Generalized Fractal Kinetics in Complex Systems (Application to Biophysics and Biotechnology)

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Abstract

We derive a universal function for the kinetics of complex systems characterized by stretched exponential and/or power-law behaviors. This kinetic function unifies and generalizes previous theoretical attempts to describe what has been called "fractal kinetic".

The concentration evolutionary equation is formally similar to the relaxation function obtained in the stochastic theory of relaxation, with two exponents $\alpha$ and $\eta$. The first one is due to memory effects and short-range correlations and the second one finds its origin in the long-range correlations and geometrical frustrations which give rise to ageing behavior. These effects can be formally handled by introducing adequate probability distributions for the rate coefficient. We show that the distribution of rate coefficients is the consequence of local variations of the free energy (energy landscape) appearing in the exponent of the Arrhenius formula.

The fractal ($n, \alpha$) kinetic is the applied to a few problems of fundamental and practical importance in particular the sorption of dissolved contaminants in liquid phase. Contrary to the usual practice in that field, we found that the exponent $\alpha$, which is implicitly equal to 1 in the traditional analysis of kinetic data in terms of first or second order reactions, is a relevant and useful parameter to characterize the kinetics of complex systems. It is formally related to the system energy landscape which depends on physical, chemical and biological internal and external factors.

We discuss briefly the relation of the ($n, \alpha$) kinetic formalism with the Tsallis theory of nonextensive systems.

Key words: Fractal kinetics, complex systems, nonextensive systems, energy landscape, Levy distributions, sorption in aqueous solutions.
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Introduction

The physical origin of anomalous kinetics in complex systems like glass, polymers, solutions, proteins, enzymes... has received much attention in recent years ([1][2][3][4][5]).

This is due to the observation that in many instances, the kinetics cannot be accounted for without introducing a time-dependent reaction rate coefficient to describe properly the experimental data. As in many other related problems an accurate relation between microscopic properties and the global macroscopic observables is lacking due to many-body interactions, the inevitable homogenization and coarse-graining resulting from complexity and experimental techniques. What has been done in practice to deal with this situation is to generalize formula used in simple reaction kinetics (first and second order reaction) and introduce one or several supplementary empirical parameters to fit experimental data. The aim of these works is to establish correlations between macroscopic observables and external parameters (temperature, concentration, pH, ...). Another method widely used is to consider a few reaction steps. The total rate equation is written as the sum of elementary rate equations (first or second order). Their respective weight and the rate coefficients are fitted to the data. This procedure can lead to ambiguous results and conclusions. In particular it does not reproduce power-law behaviors often encountered in these systems. In this spirit, Frauenfelder and collaborators [3] have used intuitive arguments to fit experimental biomolecular reaction data in protein materials with empirical stretched exponential or power-law functions. They trace the 'anomalous” kinetics to the distribution of the reaction rate in the Arrehnius formula. In 1988, to account for power law behavior, Kopelman [1] proposed a phenomenological fractal like kinetics to account for reactions in materials prepared as fractals. This lead more recently Savageau [2] to introduce a model where instead of introducing a time-dependence to the rate coefficient, the reactant concentrations are raised to non-integer powers.

More recently, Weron [4] and collaborators using results from their stochastic theory of relaxation in dipolar systems [6], introduced a time dependent power-law reaction rate coefficient to generalize first and second order kinetic equations in order to apply them to biomolecular reactions. Simultaneously, Mendes and collaborators [7], using results of the Tsallis nonextensive entropy theory [8] to solve non-linear differential equations, introduced the concept of a $n$-order kinetic equation whose solution has a formal expression similar to the Tsallis generalized Pareto distribution.

The purpose of the present paper is to use some results of two recent papers on non-Debye relaxation [9][10] to incorporate the ideas developed in the previous quoted works [1][3][4][7], in one unified formalism in order to the set the basis of a general theory of reaction kinetics in complex systems.
The challenge which has to be faced, in this important problem, is to give a physical or statistical meaning to the empirical parameters and, when this is possible, to relate the ”anomalous” kinetics to universality, i.e. universal scaling functions independent on the microscopic or mesoscopic detailed properties of the system.

