Chapman’s model for ozone concentration: earth’s slowing rotation effect in the atmospheric past

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Chapman’s model for ozone concentration is studied. In this nonlinear model, the photodissociation coefficients for $O_2$ and $O_3$ are time-depending due to earth-rotation. From the Kapitsa’s method, valid in the high frequency limit, we find the criterion for the existence of equilibrium solutions. These solutions are depending on the frequency, and require a rotation period $T$ which satisfies $T < T_1$ or $T > T_2$. Where the critical periods $T_1$ and $T_2$, with $T_2 > T_1$, are a function of the parameters of the system (reaction rates and photodissociation coefficients). Conjectures respect to the retardation of the earth’s rotation, due to friction, suggest that the criterion was not even verified in the atmospheric past.

Key words: Atmospheric Physics. Chemical Physics. Nonlinear Dynamic Systems. Oscillations.
1.- Introduction

The dynamics of the ozone layer in the atmosphere has different basic process like: chemical reactions, photochemical reactions and transport (diffusion, convection, etc.). In a general point of view, this dynamics is complex and requires some approximations to be studied. In this sense, we consider a photochemical model proposed by S. Chapman (Brasseur, 1986; Chapman, 1930; Wayne, 1991). This model considers a set of reactions between the oxygen components. Explicitly,

\begin{align*}
R1) & \quad O + O_2 + M \rightarrow O_3 + M, \\
R2) & \quad O + O_3 \rightarrow 2O_2, \\
R3) & \quad O_2 + h\nu \rightarrow O + O, \\
R4) & \quad O_3 + h\nu \rightarrow O + O_2.
\end{align*}

In the reaction of the ozone production R1, \( M \) denotes any atmospheric element acting as catalyzer. The reaction R2 denotes the loss of oxygen \( O \) and ozone \( O_3 \) producing molecular oxygen \( O_2 \). R3 and R4 correspond to photochemical destruction process related to the solar radiation (symbolized by \( h\nu \)).

The time evolution equations for the constituents consider the above reactions for variable concentration assuming the concentration of \( O_2 \) being stationary. Let \( X \) and \( Y \) be the concentration of \( O \) and \( O_3 \) respectively. Then, the Chapman’s model (see for instance Brasseur, 1986; Montecinos, 1998; 1999) considers the time evolution equations for the concentrations given by

\[
\frac{dX}{dt} = J_1 + J_2Y - (k_1 + k_2Y)X, \quad (1)
\]
\[ \frac{dY}{dt} = k_1 X - (J_2 + k_2 X) Y, \]  
\hspace{1cm} (2) 

where, on the right hand, the positive terms are production rates, and the negative ones are loss rates. In the nonlinear system (1,2), the quantities \( J_1 \) and \( J_2 \) are related to the reactions R3 and R4 and correspond to the photodissociation of \( O_2 \) and \( O_3 \) respectively. The important fact is that they depend on the sun’s radiation, and then, they are periodic in time with a period \( T = 24 \) hours. In this paper, and by simplicity, we assume

\[ J_i(t) = J_i^0 (1 - \cos \omega t), \quad i = 1, 2 \]  
\hspace{1cm} (3)

where \( \omega = 2\pi/T \), and \( J_i^0 \) are positive constants. On the other hand, the positive constants \( k_1 \) and \( k_2 \) in (1,2), are temperature dependent. Also they are dependent on the \( O_2 \) concentration, and related to the reaction velocity in R1 and R2 respectively (DeMore, 1994).

In this paper we propose an analytical study of the nonlinear model (1-3). In a general point of view, the study of this system is a difficult task, nevertheless, some interesting results can be find in the high frequency (\( \omega \)) limit. In fact, we use a method proposed originally by Kapitsa (Landau, 1982) for a mechanical particle in a field with rapid temporal oscillations in the parameters and nonlinear terms. We find explicitly the solutions of the systems (1-3) in the high frequency regime (19,20). They are the equilibrium solution for the time-averaged concentration. Calculations tell us that no solution exist in some frequency range. The study of the behavior of this model, for different frequencies, has a physical interest because earth period of rotation changes with the geological age. It is a known fact that the rotation of earth is gradually slowing down by friction. In fact, the estimated rotation velocity diminishes by 4.4 hours every billion of years (Shu, 1982).

