Iterative approach to the characteristic time
for chemical reactions of type

\[ A + B \leftrightarrow C + D \]

Homage to Alberto Santoro

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The analytic solution for the kinetic description of binary reactions can be seen as the continuum version of a basic discrete iterate mapping. This fact allows a clear definition of the reaction characteristic time which takes the backward effect into account.

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I. INTRODUCTION

In most usual laboratory and/or astrophysical conditions chemical reactions of type

\[ A + B \rightarrow C + D \]

are well described by the kinetic approach [1]. If \( n_A, n_C \) are the concentrations of species \( A \) and \( C \), and \( n = n_A + n_C \), the problem is fixed by the relative concentrations

\[ X_A = \frac{n_A}{n} \quad \text{and} \quad X_C = \frac{n_C}{n} = 1 - X_A. \] (2)

Suppose some method is given for picking particles of types \( A \) and \( C \) while sampling the system. Concentrations \( X_A(t) \) and \( X_C(t) \) are then the relative probabilities of getting particles of the corresponding species at time \( t \).

The reaction rates are typically given by the inverse times of free-flight, or velocity/(mean free path) ratios: if \( v_E \) is the average velocity of type-\( E \) particles,

\[ R(A \rightarrow C) = n_A \; v_B \; \sigma_{AB \rightarrow CD} = n \; v_B \; \sigma_{AB \rightarrow CD} \; X_A \] (3)

\[ R(C \rightarrow A) = n_C \; v_D \; \sigma_{CD \rightarrow AB} = n \; v_D \; \sigma_{CD \rightarrow AB} \; X_C, \] (4)
where $\sigma_{AB\rightarrow CD}$ and $\sigma_{CD\rightarrow AB}$ are the corresponding reaction cross-sections. The kinetic picture underlying such definitions is well known [2, 3]: in Eq.(3), for example, $v_B \sigma_{AB\rightarrow CD}$ is the effective cylindric volume presented by particle $B$ to particle $A$ per second. Particle $B$ will consequently meet $n_A v_B \sigma_{AB\rightarrow CD}$ particles $A$ per second.

The relative concentrations as functions of time are then described by the master (or gain/loss) equations

$$\frac{d}{dt} X_C = R(A \rightarrow C)X_A - R(C \rightarrow A)X_C ;$$
$$\frac{d}{dt} X_A = R(C \rightarrow A)X_C - R(A \rightarrow C)X_A .$$

Variation in the abundance of species $A$ is the abundance of species $C$ times the rate of $C$-to-$A$ transformation (which represents the gain) minus the $A$ abundance times the rate of its disappearance (the loss).

II. THE SOLUTION

Let us introduce the notations $a = n v_D \sigma_{CD\rightarrow AB}$ and $b = n v_B \sigma_{AB\rightarrow CD}$. Situations are not unusual in which both $a$ and $b$ are very nearly constant (see Section IV). In that case, it is possible to obtain general analytical solutions for the above master equations. The problem reduces to solving the differential equation

$$\frac{d}{dt} X_C(t) = -aX_C^2 + bX_A^2 = -aX_C^2 + b(1-X_C)^2 = b + (b-a)X_C^2 - 2bX_C \quad (5)$$

with constant coefficients. By their very meanings, $a > 0$ and $b > 0$. Evolution will cease when $\frac{d}{dt} X_C(t) = 0$, which suggests two candidate equilibrium values: $X_C^{(equil)} = \frac{b \pm \sqrt{ab}}{b-a} .${