1 The \((n, \alpha)\) kinetic equation

The most general chemical kinetic equation for one given species \((A)\) in a complex system composed of \(A, B, C, \ldots\) reacting atoms and molecules can be written formally as

\[
\frac{dc_A}{dt} = Kc_A^{\alpha}c_B^{\beta}c_C^{\gamma} \ldots
\]

(1)

where \(K\) is the rate coefficient and \(\alpha, \beta, \gamma\ldots\) refer to the concentrations of chemical species \(A, B, C, \ldots\) present in the reaction and the sum \(\alpha + \beta + \gamma\) is the overall order of the reaction. In some cases, the concentration \(c_B, c_C, \ldots\) can be considered as constant, thus the above equation reduces (for instance for the reactant \(A\)) to the form

\[
-\frac{dc_n(t)}{dt} = K_n c_n(t)^n
\]

(2)

In that way, the parameter \(n\) becomes the overall order of the reaction. The solution of this differential equation for one of the reactants is given by \([7]\)

\[
c_n(t) = c_n(0)[(1 + (n - 1)c_n(0)^{n-1}K_n t)]^{-\frac{1}{n-1}}
\]

(3)

which has the form of a generalized Pareto function, solution of the Tsallis entropy maximization \([8]\) and has an asymptotic power law behavior \(c_n(t) \propto t^{-1/(n-1)}\).

If we use the deformed \(n\)-exponential and \(n\)-logarithm introduced by Tsallis and collaborators in the context of nonextensive systems \([8]\):

\[
\exp_n(x) = (1 - (n - 1)x)^{-\frac{1}{n-1}} \text{ if } 1 - (n - 1)x > 0, \ 0 \text{ otherwise}
\]

and

\[
\ln_n(x) = \frac{x^{1-n} - 1}{1-n}
\]

(4)

with

\[
\exp_n(\ln_n(x)) = \ln_n(\exp_n(x)) = 1
\]

we can write the solution (3) in a more compact form:

\[
c_n(t) = c_n(0) \exp_n(-t/\tau_n)
\]

(5)
with a characteristic time:
\[ \tau_n = (c_n(0)^{n-1} K_n)^{-1} \]  \hspace{1cm} (6)

This will allow the definition of an effective time-dependent rate coefficient:
\[ -\frac{dc_n(t)}{dt} = c(0) \frac{1}{\tau_n} (\exp_n(-t/\tau_n))^n \]  \hspace{1cm} (7)
\[ = c(0) \frac{1}{\tau_n} (1 + (n - 1)(t/\tau_n))^{-\frac{1}{n-1}} \]
\[ = \mathcal{K}_n(t) c_n(t) \]

with
\[ \mathcal{K}_n(t) = \frac{1}{\tau_n} (1 + (n - 1)(t/\tau_n))^{-1} \]  \hspace{1cm} (8)

For \( t << \tau_n \), one has a slowing down of the effective rate:
\[ \mathcal{K}_n(t) = \frac{1}{\tau_n} (1 - (n - 1)(t/\tau_n)) \]  \hspace{1cm} (9)

and for \( n \neq 1 \), \( t >> \tau_n \)
\[ \mathcal{K}_n(t) \propto (1/(n - 1)) t^{-1} \]  \hspace{1cm} (10)

This behavior is a manifestation of what has been call aging [11] which appears as soon as \( n \neq 1 \). For \( n = 1 \), one recovers the exponential behavior with \( \mathcal{K}(t) = 1/\tau \).