For explicit calculations, we assume the following values for the parameters:

\[ J_1^0 \sim 10^7 [1/s]; \quad J_2^0 \sim 10^{-3} [1/s]; \quad k_1 \sim 10 [1/s]; \quad k_2 \sim 2.5 \times 10^{-15} [1/s], \]  
\hspace{1cm} (4)
corresponding to the values for the ozone layer altitude at, more or less, 35 km.

Finally we note that the case of small frequency ($\omega \rightarrow 0$) can be solved. In fact, here the parameters $J_i(t)$ evolve slowly with time and then, they can be assumed as constant in the integration process of (1,2). So the solutions corresponding to the 'fixed point' ($\frac{dx}{dt} \sim \frac{dy}{dt} \sim 0$, for definitions see (Seydel, 1988; Wio, 1997)) are

$$Y = -\frac{J_1}{4J_2} + \sqrt{\left(\frac{J_1}{4J_2}\right)^2 + \frac{k_1J_1}{2k_2J_2}}.$$  \hspace{1cm} (5)$$

$$X = \frac{Y}{k_1 - k_2Y} J_2(t).$$ \hspace{1cm} (6)$$

Namely, in this approximation, the variable $Y$ is constant and $X$ varies linearly with the dissociation coefficient. Moreover, the solutions (5,6) are consistent with the numerical solution in the stratosphere (Fabian, 1982; Montecinos, 1996). We note that, from (5), it is easy to show that the variable $Y$ satisfies $Y \leq \frac{k_1}{k_2}$. In fact, it is a general bound for the solution of the systems (1,2) (Montecinos, 2000).

2.- The method of Kapitsa

As said before, we shall study the system (1-3) in the high frequency regime. High frequency means here small period of oscillations $T$ respect to the relaxation-time $T_R$ for the slow variables.

Assume the separation of the concentrations $X$ and $Y$ in a slow temporal variation ($x$ and $y$) and other fast ($\varepsilon$ and $\eta$, respectively). Namely,

$$X = x + \varepsilon; \quad Y = y + \eta,$$ \hspace{1cm} (7)$$

where the fast variables are periodic with temporal average zero, namely,
The equation (1) can be re-written like
\[
\frac{dx}{dt} + \frac{d\varepsilon}{dt} = J_1^0 + J_2^0 y - (k_1 + k_2 y) x - (J_1^0 + J_2^0 y) \cos \omega t + (J_1^0 - J_2^0 \cos \omega t - k_2 x) \eta - (k_1 + k_2 y) \varepsilon - k_2 \varepsilon \eta, \tag{9}
\]
and equation (2) becomes
\[
\frac{dy}{dt} + \frac{d\eta}{dt} = k_1 x - (J_2^0 + k_2 x) y + J_2^0 y \cos \omega t - (J_2^0 + k_2 x - J_2^0 \cos \omega t) \eta + (k_1 - k_2 y) \varepsilon - k_2 \varepsilon \eta. \tag{10}
\]
On the other hand, the fast variables are only related to rapid oscillation (Landau, 1982). In this way, from the above expression (9,10), they are assumed to be a solution to the differential equations:
\[
\frac{d\varepsilon}{dt} = -(J_1^0 + J_2^0 y) \cos \omega t; \quad \frac{d\eta}{dt} = J_2^0 y \cos \omega t. \tag{11}
\]
At this point a remark becomes necessary. The expression (7), complemented with the above equations (11), defines a change of variables without approximations. Nevertheless, the differential equations (11) are suggested by the direct oscillatory term in (9) and (10). Kapitsa's method consider the equations for \(\frac{d\varepsilon}{dt}\) and \(\frac{d\eta}{dt}\) as approximated.

