ. The photodissociation and The absorption cross sections are taken from Photo Rate Coefficient Database.2(10) As shown in [], the solar radiation intensity spectrum is shown in [], in view of the fact that ultraviolet rays play a major role in photochemical escape, and the intensity of components with wavelengths shorter than 300nm in sunlight is very weak , So ν=300nm can be taken.a is a constant, which can be estimated as:a Based on this, a system of differential equations about the reactants and products of the photochemical reaction can be established:

$$\frac{\mathrm{d}n_1}{\mathrm{d}t} = -k_1 n_1 - \alpha_{esp1} \tag{16}$$

$$\frac{\mathrm{d}n_2}{\mathrm{d}t} = -k_2 n_2 + k_1 n_1 - \alpha_{esp2} \tag{17}$$

$$\frac{\mathrm{d}n_3}{\mathrm{d}t} = k_2 n_2 - \alpha_{esp3} \tag{18}$$
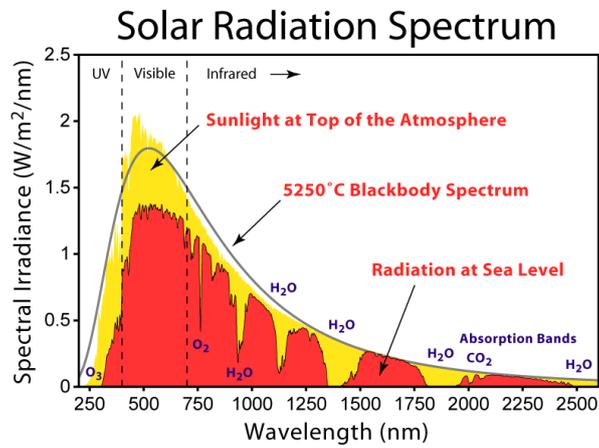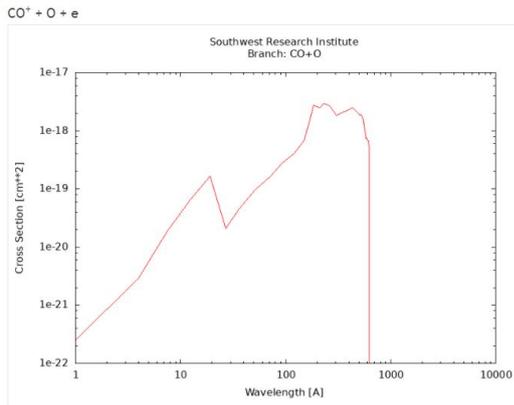

Figure 2 Solar spectrum

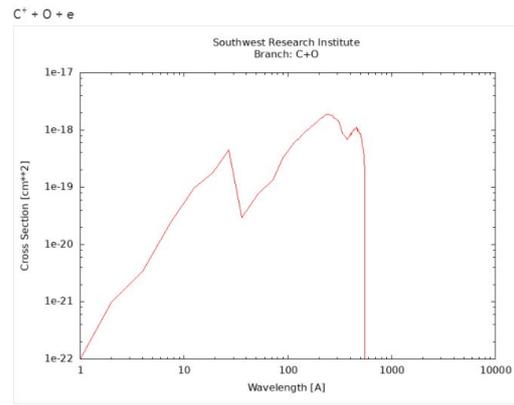Figure 3 photodissociation cross section of carbon dioxide

Figure 4 photodissociation cross section of carbon oxide

Among them, n_1, n_2, n_3 represents the number density of CO_2, CO, C. In addition, for each component, the part lost due to Jeans escape should be subtracted separately: $\alpha_{esp1}, \alpha_{esp2}, \alpha_{esp3}$. According to the equation(12)and the data in the figure(3)(4), the rate constant of each reaction

can be calculated as follows:

$$k_i = \frac{a \int_\lambda \sigma_n^{pd}(\lambda) F(r,\lambda) d\lambda \int_{R_1}^{\infty} 4\pi r^2 e^{-\frac{r-R_0}{H}} dr}{\int_{R_0}^{R_1} 4\pi r^2 e^{-\frac{r-R_0}{H}} dr}, i = 1,2 \tag{19}$$

Because the photochemical reaction mainly occurs near the exosphere, where the gas molecules are already relatively sparse. Therefore, the range of photochemical reaction takes the height corresponding to exophere to positive infinity, and the part used to calculate the increase or decrease of the particle number is taken below the height corresponding to exophere.

For the part of particle energy, we calculate according to the two-body particle model:
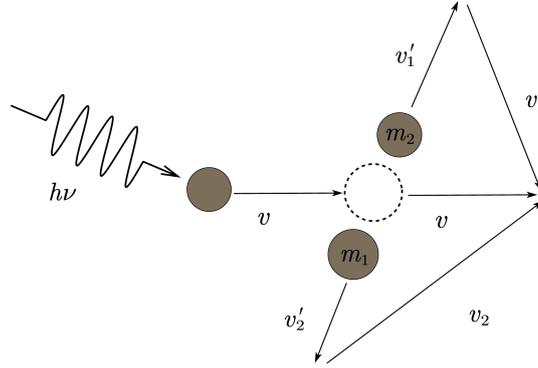

Figure 5 two-body particle model

Where v is the velocity of the reactant molecules, v_1, v_2 are the velocity of the product particles, and m_1, m_2 are their masses, and v_1', v_2' are their velocity relative to the center of mass. According to the law of conservation of momentum, law of conservation of energy and Koenig's theorem, there are:

$$v_1' = \sqrt{\frac{2m_2 E_c}{m_1(m_1 + m_2)}} \tag{20}$$

$$v_2' = \sqrt{\frac{2m_1 E_c}{m_1(m_1 + m_2)}} \tag{21}$$

$$v_1 = \sqrt{v_1'^2 + v^2 - 2vv_1'^2 \cos\theta} \tag{22}$$

$$v_2 = \sqrt{v_2'^2 + v^2 + 2vv_2'^2 \cos\theta} \tag{23}$$

$$E_c = h\nu \tag{24}$$

Where θ is randomly distributed We combine the jeans escape model in section 4.1 and use matlab to solve the above differential equations(16)(17)(18)and equations(20)(21)(22)(23), we can get the velocity distribution of the resulting particles CO, C, O and the quality of each component under the influence of the photochemical escape effect Changes over time. See section 5.