These results do not exhibit the \( t < \tau \) power law time dependence of the reaction rate which describes adequately the experimental data of many complex systems [4][12][13][14][15]. This behavior can appear quite naturally if we introduce in (6), instead of the \( n \)-exponential, a \( n \)-Weibull function introduced by Mendes [16] and used also in the theory of relaxation [9][10]
\[ c_{n,\alpha}(t) = c(0) \exp_n((-t/\tau_{n,\alpha})^\alpha) = c(0)[(1 + (n - 1) (t/\tau_{n,\alpha})^\alpha)^{-\frac{1}{\alpha-1}}] \]  \hspace{1cm} (11)

with a characteristic time:
\[ \tau_{n,\alpha} = [K_{n,\alpha} c(0)^{n-1}]^{-1/\alpha} \]  \hspace{1cm} (12)

The effective time-dependent rate coefficient \( \mathcal{K}_{n,\alpha}(t) \) now reads
\[ \mathcal{K}_{n,\alpha}(t) = \alpha \frac{t^{\alpha-1}}{\tau_{n,\alpha}^\alpha} (1 + (n - 1)(t/\tau_{n,\alpha})^\alpha)^{-1} \]  \hspace{1cm} (13)

Equation (11) is solution of a fractional differential equation:
\[ -\frac{dc_{n,\alpha}(t)}{dt^{\alpha}} = K_{n,\alpha} c_{n,\alpha}(t)^n \]  \hspace{1cm} (14)
by introducing a fractional time index $\alpha$ and a non-integer reaction order $n$. Fractional derivation and fractal time concepts have been introduced in physics (diffusion in disordered and porous media, random walks ...[17]) in the theory of dielectric response [20][18][10] and in economy [19].

The effective rate coefficient $K_{n,\alpha}(t)$ has the two asymptotic behaviors

$$
\begin{align*}
\text{for } t \to 0 & \quad K_{n,\alpha}(t) \propto t^{\alpha-1} \\
\text{for } t \to \infty & \quad K_{n,\alpha}(t) \propto t^{-1}
\end{align*}
$$

For $t \to 0$, we get the same power-law variation of the rate coefficient as in the work of Weron et al. [4] as well as in the fractal phenomenological description of non-homogeneous reaction dynamics called fractal-like kinetics [1], if we identify the Kopelman fractal parameter $h < 1$ with $1 - \alpha$. As noted in [5], the concept of effective time-dependent rate constant breaks down for $t \to 0$, $\alpha < 1$, since in that limit $K_{n,\alpha}(t)$ diverges. The general solution (11) of the fractional differential equation (14) does not suffer from such difficulty and is well defined in the positive time domain. In any case, as for real geometric fractals, for physical reasons, there is in each case a natural small time cut-off.

The two asymptotic behaviors of the concentration evolutionary law equation (11) are:

$$
c_{n,\alpha}(t) = c(0)[(1 - (t/\tau_{n,\alpha})^\alpha + ...]
$$

independent of $n$ for $t << \tau_{n,\alpha}$, while for $n \neq 1$ and $t >> \tau_{n,\alpha}$

$$
c_{n,\alpha}(t) = c(0)(n-1) (t/\tau_{n,\alpha})^{-\alpha/(n-1)}
$$

The ratio of the the two asymptotic exponents $\alpha$ and $\alpha/(n-1)$ yields the value of the apparent order of the reaction $n$.

For special values of the two parameters $n$ and $\alpha$, some other typical solutions are recovered

a. If $n = 1, \alpha = 1$, we have

$$
-\frac{dc(t)}{dt} = K_1 c(t) \quad \rightarrow \quad c(t) = c(0) \exp(-K_1 t)
$$

which is a first order kinetic

b. If $n = 1, \alpha \neq 1$, we have

$$
-\frac{dc_\alpha(t)}{dt^\alpha} = K_\alpha c_\alpha(t) \quad \rightarrow \quad c_\alpha(t) = c(0) \exp(-K_\alpha t^\alpha)
$$

which is a "Weibull kinetics". If $0 < \alpha < 1$, it is a "stretched exponential kinetic".
c. If \( n \neq 1 \), \( \alpha = 1 \), equations (11) gives
\[
c_q(t) = c_n(0)[(1 + (n - 1)c_n(0)^{n-1}K_n t)^{-\frac{1}{n-1}} - c(0)^{n-1}K_n t] = \exp_n(-c(0)^{n-1}K_n t) \tag{20}
\]
which is solution of (2).

d. If \( n = 2 \), \( \alpha = 1 \), we have
\[
-\frac{dc(t)}{dt} = K_2c^2(t) \rightarrow 1/c(t) - 1/c(0) = K_2t \tag{21}
\]
This is the second order kinetic.

e. If \( n = 2 \), \( \alpha \neq 1 \), we have
\[
-\frac{dc_\alpha(t)}{dt^{\alpha}} = K_{2,\alpha}c_\alpha(t)^2 \rightarrow c_\alpha(t) = c(0)[(1 + c(0)(K_{2,\alpha} t)^\alpha)^{-1}] \tag{22}
\]
This is a generalized second order kinetic.