Once equilibrium is attained, the backward reaction is as important as the forward reaction and Eq.(5) is, of course, better written with a two-sided arrow,

$$A + B \leftrightarrow C + D . \quad (6)$$

The $X_C^2$ term in the right-hand side of [5] is present only if $a \neq b$. In that case the solution is

$$X_C(t) = \frac{1}{b-a} \left\{ b - \sqrt{ab} \tanh \left[ \sqrt{ab} t + K \right] \right\} . \quad (7)$$
with $K$ an integration constant whose determination will later provide our main result. As $\lim_{x \to \infty} \tanh(x) = 1$, this solution tends indeed to one of the above candidate equilibria:

$$X_C(\infty) = \frac{b - \sqrt{ab}}{b - a} = \frac{\sqrt{b}}{\sqrt{b} + \sqrt{a}} = \frac{v_B \sigma_{AB \to CD} - \sqrt{v_B v_D \sigma_{CD \to AB} \sigma_{AB \to CD}}}{v_B \sigma_{AB \to CD} - v_D \sigma_{CD \to AB}}.$$  \hspace{1cm} (8)

The solution for $X_A(t) = 1 - X_C(t)$ is obtained by simply exchanging parameters $a$ and $b$. Equilibria probabilities are related by

$$\frac{X_C(\infty)}{X_A(\infty)} = \frac{\sqrt{b}}{\sqrt{a}} = \frac{\sqrt{v_B \sigma_{AB \to CD}}}{\sqrt{v_D \sigma_{CD \to AB}}}.$$ \hspace{1cm} (9)

Only to provide some intuitive guidance, plots for toy models $(a, b) = (2, 1/2)$ and $(a, b) = (2, 50)$ are shown in Figures 1 and 2.

An analogous result relates $X_B$ to $X_D$. Contact with the usual equilibrium approach \[4, 5\] can be made through a few simple considerations. In the equilibrium classical (nonrelativistic, non–quantal) case, particle $C$ (for example) will have concentration $n_C = g_C \frac{e^{\nu_C / kT}}{\lambda_C}$.
where \( g_C \) counts the values taken by “internal” degrees of freedom (spin, isospin, etc), \( \lambda_C \) is the de Broglie thermal wavelength of particle \( C \) (\( \lambda_C = \hbar \sqrt{\frac{2\pi}{m_C kT}} \)) and \( \mu_C \) is its chemical potential. The equilibrium condition is \( \mu_A + \mu_B = \mu_C + \mu_D \) or, in terms of the fugacities \( z = e^{\mu/kT} \), \( z_A z_B = z_C z_D \). Direct comparison with the above result leads to

\[
\frac{g_C g_D}{g_A g_B} \left[ \frac{m_C m_D}{m_A m_B} \right]^{3/2} = \sqrt{\frac{v_A v_B}{v_C v_D}} \frac{\sigma_{AB \rightarrow CD}}{\sigma_{CD \rightarrow AB}}.
\]

If we use the equipartition formula \( v_B = \sqrt{\frac{3kT}{m_B}} \),

\[
\frac{g_C g_D}{g_A g_B} \left[ \frac{m_C m_D}{m_A m_B} \right]^{5/4} = \frac{\sigma_{AB \rightarrow CD}}{\sigma_{CD \rightarrow AB}}.
\]

We see that the cross-sections have, in this case, just to account for kinematic factors. If we take naively \( m_A = m_C, m_B = m_D, g_A = g_C, g_B = g_D \), the expected trivial equilibrium requirement follows: \( \sigma_{AB \rightarrow CD} = \sigma_{CD \rightarrow AB} \).

Situation \( a = b \), which must be considered separately, would turn up in the peculiar case \( v_D \sigma_{CD \rightarrow AB} = v_B \sigma_{AB \rightarrow CD} \); the volume spanned by \( D \) per unit time, as seen by \( C \), equals the volume spanned by \( B \) per unit time, as seen by \( A \). The solution of Eq.(5) would, in that case, be

\[
X_C(t) = \frac{1}{2} + e^{-2bt}(X_0 - \frac{1}{2})
\]

with, naturally enough, the probabilities tending to equilibrium at \( X_C = X_A = \frac{1}{2} \). An example would be an “elastic” reaction of type

\[
A + B \rightarrow A + B,
\]

with the same cross-section \( \sigma \) in both sides. The crossed reaction \( A + B \rightarrow B + A \) would be accounted for by the general case, as \( a = n v_A \sigma \neq b = n v_B \sigma \), equilibrium being given by the condition \( \frac{X_B}{X_A} = \sqrt{\frac{v_B}{v_A}} \).