5 Simulation

5.1 Simulation of Jeans escape

Because the gas in the Martian escape layer is relatively rare, it can be regarded as an ideal gas. From the microscopic pressure formula: (k is Boltzmann constant)

$$p = nkT \tag{25}$$

According to eq[6], the number of gas molecules Fe passing through per unit time per unit area can be obtained, by

$$F = \frac{dN}{dt} = V_{eff} \frac{dn_0}{dt} \tag{26}$$

Substitution can get:

$$\frac{dn_0}{dt} = \frac{n(r_{exo})U}{2\sqrt{\pi}V_{eff}}\left(\left(\frac{v}{U}\right)^2 + 1\right)e^{-\left(\frac{v}{U}\right)^2} \tag{27}$$

That is, the decrease rate of a certain gas molecule is related to some parameters, so the problem is transformed into a first-order variable coefficient ordinary differential equation problem. The initial condition n0: $p(CO_2) = 0.2bar$ can be determined by eq[25]. Runge-Kutta method can be used to solve this kind of ordinary differential equation problems. Using Matlab to numerically simulate the jeans escape of Mars by the fourth to fifth step variable step length Runge-Kutta method, substituting the data of the main carbon dioxide gas in Mars, the results are as follows:
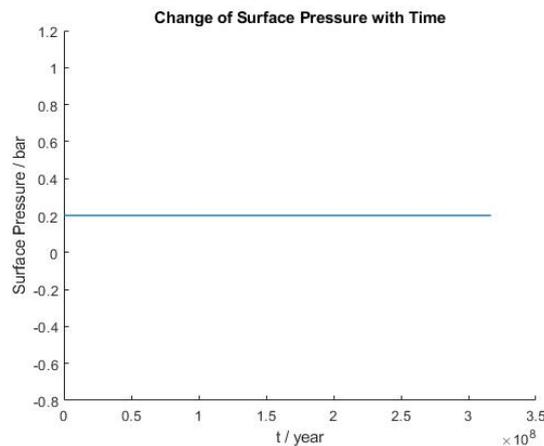

Figure 6 Jeans escape of carbon dioxide

It can be seen that in a fairly long period of time, within the range of 1e-15 solution accuracy, the number density of CO2 molecules hardly changes with time. This is because the average velocity of molecules of the same weight as CO2 is relatively small, and it is difficult to escape the Martian atmosphere through the Jeans escape method.

For comparison, substituting the relevant parameters of hydrogen and selecting the same initial conditions as carbon dioxide, we get:
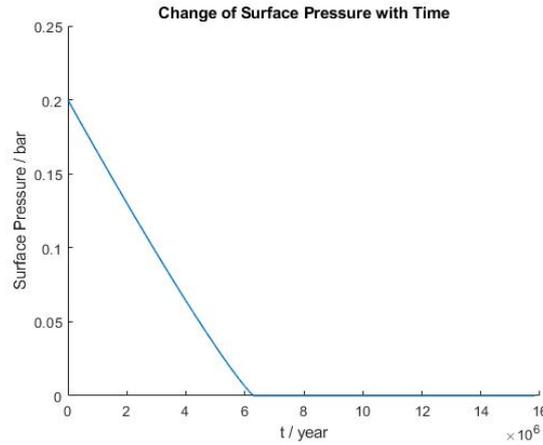
Figure 7 Jeans escape of hydrogen

It can be found that under the same atmospheric pressure, the escape rate of carbon dioxide is much smaller than that of hydrogen.

5.2 Simulation of Sputtering escape

Sputtering is a phenomenon in which particles in the solar wind (mainly H^+ ions) collide with atmospheric molecules at a high speed, which changes the velocity distribution of atmospheric molecules. We first use the Monte Carlo dynamics simulation method to study the collision of two particle swarms. In order to simplify the model, we think that every particle is a particle, and because the gas in the Martian escape layer is very thin, we think that there is no interaction between the particles in each particle group, and only elasticity with the particles of another particle group. collision. The main process is:

(1) Generate a certain number of random points. In order to make the result statistically significant, the number is generally above 1e4.

(2) Set the velocity distribution of A particle group (corresponding to gas molecules) to Maxwell's velocity distribution law, and B particle group (corresponding to the solar wind) has a velocity in a certain direction in space.

(3) The particles between the two particle swarms collide.

(4) Count the velocity distribution before and after the collision.
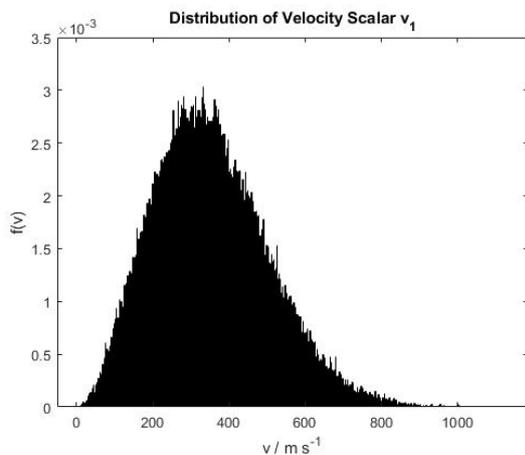
The results are as follows:

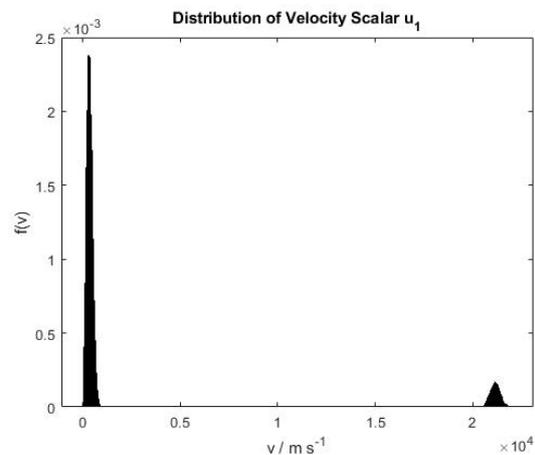Figure 8 Gas velocity distribution of gas before collision

Figure 9 Gas velocity distribution of gas after collision

After several simulations with changing conditions, it can be concluded that after the gas is hit by high-speed solar wind particles, some of the particles are accelerated to a higher energy state, and the percentage is related to the average number of collisions. When the average number of collisions is 1, the number of accelerated particles is exactly equal to the number of particles in the solar wind. We use computer programming methods to find the average number of collisions. Considering the elastic collision between solar wind particles and molecules, the speeds of both have changed. The changed solar wind particles continue to collide with other molecules until the speed of the solar wind particles is less than the escape velocity. This can be achieved by Matlab's loop statement. After substituting relevant data, the maximum number of collisions between solar wind particles and molecules can be found to be 32 times. However, the effective number of collisions for the gas to escape is not equal to the maximum number of collisions. Only molecules with velocity components in the direction away from Mars can escape, so the effective number of collisions is half of the maximum number of collisions, that is, 16 times.

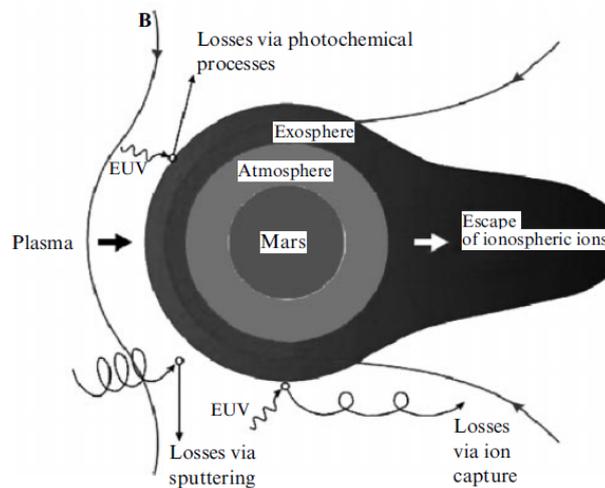Record the effective number of collisions as K, and consider the interaction between Mars and the sun:

Figure 10 Sputtering escape

The number of molecules that each solar wind particle can accelerate is K, so consider the deltat process and list the equations:

$$n_{sw}\pi R_1^2 v \mathrm{d}t = \frac{1}{K}\mathrm{d}N = \frac{1}{K}\mathrm{d}(n_0 V_{eff}) \tag{28}$$

That is the differential equation:

$$n_{sw}\pi R_1^2 v K \frac{1}{V_{eff}} = \frac{\mathrm{d}(n_0)}{\mathrm{d}t} \tag{29}$$

Considering that the radius of the Martian escape layer will change within the time range of the solution, this equation is a first-order variable coefficient ordinary differential equation. Using the fourth to fifth order Runge-Kutta method to solve the differential equation can be obtained:
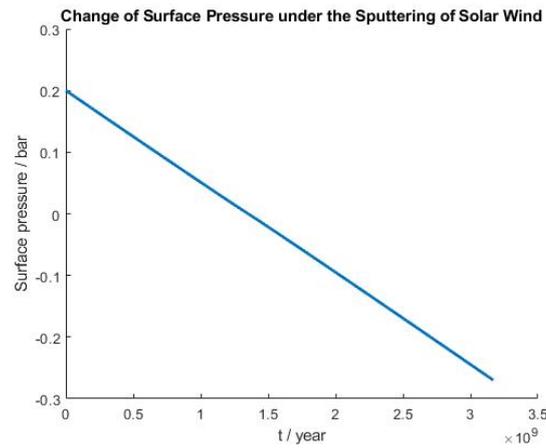
Figure 11 Change of Surface Pressure Under the Sputtering of solar wind

It can be found that even when the radius of the escape layer changes with time, the relationship between air pressure and time is still approximately linear.

5.3   Simulation of Photochemical escape

For the first-order ordinary differential equations of eq[16][17][18],the escape factor is not considered at first, and the fourth to fifth-order variable-step adaptive Runge-Kutta algorithm is used to solve the equations. Since only the photochemical effect near the exosphere is considered, the initial carbon dioxide content is much higher than CO, O, C and other particles, so the initial conditions are set to $n(CO_2) = 0, n(CO) = 0, n(O) = 0$

Solve to obtain the molecular number density of each substance as:
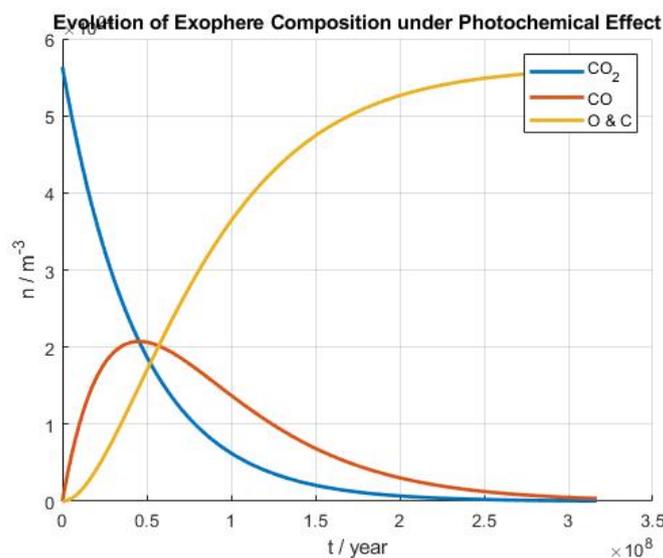
Figure 12 Evolution of Exophere Composition under Photochemical Effect