Cases (b) and (e) have been discussed in [4].

It is important to note that as soon as \( n \neq 1 \), the time dependence of the kinetics depends on the initial concentration.

We will call the kinetic giving rise to the concentration evolutionary law (11), the \((n, \alpha)\) kinetic:
\[
c_{n,\alpha}(t) = c(0)[(1 + (n - 1) (t/\tau_{n,\alpha})^\alpha)^{-\frac{1}{n-1}}] \tag{23}
\]
\[
\tau_{n,\alpha} = [c(0)^{n-1}K_{n,\alpha}]^{-1/\alpha} \tag{24}
\]
is the characteristic time of the complex kinetic. It depends on the initial concentration and the two exponents \( n \) and \( \alpha \). For \( n \to 1 \), \( c_{n,\alpha}(t) \) tends to a Weibull exponential with \( \tau_{1,\alpha} = [K_{1,\alpha}]^{-1/\alpha} \). One can define a "half-reaction time" \( \tau_{1/2} \) which is the time necessary to transform half of the relevant quantity by solving the equation
\[
(1 + (n - 1)(\tau_{1/2}/\tau_{n,\alpha})^\alpha)^{-1/(n-1)} = 1/2 \tag{25}
\]
which gives using the definition of \( \ln_n(x) \) (4):
\[
\tau_{1/2} = \tau_{n,\alpha}(\ln_n 2)^{1/\alpha} \tag{26}
\]
Kinetics are "memoryless" only when \( n = \alpha = 1 \). If \( n = 1 \), kinetics are "memoryless" in the fractal time \( t_f = t^\alpha \) since with the change of variable, the Weibull function reduces to a memoryless exponential.
One can introduce in this problem a "response function" as it is done in Weron et al. [4] for $n = 1$ and $n = 2$. We have more generally for any real $n$:

$$f(t) = -\frac{1}{c(0)} \frac{dc_{n,\alpha}(t)}{dt} = \alpha \frac{t^{\alpha-1}}{\tau_{n,\alpha}} (1 + (n - 1)\left(\frac{t}{\tau_{n,\alpha}}\right)^{\alpha} - \frac{1}{\alpha - 1})^{-1}$$

(27)

this function has the two asymptotic behaviors:

\[
\begin{align*}
\text{for } t \to 0 & \quad f(t) \propto (t/\tau_{n,\alpha})^{\alpha-1} \\
\text{for } t \to \infty & \quad f(t) \propto (t/\tau_{n,\alpha})^{-(\alpha/n - 1)} \quad n \neq 1
\end{align*}
\]

(28)

For $n = 1$ and $n = 2$, they coincide with those of [4].

2 Arrhenius law and exponential conspiracy

The results of the previous section can be understood physically as a consequence of what is has been called "exponential conspiracy", an expression coined by Boucheau [21] and proposed as exercise in textbooks on probability theory (for example [22]). It is generally accepted that the temperature dependence of the reaction rate $K$ has an Arrhenius form which we will write:

$$K = K_0 \exp(\pm E/kT)$$

(29)

$K_0$ is the pre-exponential factor and $E$ the relevant energy (in thermodynamics systems this energy is the Gibbs free energy which depends on the enthalpy (heat of reaction) and the entropy: $G = H - TS$). The sign + corresponds to an "exothermic" reaction (i.e. the energy corresponds to an attraction energy and the rate decreases with the temperature). This is the case for instance in physisorption, when the overall adsorption enthalpy resulting from adsorption and desorption is positive. The sign - corresponds to an "endothermic" reaction and $E$ is an activation energy barrier to be overcome. In that case the rate increases with temperature. We have written the two terms "exothermic" and "endothermic", because due to the variation of entropy with $T$, paradoxically in some complex systems, an endothermic reaction can occur without activation energy (see for instance [23]).