III. CHARACTERISTIC TIME

There are two main approaches to evolving systems. We have above used the first: time evolution is described by a continuous curve of type \( X_t = f^{<t>}(X_0) \), solution of some differential equation. In the second, evolution is described by the successive iterations of a mapping [6-8]. The state is known at each step, as if the “time” parameter of the system were
defined only at discrete values. We can go from the first approach to the second by taking the intersections leading to a Poincaré map. This approach supposes a characteristic time — the time of a unit step. If a continuous description can be shown to be the interpolation of a discrete mapping [9], a clear notion of characteristic time obtains. There is, however, a strong requirement: that interpolation must preserve the notion of iteration all along. This requirement is encapsulated in the so-called semigroup conditions [10]. For a function \( f(x,t) \equiv f^{<t>}(x) \) describing the dynamical flow of a system, these conditions are

\[
f^{<t>}[f^{<t'}>(x)] = f^{<t'}>[f^{<t>}(x)] = f^{<t+t'>}(x) ;
\]

\[
f^{<0>}(x) = x.
\]

A sufficient condition for that is that the solution have the form

\[
g(x,t) = F^{<-1>}[c^t F(x)],
\]

for some function \( F(x) \), its inverse \( F^{<-1>}(x) \) and a constant \( c \). This would mean that \( F(x) \) solves the Schröder functional equation

\[
F[g(x)] = c F(x).
\]

This can be translated into the additive form \( f[g(x)] = c + f(x) \) by taking \( f(x) = \ln[F(x)] \) — what matters is that the semigroup conditions be respected.

Let us now notice that the integration constant \( K \) in (7) can be obtained by simply taking the inverse function at \( t = 0 \). That solution assumes then the form

\[
X_C(t) = \frac{1}{b-a} \left\{ b - \sqrt{ab} \tanh \left[ \sqrt{ab} t + \text{arctanh} \left( \frac{b + (a-b) X_C(0)}{\sqrt{ab}} \right) \right] \right\}.
\]

This is actually the continuum form of an iterate discrete mapping, and fulfills the semigroup requirement. In more detail: introduce the notations \( f \circ g \) for the composition of functions \( f \) and \( g \), \( f^{<m>} \) for the \( m \)-th iterate of \( f \) and \( f^{<-1>} \) for the function inverse to \( f \). Then, with the functions

\[
w^{<-1>}(z) = \frac{1}{a-b} \left( -b + \sqrt{ab} \tanh z \right), \quad v = w^{<-1>} \circ f \circ w, \quad f(u) = \sqrt{ab} + u,
\]

expression (18) is in effect the continuum version of

\[
X_p(m) = v^{<m>} (X_p(0)) = w^{<-1>} \circ f^{<m>} \circ w (X_p(0)).
\]
The quantity

\[ \tau = (ab)^{-1/2} = \frac{1}{n \sqrt{v_B v_D} \sigma_{CD \rightarrow AB} \sigma_{AB \rightarrow CD}} \]  

(21)

is the one-step time in the iteration and indicates the time interval in which the reaction process does make significant progress.

Solution (12) for the special \( a = b \) case has already been written in iterative form, with \( w^{<1>}(z) = \frac{1}{2} + z \) and characteristic time \( \tau = (2b)^{-1} = (2n v_B \sigma_{AB \rightarrow CD})^{-1} = (2n v_D \sigma_{CD \rightarrow AB})^{-1} \), half the time of free flight.