In order to calculate the influence of this chemical reaction on molecular escape, we performed the following two-step simulation. The first is to simulate the velocity distribution of the product particles after the reaction. Starting from the Maxwell's distribution law followed by atmospheric CO2 molecules, the velocity distribution of the product represented by the two-step reaction (13) (14) equations (22) (23) is obtained using Monte Lalo dynamics simulation,

The second step is to use the existing jeans escape model to study the escape rate of the particles generated by the photochemical reaction. It can be obtained from(22)(23)that for any velocity distribution(figure15-18), a differential equation about escape rate can be obtained after substituting the average velocity U. After obtaining the average velocity from the above velocity distribution, substituting it into the Jeans escape model, and considering the generation of particles in the chemical reaction, the following equation is obtained:

$$\frac{dn}{dt}V_{eff} = F + Prd \tag{30}$$

Among them, Prd is the generation rate. For the CO density curve that only considers the reaction generated in the figure (12), the finite difference method is used to numerically differentiate the obtained data, and the rate of change of the number density of CO over time can be obtained. The same method as above are used to solve ordinary differential equations. The results are as follows:
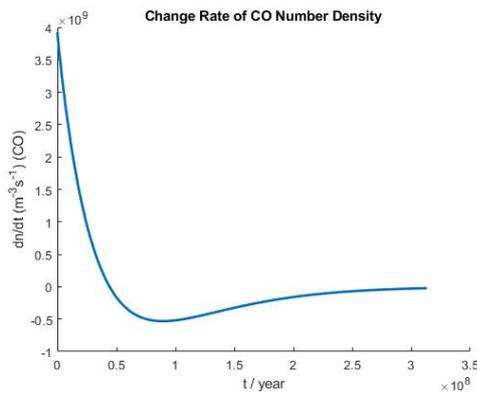

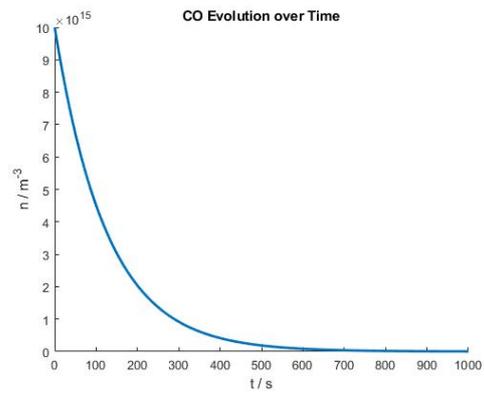Figure 13 Change Rate of CO Number Density
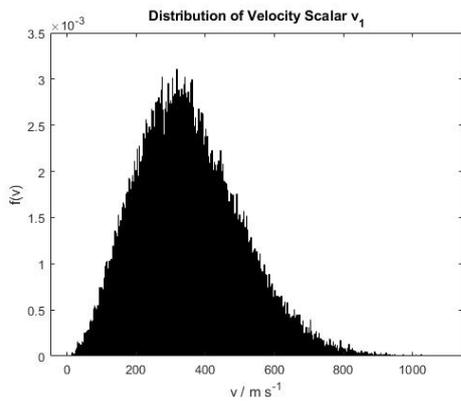

Figure 14 CO evolution over time
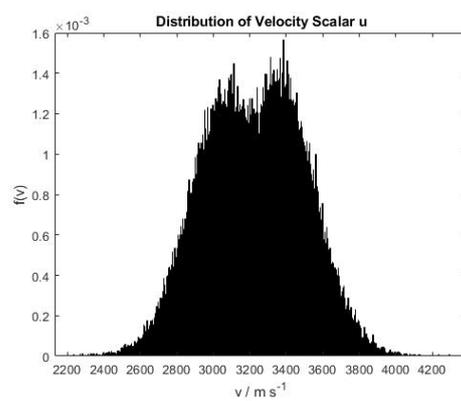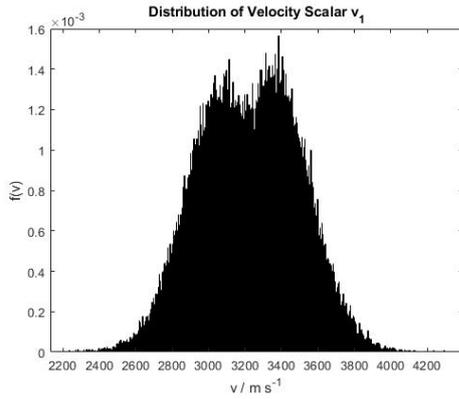

Figure 15

Figure 16

Figure 17
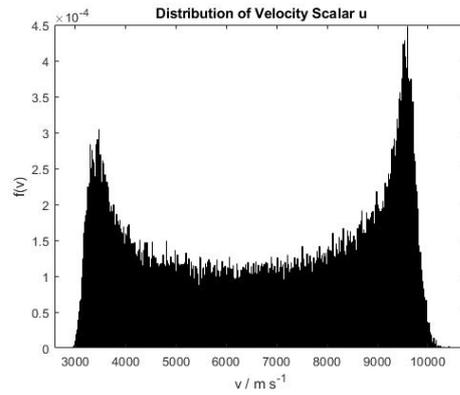
Figure 18 Final rate distribution after photochemical reaction

It can be found that in a short period of time, the inventory of CO is close to 0. This is because the energy of CO generated by the chemical reaction is higher, so jeans' escape rate is very fast. Therefore, near the escape layer of Mars, the amount of CO can be ignored.