In disordered systems frozen out of equilibrium, the exponent factor $E/kT$ varies due to fluctuations of local energies and local temperatures. The distribution of energies depends on what has been called by Frauenfelder [3] the "energy landscape", a concept taken from the theory of glasses, and variations of the inverse of local temperature $(1/T)$ have been used to introduce, what has been called "super-statistics" by Beck and Cohen [24].

Here we will assume, as in the theory of heterogeneous catalysis, in the theory
of glass and in the theory of adsorption [25], that the probability distribution of the energy \( E \) varies for large values as \( \exp(-E/E_0) \). This means that the large energy values are statistically exponentially small. The reference energy \( E_0 \) is linked to the width of the energy density distribution \( f_E(E) \) [25]. With this assumption, using the basic probability theory relation

\[
f_E(E) dE = f_K(K) dK
\]  

(30)

it is straightforward to show, that the distribution of the rate coefficient \( K \), has the asymptotic form

\[
f_K(K) = \mu (K/K_0)^{-1+\mu} \quad \text{with} \quad \mu = kT/E_0
\]  

(31)

Therefore, in the ”exothermic” case (sign + in (18)),

\[K \to \infty \quad f_K(K) \sim K^{-1-\mu}\]  

(32)

while in the ”endothermic” case (sign - in (18))

\[K \to 0 \quad f_K(K) \sim K^{-1+\mu}\]  

(33)

In the first case, the distribution \( f_K(K) \) is a Pareto distribution and is the simplest density distribution belonging to the domain of attraction of the stable Lévy distributions [26][27]. If we assume that the variations of \( K \) induced by the fluctuations of \( E \) are represented by a Lévy distribution \( L_\mu(\lambda) \), one can, using the well-known relation (the Laplace transform of a one-sided Levy distribution is a stretched exponential):

\[
\int_0^\infty \exp(-\lambda Kt) L_\mu(\lambda) d\lambda = \exp (- (Kt)\mu )
\]  

(34)

obtain the generalized first order (Weibull) kinetic (case 2 with \( \mu = \alpha \)) as a compounded exponential first order kinetic . In the second case, if we use the Gamma density distribution which has the power law asymptotic behavior \( (\mu \lambda^{\mu-1}) \) for small values of \( \lambda \),

\[
g_\mu(\lambda) = \frac{\mu}{\Gamma(\mu)} (\mu \lambda)^{\mu-1} \exp(-\mu \lambda)
\]  

(35)

we obtain equation (3) with \( \mu = 1/(n-1) \)

\[
\int_0^\infty \exp(-\lambda (Kt)) g_\mu(\lambda) d\lambda = (1 + \frac{1}{\mu} (Kt)^{-\mu}
\]  

(36)

If we use the Weibull distribution, we can then write [28]

\[
\int_0^\infty \exp(-\lambda (Kt)\alpha) g_\mu(\lambda) d\lambda = (1 + \frac{1}{\mu} (Kt)^\alpha)^{-\mu}
\]  

(37)
or using a result established by Weron and collaborators in the stochastic theory of relaxation [6]:

\[
\int_0^\infty \exp(-\lambda Kt) ML_{\alpha,\mu}(\lambda) d\lambda = (1 + (1/\mu)(Kt)^\alpha)^{-\mu}
\]

where \(ML_{\alpha,\mu}(\lambda)\) is a generalized Mittag-Lefller distribution:

\[
ML_{\alpha,\mu}(\lambda) = \sum_{k=0}^{\infty} \frac{(-1)^k \Gamma(\mu + k)}{k! \Gamma(\mu) \Gamma[\alpha(\mu + k)]} (\lambda)^{\alpha(\mu + k) - 1}
\]

This last result is more difficult to interpret. It can be understood [6][9], as the result of the random character of the number of active centers, geometric frustrations and dynamic constraints or as a consequence of the interplay of "exothermic" and "endothermic" processes in the kinetics of complex materials. In conclusion, the \((n, \alpha)\) kinetic equation, can be obtained formally by introducing an adequate distribution for the exponent of the Arrhenius law as conjectured by Fraunfelder [3].