IV. FINAL COMMENTS

The assumption used above — that \( a \) and \( b \) are constant — actually mean that time \( (ab)^{-1/2} \) is short in comparison with any other “macroscopic” time-scale involved. Such a “macroscopic” time can, for instance, be the time in which temperature and/or volume of the system change appreciably under the influence of some external agent. For reactions of cosmological interest, as those involved in primordial nucleosynthesis, it is the inverse rate of expansion, or inverse Hubble function. The quantities (velocities and cross sections) appearing in Eq. (8) will depend on such large-scale time. The first criterion for the validity of the above results is, consequently, that \( (ab)^{-1/2} \) be very short in comparison to those times. In order to use the equilibrium formulae, it would be necessary that equilibrium be attained in not too many steps.

It is usual to take the average time of free flight \( \tau = (n \sigma v)^{-1} \) as an order-of-magnitude indication of the lapse necessary for thermalization to be established. It gives a rough measure of the time between two “hits” in the reaction. This parameter, however, turns up under conditions quite different from those supposed above [2]. It is conceived for an arrangement by which particles of type \( A \) impinge with constant velocity \( v_A \) upon a medium formed by particles of type \( B \) with constant number density \( n_B \). With (constant) cross section \( \sigma_{AB} \), the mean free path of an \( A \) particle in the medium will be \( \lambda_A = \frac{1}{n_B \sigma_{AB}} \), and the corresponding time of free flight, \( \tau_A = \frac{\lambda_A}{v_A} = \frac{1}{n_B v_A \sigma_{AB}} \). The number of unscattered (that is, keeping the same momentum direction) particles \( A \) will then be given by

\[ \frac{dn_A}{dt} = -\frac{n_A}{\tau_A} \]
This is a pure-loss equation, quite the same as that for radiative decay. Eventual reproduction of particles $A$ with the original momentum by other scatterings is neglected, so that there is no gain. The solution is, of course, the radiative decay formula

$$n_A(t) = n_A(0) e^{-\frac{t}{\tau_A}} .$$

This corresponds, up to normalizations, to the special solution (12). Expression (21),

$$\tau = \frac{1}{(n_A + n_C) \sqrt{v_B v_D \sigma_{AB \rightarrow CD} \sigma_{CD \rightarrow AB}}} = \frac{\sqrt{n_A n_C}}{n \sqrt{R(A \rightarrow C) R(C \rightarrow A)}} ,$$

coming from gain-loss considerations, takes also the backward reaction into account and provides, in principle at least, a far better measure of the reaction characteristic time.

[1] A deep discussion of the conditions which are supposed to be satisfied can be found in R. Balescu, Statistical Dynamics, Imperial College Press, London, 1997. The chemists’ approach is described in J.E. Leffler and E. Grunwald, Rates and Equilibria of Organic Reactions, Dover, New York, 1989, where a very clear exposition is made of the “cage effect” and the consequent diffusive regime, which will not be of our concern here.

[2] See for example M. Born, Atomic Physics, 7th. ed. (Blackie & Son, London, 1962).

[3] Ya. B. Zeldovich and I. D. Novikov, Relativistic Astrophysics I: Stars and Relativity (University of Chicago Press, Chicago, 1971).

[4] L. D. Landau and E. M. Lifschitz, Statistical Mechanics (Pergamon Press, Oxford, 1974).

[5] D. A. McQuarrie, Statistical Mechanics (Harper & Row, New York, 1976).

[6] S. N. Rasband, Chaotic Dynamics of Nonlinear Systems, J. Wiley, New York, 1989.

[7] J. L. McCauley, Chaos, Dynamics and Fractals, Cambridge University Press, Cambridge, 1993.

[8] E. Ott, Chaos in Dynamical Systems, Cambridge University Press, Cambridge, 1994.

[9] R. Aldrovandi, Special Matrices of Mathematical Physics, World Scientific, Singapore, 2001.

See Chap.2 for the two dynamical pictures and, for the relationship between iterates and Schröder’s equation, §15.2.

[10] R. Aldrovandi and L.P. Freitas, J. Math. Phys. 39 (1998) 5324.