According to the reaction equation eq, when the CO inventory is close to 0, the rate of C and O formation in the second step of the reaction is close to 0. And because the jeans escape rate of C and O is faster than that of CO, the inventory of C and O is also close to zero in a short period of time. The rate of O produced in the first reaction is the same as that of CO, and the jeans escape rate of O is faster than that of CO, so the stock of O produced in the first reaction is also close to 0.

5.4   Calculation of total effect

Since the main component of the Martian atmosphere is CO2, and the jeans effect of CO2 is not significant, the photochemistry and sputtering effects are mainly considered. From the above analysis, we can get the function $p_1(t)$ and $p_2(t)$ of pressure and time when these two effects are considered independently. When considering the total effect, the pressure function is: $p_{sum}(t) = 0.2 - (0.2 - p_1(t) + 0.2 - p_2(t))$ Use Matlab Plot the above solution results:

Figure 19 Change of Surface Atmospheric Pressure over Time

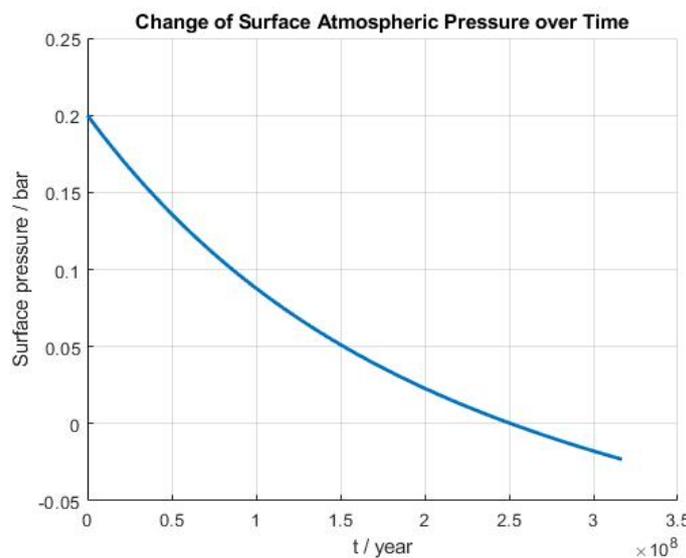It is the evolution over time of the pressure generated by the Martian atmosphere on the surface under the conditions considered in the topic.

From the above results, it can be concluded that the time for the pressure to decrease to 0.1 bar is about 8.6422×10^7 years.

6   Results

Through our analysis and calculations, we know that among the three factors, photochemical escape contributes the most to the reduction of CO2 in the hypothetical Martian atmosphere. Sputtering escape is second, and the CO2 escape speed it causes is about one-tenth of the former. The Kings escape contributes the least to the reduction of CO2, almost negligible.

Our final result is: the time for the pressure to decrease to 0.1 bar is about 8.6422×10^7 years.

7   Discussion / Conclusions

7.1   Conclusion

From Figure 13, it can be seen that the atmospheric pressure of 0.2bar on Mars has decreased to 0.1bar after about 70-90 million years, which is only the result of considering three main mechanisms, including thermal escape, solar windsputtering and photochemical reaction.

7.2   Strength

• We have considered three main mechanisms that affect the atmosphere, and simulated these processes by Monte Carlo dynamics simulation and other calculation methods, and presented the results clearly.

• Our simplified model of atmospheric escape layer can help us to master the evolution law of planetary atmosphere more clearly.

• Our calculation proves that it is difficult to maintain the way of increasing the atmospheric pressure of Mars on the cosmic time scale, and it may be necessary to take other measures to reshape the atmosphere of Mars.

7.3   Weakness

•In our model, we only considered the escape of gas particles in the escape layer, ignoring the influence of ionosphere and troposphere.

• Sedimentation processes such as adsorption and cooling of sand and dust may accelerate the reduction of atmospheric pressure, which is not considered in our model.

•Perhaps in the actual environment where Mars is located, an asteroid impact with a certain probability will have a fundamental impact on the atmospheric environment.

8   Outlook / Future Work

Studying the evolution of the Martian atmosphere is of great significance in many aspects. From a theoretical point of view, this helps us understand the meteorological laws of planets including the Earth and study the evolution of planets. From a practical point of view, it is helpful for us to study how to modify the climate on the planet, which may be of great value to the exploration and development of human alien habitats.

The mechanisms we studied in this article is actually very complicated, and the complexity of the model has a lot of room for improvement. The use of electromagnetic theory to construct a three-dimensional solar wind electromagnetic field and the use of three-dimensional Monte Carlo methods to simulate the collision and scattering of atmospheric particles are all very good research directions.