3 Probabilistic interpretation of the \((n, \alpha)\) kinetic equation

A comparison with the stochastic theory of relaxation [6][4][9][10] is of interest to understand the physical meaning of equation (23). We first note that

\[
c_{n,\alpha}(t) = c(0)[(1 + (n - 1) (t/\tau_{n,\alpha})^\alpha)^{-1 - \mu}
\]

is related to the Burr XII distribution function \((B_{a,b,c}(x) = 1 - (1 + ax^b)^{-c}, x > 0)\) [28], named by reference to the number it occupies in the main Table of Burr’s original paper [29]). If we introduce an effective random reaction waiting time \(\tilde{\theta}\), the quantity \(c_{n,\alpha}(t)/c(0)\) can be viewed as the probability that the reactant has not yet reacted at time \(t\):

\[
c_{n,\alpha}(t)/c(0) = \Pr(\tilde{\theta} > t) = 1 - \int_0^t f_{n,\alpha}(\tilde{\theta}) d\tilde{\theta}
\]

where

\[
f_{n,\alpha}(\tilde{\theta}) = \frac{\tilde{\theta}^{\alpha-1}}{\tau_{n,\alpha}} (1 + (n - 1)(\tilde{\theta}/\tau_{n,\alpha})^\alpha)^{-1 - \mu - \frac{1}{n-1} - 1}
\]

This distribution belongs to the domain of attraction of the Levy distribution with a tail exponent \(\mu = \alpha/(n - 1)\) and therefore generalizes the Pareto or Zipf-Mandelbrot distributions used in fractal reactions kinetics of previous works [5]. If \(\mu < 1\), an expectation value of \(\tilde{\theta}\) cannot be defined and an escort probability function [30] has to be used to determine \(\tau_{n,\alpha}\) from the knowledge of \(f_{n,\alpha}(\tilde{\theta})\).
If $\alpha = 1$, the probability density function (41) reduces to the Tsallis generalized Pareto distribution [8] if $(n - 1) = (q - 1)/(2 - q)$ i.e. $n = 1/(2 - q)$

$$f_{q}(\tilde{\theta}) = \frac{1}{\tau_{n,\alpha}}(1 + (q - 1)/(2 - q)\frac{\tilde{\theta}}{\tau_{n,\alpha}})^{-\frac{1}{q-1}}$$

which maximizes the Tsallis entropy of the random variable $\tilde{\theta}$.

The relation between the $(n, \alpha)$ kinetics and the nonextensivity of the entropy and the formal relation of the reaction order $n$ with the Tsallis entropy index $q$ is worth further investigations. The characteristics of the complex systems studied in the present work (see the introduction) are similar to the ones (frozen non-equilibrium states with memory effects and long range correlations) of what has been called nonextensive systems by the Tsallis school [8].

4 Application to biotechnology and biophysics

In this last section, we give some examples of problems in the field of biotechnology and biophysics, where we think the application of the $(n, \alpha)$ kinetics can open new paths to understand anomalous kinetics from the point of view of the theory of complex systems.

4.1 Sorption of dissolved contaminants in liquid phase

The sorption (adsorption, chemisorption, biosorption) of pollutants from aqueous solutions plays a significant role in water pollution control. It is therefore important to be able to predict the rate at which contamination is removed from aqueous solutions and how this rate depend on physical, chemical, biological and environment variables in order to design an appropriate treatment plant. Sorption of dissolved contaminant is a complex phenomena caused by several mechanisms including London-van der Waals forces, Coulomb forces, hydrogen bonding, ligand exchange fluctuations, chemisorption, dipole-dipole forces and hydrophobic forces and biosorption for biological materials. Therefore these systems can be considered to belong to the class of complex systems [31]. The quantity adsorbed at time $t$, $q_t$ is defined as