In one period, the slow variables are essentially constants and the fast have zero average (8), then, the time average of the equation (9) becomes.
\[
\frac{dx}{dt} = J_1^0 + J_2^0 y - (k_1 + k_2 y) x - J_2^0 \langle \eta \cos \omega t \rangle_T - k_2 \langle \varepsilon \eta \rangle_T, \tag{12}
\]
and, for equation (10), we obtain
\[
\frac{dy}{dt} = k_1 x - (J_2^0 + k_2 x) y + J_2^0 \langle \eta \cos \omega t \rangle_T - k_2 \langle \varepsilon \eta \rangle_T. \tag{13}
\]
Nevertheless, since equations (11) can be solved exactly,

\[ \varepsilon(t) = -\frac{1}{\omega} (J_1^o + J_2^o y) \sin \omega t; \quad \eta(t) = \frac{J_2^o}{\omega} y \sin \omega t, \quad (14) \]

the evolution equations for the slow variables become

\[ \frac{dx}{dt} = J_1^o + J_2^o y - (k_1 + k_2 y) x + \frac{J_2^o k_2}{2\omega^2} y (J_1^o + J_2^o y), \quad (15) \]

and

\[ \frac{dy}{dt} = k_1 x - (J_2^o + k_2 x) y + \frac{J_2^o k_2}{2\omega^2} y (J_1^o + J_2^o y). \quad (16) \]

This set of equations are the basis for our analytical results. They are restricted to the high frequency approximation. This approximation becomes given by the ‘expansion’ in \(1/\omega^2\) related to the last term in (15,16). Remark that it is an autonomous nonlinear system and then, without the explicit temporal dependence. This transformation, from a set of equations with time-periodic parameters, to other autonomous, is related to the Kapitsa original ideas (Landau, 1982).

In a general frame of work, the system (15,16) is complex. Moreover, the approximation of high frequency is valid when the relaxation time \(T_R\), of the equations (15,16), is bigger than \(2\pi/\omega\). This comparison is a difficult task, nevertheless, the case \(J_2^o = 0\) can be solved exactly to estimate the validity of the approximation. It corresponds formally to eliminate the dissociation of \(O_3\). The asymptotic solution of the non-autonomous system (1-3) is (Montecinos, 2000).

\[ X = \frac{J_1^o}{2k_1} - \frac{J_1^o}{\sqrt{4k_1^2 + \omega^2}} \cos(\omega t - \phi), \quad Y = \frac{k_1}{k_2}, \quad (17) \]

where the phase \(\phi\) is given by the relation: \(\tan \phi = \omega/2k_1\). On the other hand, combining the equations (15,16) with (7), in the high frequency approximation we found that the equilibrium solution given by the Kapitsa’s method is:

\[ X = \frac{J_1^o}{2k_1} - \frac{J_1^o}{\omega} \sin \omega t; \quad Y = \frac{k_1}{k_2}, \quad (18) \]
It is direct to show that the exact solution (17) reduces to (18) in the high frequency limit. Moreover, the relaxation time $T_R$ can be calculated here analytically. It is given by $T_R = 1/2k_1$. So, we expect that the high frequency approximation (15,16) is valid when $4\pi k_1 \ll \omega$.

3.- Existence of equilibrium solutions

In this section we are concerned with the fixed point solution (Seydel, 1988; Wio, 1997) of the autonomous set (15,16). This system have an equilibrium point $(x_o, y_o)$, defined by $\frac{dx}{dt} = \frac{dy}{dt} = 0$, and given by the solution of the equations:

$$k_2 J_o^0 \left(2 - \frac{k_1 J_o}{\omega^2}\right) y_o^2 + k_2 J_1^0 \left(1 - \frac{k_1 J_o}{\omega^2}\right) y_o - k_1 J_1^0 = 0,$$

and

$$x_o = \frac{(J_1^0 + J_2^0 y_o) \left(1 + \frac{k_2 J_o}{\omega^2} y_o\right)}{(k_1 + k_2 y_o)}.$$

Equations (19) and (20) define the homogeneous equilibrium solution of the autonomous system (15) and (16) and then, with (7) and (14), we have the solution of the systems (1,2) in the high frequency regime.