9 Appendix

9.1   MATLAB Code

This code calculates the Jeans escape:

```matlab
clear;clc;close all;
tic;

%constants
year=3600*24*365.25;% seconds in a year
G=6.67259e-11;% gravitational constant
M_mars=6.4171e23;% kg
R_mars=3389.5e3;% m
g=G*M_mars/(R_mars^2);% gravitational acceleration on the surface of Mars
k=1.380649e-23;%Boltzmann constant
R_ugc=8.31446261815324;% universal gas constant
tmax=5e14;% time range

% Calculate
T_es=257;% temperature of exosphere
t_T=linspace(0,tmax,10);
T_es=257+0/tmax*t_T;
T0=T_es;
p0=0.2e5;
n0=p0/(k*T0(1));

% data of molecules
M=2/1000;% molar mass of H2
d=0.289e-9;%d=31e-12;% radius of H2
% M=44/1000;% molar mass of CO2
% d=233e-12;% CO2
% M=16/1000;% molar mass of O
% d=0.074*1e-9;% radius of O
% M=12/1000;% molar mass of C
% d=91*1e-12;% radius of C

% function
H=R_ugc*T_es/(M*g);% pressure scale height of H2

% solve the ode
tspan=linspace(0,tmax,10000);
[t,n]=ode45(@(t,n) fun_ode(t,n,R_mars,M_mars,R_ugc,G,H,d,M,T_es,t_T),tspan,n0);
p=k*n'.*interp1(t_T,T0,tspan);
```

```matlab
% Time required to reduce to half
[~,index]=min(abs(p-p0/2));
t_result=t(index);
disp('The result is (year): ');
disp(t_result/year);
% print the figure
figure();hold on;
plot(t/year,p/1e5,'LineWidth',1);
xlabel('t / year');ylabel('Surface Pressure / bar');
title('Change of Surface Pressure with Time');
toc;

function dy=fun_ode(t,y,R_mars,M_mars,R_ugc,G,H,d,M,T_es,t_T)
T_es=interp1(t_T,T_es,t);
H=interp1(t_T,H,t);
R_es=R_mars+H*log(H*sqrt(2)*pi*d.^2*y);
% solve the V_eff
dV=@(r) 4*pi*r.^2.*exp(-(r-R_mars)./H);
V_eff=integral(dV,R_mars,R_es);
% parameters
u=sqrt(8/pi*R_ugc.*T_es./M);% most probable rate
v=sqrt(2*G.*M_mars./R_es);% escape velocity
dy=-4*pi*R_es.^2./V_eff.*y.*exp(-(R_es-R_mars)/H).*...
u/(2*sqrt(pi)).*exp(-(v/u).^2).*(1+(v/u).^2);
end
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% This code calculates the Particle swarm collision problem:
clear;clc;close all;

%constants
R_mars=3389.5e3;% m
R_ugc=8.31446261815324;% universal gas constant
T=257;% temperature

% parameters
M=44/1000;% H
v_sw=475.8e3;
n_sw=1.83e6;
n_atm=5.64e22;

% calculate
v_crit=5.02e3;
t=1;

% Maxwell Distribution.
f_dis=@(x) (M/(2*pi*R_ugc*T)).^(1/2).*exp(-M*x.^2/(2*R_ugc*T));

m1=M;m2=1/1000;
```

```matlab
N1=1e5;
N2=10e3;

vmax=1e5;
v1(:,1)=randf(f_dis,N1,[-vmax,vmax]);% The speed vector of Martian gas molecule
v1(:,2)=randf(f_dis,N1,[-vmax,vmax]);
v1(:,3)=randf(f_dis,N1,[-vmax,vmax]);
v2(:,1)=v_sw+5e3*(2*rand(N2,1)-1);% The speed of solar wind
v2(:,2)=zeros(size(v2(:,1)));
v2(:,3)=zeros(size(v2(:,1)));
v1_mod=vecnorm(v1');


FDH(v1_mod,1000,'Distribution of Velocity Scalar v_1');

[u1,u2]=particles_collision(m1,v1,m2,v2);
u1_mod=vecnorm(u1');
FDH(u1_mod,1000,'Distribution of Velocity Scalar u_1');
u2_mod=vecnorm(u2');
FDH(u2_mod,1000,'Distribution of Velocity Scalar u_2');

m1_crit=sum(v1_mod>v_crit);
n1_crit=sum(u1_mod>v_crit);
rate=(n1_crit-m1_crit)/m1_crit;
disp(n1_crit/N1);
% disp(rate);




function [u1,u2]=particles_collision(m1,v1,m2,v2)
m2=m2*ones(size(v2));m1=m1*ones(size(v1));
m2=[m2;zeros(size(m1,1)-size(m2,1),size(m1,2))];
v2=[v2;zeros(size(m1,1)-size(v2,1),size(m1,2))];
[u1,u2]=elastic_collision(m1,v1,m2,v2);
end

function [u1,u2]=elastic_collision(m1,v1,m2,v2)
u1=((m1-m2).*v1+2.*m2.*v2)./(m1+m2);
u2=((m2-m1).*v2+2.*m1.*v1)./(m1+m2);
end

function X = randf(f,N,b)
% Generate N samples distributed with f on interval b
% M is the maximum value of the distribution function on the interval
n = 0;
X = zeros(N,1);
counter = 0;
% f_oppo=@(x) -f(x);
% M=particleswarm(f_oppo,1,b(1),b(2));
M=f(0);
```

```matlab
    while n < N && counter < 1000
        x = b(1) + rand(2*N,1)*diff(b);
        uM = M*rand(2*N,1);
        x = x(uM < f(x));
        if isempty(x)
            error('No Points Sampled')
        end
        X(n+1:min([n+length(x),N])) = x(1:min([length(x),N - n]));
        n = n + length(x);
        counter = counter+1;
    end
end

function FDH(y,tin,tit)
% Give a frequency distribution histogram
figure();
histogram(y,tin,'Normalization','pdf');
xlabel('v / m s^{-1}');ylabel('f(v)');
title(tit);
end
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%5
%the effect of photochemical process on Jeans escape
clear;clc;close all;
tic;

year=3600*24*365.25;% seconds in a year
M=8/1000;% molar mass of O
d=0.074*1e-9;% radius of O
n0=5.6366e24;%
T=257;