$$q_t = \frac{(c_0 - c_t)V}{W}$$

(42)

where $c_0$ is the initial concentration of the solution, $c_t$, the concentration at time $t$, $V$, the volume of the solution and $W$, the weight of the adsorbent.
In this context, the kinetic equations are determined with reference to the quantity of dissolved contaminant necessary to reach equilibrium (for ex. [23]). We have then

\[ q_t = q_e (1 - \exp(-K_1 t)) \quad (43) \]

where \( q_e \) is the mass of solute adsorbed at equilibrium, \( q_t \) is the mass of solute adsorbed at time \( t \) and \( K_1 \) is the rate coefficient. Equation (43) is called pseudo first-order equation by contrast to the simple exponential first-order equation (18).

In the same way, one can define a pseudo second-order reaction:

\[ \frac{1}{q_e - q_t} = K_2 t + \frac{1}{q_e} \quad (44) \]

In agreement with the ideas developed in sections 1 and 2, we can introduce the pseudo-\((n, \alpha)\) equation

\[ q_t(\alpha, n) = q_e [1 - (1 + q_e^{n-1}(n - 1)K_{n,\alpha} t^\alpha)^{-\frac{1}{n-1}}] \quad (45) \]

which reduces to (43) for \( n = 1, \alpha = 1 \) and to (44) for \( n = 2, \alpha = 1 \). We can write (45) more compactly using the definition (4) of the deformed exponential \( \exp_n(x) \),

\[ r_{n,\alpha}(t) = q_t(\alpha, n)/q_e = 1 - \exp_n((t/\tau_{n,\alpha})^\alpha) \quad \text{with} \quad \tau_{n,\alpha} = (q_e^{n-1}K_{n,\alpha})^{-1/\alpha} \quad (46) \]

The definition of the deformed logarithm (4) associated with \( \exp_n(x) \) allows us to write the following relation

\[ R(t) = \log\left(\frac{(1 - r_{n,\alpha}(t))^{1-n} - 1}{n - 1}\right) = \alpha \log(t) - \alpha \log(\tau_{n,\alpha}) \quad (47) \]

which can be used to make a linear fit of the data \( r_{n,\alpha}(t) = q_t(\alpha, n)/q_e \) and obtain the values of \( \alpha \) and \( \tau_{n,\alpha} \). The value of \( n \) to be chosen is the one which can give the better fit in the Log-Log plot.

In two different collaborations we have analyzed the kinetics of various pollutants (phenol, tannic acid, gallic acid, melanoidine on activated carbon [32] and various dyes pollutants from the textile industry on biological materials (algaes and agaves) [33]. It appears that, quite generally the data can be fitted quite well to pseudo-\((n, \alpha)\) kinetic. For \( t << \tau \), the concentration \( q_e(n, \alpha) \) does not depend on \( n \) (cf eq.16) and can be fitted to a \( n \)-independent power law \( q_e(n, \alpha) \propto t^\alpha \). The value of \( n \) (i.e. the overall order of the reaction) has to be determined from the large time (near saturation) behavior of the kinetics. Contrary to the usual practice in that field, we found that the exponent \( \alpha \), which is implicitly equal to 1 in the traditional analysis of kinetic data [23] in terms of a pseudo-first or -second order reaction, is more appropriate to characterize the kinetics of sorption of dissolved contaminants in liquid phase.
It yields a better fit and moreover it is related to the system energy landscape which varies with external parameters. In Fig.1, we show an example (adsorption kinetic on activated carbon of mélanoidine, a dye formed in the crystallization process of sacharose [32]) where the best fit is obtained with a pseudo-(1.5,α) kinetic equation. One cannot fit properly the data with a quasi-first or second-order kinetic where α = 1. This is understandable since one observes that for small t, \( q_e(n, \alpha) \propto t^{0.56} \). The dependence of the two quantities α and n on the physical, chemical environmental and biological parameters of the couple adsorbent-pollutant (pH, T, clustering, ligand field and architecture of large biomolecules...) is the subject of current studies [32][33].