The existence of real solutions, for the second degree equation (19), requires the inequality

$$\frac{1}{\omega^4} - \frac{4}{k_2 J_1^0} \left(1 + \frac{k_2 J_1^0}{2k_1 J_2^0}\right) \frac{1}{\omega^2} + \frac{8}{k_1 k_2 J_1^0 J_2^0} \left(1 + \frac{k_2 J_1^0}{8k_1 J_2^0}\right) \geq 0,$$

which corresponds to an inequality of second degree for $1/\omega^2$. Namely, there is no equilibrium solution of (15,16) if and only if,

$$\frac{2}{k_2 J_1^0} + \frac{1}{k_1 J_2^0} - \frac{2}{k_2 J_1^0} \sqrt{1 - \frac{k_2 J_1^0}{k_1 J_2^0}} \leq \frac{1}{\omega^2} \leq \frac{2}{k_2 J_1^0} + \frac{1}{k_1 J_2^0} + \frac{2}{k_2 J_1^0} \sqrt{1 - \frac{k_2 J_1^0}{k_1 J_2^0}}.$$
If we assume the condition

\[
\frac{k_2 J_1^o}{k_1 J_2^o} \ll 1,
\]

valid for the parameters (4) of section 1, the inequality (22) can be re-written for the period \( T \). In fact, there is no equilibrium solution of the system (15,16) when

\[
T_1 \leq T \leq T_2 \quad \text{(no solution)},
\]

where

\[
T_1 = 2\pi \sqrt{\frac{2}{k_1 J_2^o}}; \quad T_2 = 4\pi \sqrt{\frac{1}{k_2 J_1^o}}.
\]

4.- Earth’s slowing rotation and the existence of solution

It is interesting that the inequality (24) gives a region where no solution exist. Here we must take care because no oscillating solution like (7) exist. In fact, (24) splits the \( \omega \)-space parameter in three regions: (i) The region defined by \( T < T_1 \) where a real positive solution \((y_o > 0)\) of equation (15) exist, with a negative one \((y_o < 0)\). (ii) The region defined by (24), where no solution of (15) exist. (iii) The region defined by \( T > T_2 \) where solutions are negative \((y_o < 0)\). From (5,6), we known that in the slow frequency limit (region (iii)) a real positive solution exist. Then, Kapitsa’s method does not work well in this region, nevertheless, at least it says that an oscillating solution exist.

At this point we can formulate the following question: since the earth-rotation has diminished by friction, how has the change in rotation affected
the existence of the ozone layer ?. This question seems appropriate because the Kapitsa’s method tells us that the frequency of rotation and the ozone concentration are related. Using the parameter values (4), of section 1, we can estimate the critical period (24) : $T_1 \sim 0.02$ hours and $T_2 \sim 22$ hours. It is interesting that the actual period $T = 24$ hours, is in the region of permitted solution ($T > T_2$). Moreover this is suggestive: from the retardation of earth rotation velocity data (4.4 hours/billion of years, (Shu, 1982)), a simple calculation tells us that before $\frac{24-22}{4.4} \sim 0.46$ billons years no solution existed because we were in the region (24). This is a surprising estimation if we consider that actually the ozone layer is believed to have been in existence 0.7 billion years (Graedel, 1993).

5.- Conclusions

We have considered the Chapman’s model for ozone production (1,2). In this nonlinear model, the parameters related to photodissociation are periodic in time (3). We were interested at the analytical study of this model by using the high frequency approximation, due to Kapitsa. Namely, we have considered the autonomous system (15,16), depending on the frequency, for the averaged variable concentrations. The existence of equilibrium solutions (fixed points (19,20)) is depending on the frequency. In fact, there are two critical period $T_1$ and $T_2$ so that for $T_1 < T < T_2$ there is no equilibrium solution (24).

The values for the parameters (4), in section 1, give the condition of no-existence (24): $0.02$ hours $\leq T \leq 22$ hours, and then compatible with the actual earth’s period of rotation, and existence of the ozone layer. Moreover, considering the earth’s slowing rotation motion due to friction (4.4 hours every billion of years, (Shu, 1982)), we estimate that the ozone existence condition is verified after $\frac{24-22}{4.4} \sim 0.46$ billion years (section 4). This is a good estimation if we consider the simplicity of the autonomous model given by equations (15,16). The age of the ozone layer is 0.7 billions of years (Graedel, 1993)).
Before to ending a remark, equations (15) and (16) are very adequate to the study of diffusion process, which was neglected in the original equations (1) and (2). In fact, because they are not time depending, when we add spatial diffusion terms $D\frac{d^2}{dx^2}X$ and $D\frac{d^2}{dx^2}Y$, they become similar to reaction-diffusion-equations.

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