tmax=1e16;
[t,n]=Change_in_molecules(M,d,[n0,0,0],T,tmax);
figure();hold on;
plot(t/year,n,'LineWidth',2);
ylabel('n / m^{-3}');xlabel('t / year');
legend('CO_2','CO','O & C');
title('Evolution of Exohere Composition under Photochemical Effect');
grid on;
hold off;

prd=diff(n(:,2))./diff(t);
t_prd=t(1:end-1);
figure();hold on;
plot(t_prd/year,prd,'LineWidth',2);
xlabel('t / year');ylabel('dn/dt (m^{-3}s^{-1}) (CO)');
title('Change Rate of CO Number Density');
% data of molecules
% M=2/1000;% molar mass of H2
% d=0.289e-9;%d=31e-12;% radius of H2
% M=44/1000;% molar mass of CO2
```

```matlab
% d=(0.35+0.51)/2*1e-9;% radius of CO2
% M=16/1000;% molar mass of O
% d=0.074*1e-9;% radius of O
% M=12/1000;% molar mass of C
% d=91*1e-12;% radius of C
M=28/1000;% molar mass of CO
d=113*1e-12;% radius of CO



%constants
year=3600*24*365.25;% seconds in a year
G=6.67259e-11;% gravitational constant
M_mars=6.4171e23;% kg
R_mars=3389.5e3;% m
g=G*M_mars/(R_mars^2);% gravitational acceleration on the surface of Mars
k=1.380649e-23;%Boltzmann constant
R_ugc=8.31446261815324;% universal gas constant

tmax=1e3;
% Calculate
t_T=linspace(0,tmax,10);
T_es=257;% temperature of exosphere
T0=T_es;
p0=0.2e5;
n0=p0/(k*T0);% n is the number density of molecules on the surface of Mars
n0=1e16;

% function
H=R_ugc*T_es/(M*g);% pressure scale height of H2



% solve the V_eff
R_es=R_mars+H*log(H*sqrt(2)*pi*d.^2*n0);
dV=@(r) 4*pi*(r.^2).*exp(-(r-R_mars)./H);
V_eff=integral(dV,R_mars,R_es);
V_eff=real(V_eff);



% solve the ode of changing
% fun_ode=@(t,y) -4*pi*R_ex^2/V_eff*y*exp(-(R_ex-R_mars)/H)*u/(2*sqrt(pi)).*ea
tspan=linspace(0,tmax,200);
opts=odeset('RelTol',1e-3);
[t,n]=ode45(@(t,n) fun_ode(t,n,R_mars,M_mars,R_ugc,G,H,d,M,V_eff,R_es,prd,t_prd
p=n*k*T_es;

[~,index]=min(abs(p-p0/2));
t_result=t(index);
% disp('The result is (year): ');
% disp(t_result/year);
```

```matlab
% print the figure
figure();hold on;
plot(t,n,'LineWidth',2);
xlabel('t / s');ylabel('n / m^{-3}');
title('CO Evolution over Time');

toc;

function dy=fun_ode(t,y,R_mars,M_mars,R_ugc,G,H,d,M,V_eff,R_es,prd,t_prd)

% R_es=R_mars+H*log(H*sqrt(2)*pi*d.^2*y);

% parameters
% u=sqrt(8/pi*R_ugc.*T_ex./M);% most probable rate

u=6.7260e3;% Get from Change_in_molecules.m
v=(2*G.*M_mars./R_es).^(1/2);% escape velocity

prd=interp1(t_prd,prd,t);% the productivity of a gas
dy=prd-4*pi*R_es.^2./V_eff.*y.*exp(-(R_es-R_mars)/H).*u/(2*sqrt(pi)).*exp(-(v/u
% disp(dy);
end




%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%change of velocity distribution during photochemical reaction
clear;clc;close all;
tic;

% constants
v_es=5.027e3;
R_ugc=8.31446261815324;% universal gas constant

M=44/1000;% CO2
k=3209;% CO
% M=16/1000;
% k=5615;% m/s O

% premeters
T=257;% temperature

% Maxwell Distribution.
f_dis=@(x) (M/(2*pi*R_ugc*T)).^(1/2).*exp(-M*x.^2/(2*R_ugc*T));

Num=1e5;
vmax=1e5;
theta=2*pi*rand(Num,1)';
v1(:,1)=randf(f_dis,Num,[-vmax,vmax]);% The speed vector of Martian gas molecu
v1(:,2)=randf(f_dis,Num,[-vmax,vmax]);
```

```matlab
    v1(:,3)=randf(f_dis,Num,[-vmax,vmax]);
    v1_mod=vecnorm(v1');

    u=sqrt(v1_mod.^2+k^2+2*k.*cos(theta).*v1_mod);
    FDH(v1_mod,1000,'Distribution of Velocity Scalar v_1');
    FDH(u,1000,'Distribution of Velocity Scalar u');

    v1_mod=u;
    k=6144;% C
    % k=4608;% m/s O

    u=sqrt(v1_mod.^2+k^2+2*k*cos(theta).*v1_mod);
    FDH(v1_mod,1000,'Distribution of Velocity Scalar v_1');
    FDH(u,1000,'Distribution of Velocity Scalar u');


    rate_es=sum(u>=v_es)/Num;
    disp(rate_es);% the ratio of velocity to escape velocity
    disp(mean(u));% average velocity

    toc;

    function X = randf(f,N,b)
    % Generate N samples distributed with f on interval b
    % M is the maximum value of the distribution function on the interval
    n = 0;
    X = zeros(N,1);
    counter = 0;
    % f_oppo=@(x) -f(x);
    % M=particleswarm(f_oppo,1,b(1),b(2));
    M=f(0);
    while n < N && counter < 1000
        x = b(1) + rand(2*N,1)*diff(b);
        uM = M*rand(2*N,1);
        x = x(uM < f(x));
        if isempty(x)
            error('No Points Sampled')
        end
        X(n+1:min([n+length(x),N])) = x(1:min([length(x),N - n]));
        n = n + length(x);
        counter = counter+1;
    end
    end


    function FDH(y,tin,tit)
    % Give a frequency distribution histogram
    figure();
    histogram(y,tin,'Normalization','pdf');
    xlabel('v / m s^{-1}');ylabel('f(v)');
    title(tit);
```

```matlab
    end


    %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%5
    % In the process of photochemistry, solve the differential
    % equation of the change of the number of particles
    function [t,n]=Change_in_molecules(M,d,n_ini,T,tmax)
    % Calculate the chemical reaction in the photochemical process
    % and the concentration of each substance by ordinary differential equation
    % M is the molar mass of atom
    % d is the diameter of atom
    % n_ini is the the initial number density of the three substances
    % T is temperature
    % tmax is the time range

    % constants
    G=6.67259e-11;% gravitational constant
    R_mars=3389.5e3;% m, radius of Mars
    M_mars=6.4171e23;% kg
    g=G*M_mars/(R_mars^2);% gravitational acceleration on the surface of Mars
    r_mars=227940000e3;% m, distance from mars to sun
    T_solar=5500+273.15;% K, temperature of the sun
    R_ugc=8.31446261815324;% universal gas constant
    sigma=5.670373e-8;% Stefan-Boltzmann constant

    %cauculate the H
    H=R_ugc*T/(M*g);

    % calculate the V_eff
    n0=n_ini(1);
    R_es=R_mars+H*log(H*sqrt(2)*pi*d.^2*n0);
    dV=@(r) 4*pi*r.^2.*exp(-(r-R_mars)./H);
    V_eff2=integral(dV,R_es,+Inf);
    dV=@(r) 4*pi*r.^2.*exp(-(r-R_mars)./H);
    V_eff1=integral(dV,R_mars,R_es);

    % Calculate the integral
    Phi_ener=0.5*sigma*T_solar^4*(pi*R_mars^2)^2/(4*pi*r_mars^2);
    inte1=1/2*1000e-10*1e-18*1e-4;
    inte2=1/2*1000e-10*1e-18*1e-4;

    % calculate the k
    k1=V_eff2*inte1*Phi_ener/V_eff1;
    k2=V_eff2*inte2*Phi_ener/V_eff1;
    k1=k1*1e13;
    k2=k2*1e13;

    % solve the ode
    opts=odeset('RelTol',1e-5);
    tspan=[0 tmax];
```

```matlab
    [t,n]=ode45(@(t,y) fun_ode_chem(t,y,k1,k2),tspan,n_ini,opts);

    % the differential equation
    function dn=fun_ode_chem(t,n,k1,k2)
    dn=zeros(3,1);
    dn(1)=-k1*n(1);
    dn(2)=k1*n(1)-k2*n(2);
    dn(3)=k2*n(2);
    end

end


%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%5
% Calculate the sputtering process of the solar wind
function [t,y_bar]=Sputtering()

% constants
year=3600*24*365.25;% seconds in a year
bar=1e5;
G=6.67259e-11;% gravitational constant
k=1.380649e-23;%Boltzmann constant
R_ugc=8.31446261815324;% universal gas constant
T=200;% temperature
M_mars=6.4171e23;% kg
R_mars=3389.5e3;% m
g=G*M_mars/(R_mars^2);% gravitational acceleration on the surface of Mars

% parameters
v_sw=475.8e3;% velocity of solar wind
n_sw=1.83e6;% nmber density of solar wind
n_atm=5.64e22;
K=16;% Number of collisions
tmax=1e17;% time range

% M=44/1000;% molar mass of CO2
% d=(0.35+0.51)/2*1e-9;% radius of CO2
M_O=16/1000;% molar mass of O
d_O=0.074*1e-9;% radius of O

M=M_O;
d=d_O;
p0=0.2*bar;
n0=p0/(k*T);% n is the number density of molecules on the surface of Mars

% solve the ode
tspan=[0 tmax];
[t,y]=ode45(@(t,y)ode_jianshe(t,y,g,R_ugc,R_mars,d,M,T,n_sw,v_sw,K),tspan,n0);

% Mapping and visualization
```

```matlab
t_year=t/year;
y_bar=y*k*T/bar;
figure();hold on;
plot(t_year,y_bar,'LineWidth',2);
xlabel('t / year');ylabel('Surface pressure / bar');
title('Change of Surface Pressure under the Sputtering of Solar Wind');
hold off;


function dy=ode_jianshe(t,y,g,R_ugc,R_mars,d,M,T,n_sw,v_sw,K)

%cauculate the H
H=R_ugc*T/(M*g);

% calculate the V_eff
R_es=R_mars+H*log(H*sqrt(2)*pi*d.^2*y);
dV=@(r) 4*pi*r.^2.*exp(-(r-R_mars)./H);
V_eff=integral(dV,R_mars,R_es);

R_es=1.5*R_mars;

% if imag(log(sqrt(2)*pi*d.^2.*H.*y))~=0
dy=-n_sw.*K*pi*v_sw./real(V_eff).*(R_mars+H.*real(log(sqrt(2)*pi*d.^2.*H.*y))).^
end
end




%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Pressure change in photochemical process
function [t,p_bar]=Photochemistry()
year=3600*24*365.25;% seconds in a year
k=1.380649e-23;% Boltzmann constant
% M=16/1000;% molar mass of O
% d=0.074*1e-9;% radius of O
M=44/1000;% molar mass of CO2
d=233e-12;% CO2
n0=5.6366e24;%
T=257;
tmax=1e16;
[t,n]=Change_in_molecules(M,d,[n0,0,0],T,tmax);
p_bar=n(:,1)*k*T/1e5;

figure();hold on;
plot(t/year,p_bar,'LineWidth',2);
ylabel('Surface pressure / bar');xlabel('t / year');
legend('CO_2');
title('Evolution of CO_2 under Photochemical Effect');
hold off;
```

```
    end
```

```
    end
```

10   References

References

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