4.2 Kinetics in photosynthesis processes

In this subsection, we want to show how the fractal \((n, \alpha)\) rate equation (41) can be used in situation where a two-steps first order equation has been used to fit the kinetics of photosynthesis processes. The example chosen is the kinetics of the conversion of protochlorophyllide into chlorophyllide. The method used to follows the kinetics in that problem is the observation of spectral changes recorded by the technique of spectrofluorometry under short-time illumination. For instance in [34] the authors have observed the transformation of a 647 nm pigment (species a) by 630 nm photons. Contrary to the transformation induced by 647 nm photons, where the kinetics is first order, the transformation under 630 nm irradiation follows an unusual kinetic. It has been assumed that this particular kinetics is due to the presence of an other protochlorophyllide species (named b), i.e. a pigment with another association with the lipoproteins. We refer to the specialized literature for details [34][35][34]. The two-steps model, often used when the rate equation cannot be fitted to a first or second-order kinetics, lead Boardman, in this particular problem [35], to the following rate equation (percentage of phototransformed quantity),

\[
T(\%) = 100 - A \exp(-K_1 t) - (100 - A) \exp(-K_2 t) \quad (48)
\]

A is the proportion in % of the complex which is transformed. This formula can be fitted to the experimental data up to 85% [34]. What differs in 647 pigment and 630 nm pigment is the link with the lipoproteins. The pigment-protein links are most probably fluctuating locally due to the complexity of the organization of the molecules inside the prolamellar body. If instead of two, a distribution of ”species” is present, it is more appropriate to use, a rate equation deriving from a distribution of exponentials as the \((n, \alpha)\) rate equation. We have verified that in this particular case, (42) can fit perfectly the experimental curve, also for transformation larger than 85% (Fig.1). The two asymptotic behaviors appears to be power-law, a behavior a simple two-step mechanism cannot account for. The best fit obtained with a nonlinear
The method is given by

\[ T(\%) = 100 \left(1 - (1 + (1.9 - 1) \left(t/0.07\right)^{0.96}\right)^{-1/(1.9 - 1)}) \]  

This corresponds to a fractal-time exponent \( \alpha = 0.96 \) and a reaction order parameter \( n = 1.9 \). The characteristic time is \( \tau_a = 0.07 \) and from the inspection of the experimental curve (Fig.1), one can see that it is very close to \( \tau_{1/2} \). The linear fit \( (r(t) = T/100) \) gives the same result (Fig.2):

\[ R(t) = \text{Log}\left(\frac{1 - r(t)}{1.9 - 1}\right)^{1.9 - 1} = 0.96\text{Log}(t) - 0.96\text{Log}(0.07) \]

with a regression coefficient of 0.9997.

The temperature dependence of the transformation rate under 633 nm photons [36] indicates that both endo- and exothermic effects are competing. As we have suggested at the end of section 2, in this particular situation, fluctuations of the rate coefficient in the exponent of the Arrhenius law (29) can give rise to \((n, \alpha)\) kinetics.

### 4.3 Complexity of DNA

One method widely used to study the complexity of DNA is the so-called Cot method. The method splits the double strands of DNA into single strands by raising the temperature or by other denaturing process. One then studies the kinetics of the reassociation of dissociated single strands. Since it involves two single strands, the renaturing into the original form is assumed to follow a (2,1) kinetics \( f = c(t)/c(0) = [(1 + c(0))(Kt)]^{-1} \). This equation is the basis of the Cot analysis of the rate of renaturation of sequence heterogeneity (or complexity) of DNA. The quantity \( c(0) \) is the initial concentration of DNA, \( f = c(t)/c(0) \) the fraction of single-stranded molecules which decreases with time and \( K \) the rate constant for the reassociation of complementary strands. The value of \( c(0)t \) when \( f = 0.5 \) is known as \( c(0)t_{1/2} \).

The rate coefficient \( K \) is characteristic of a particular DNA and is related to its complexity in terms of sequence composition. The quantity \( c(0)t_{1/2} \) is the reciprocal of \( K \) and can therefore be used as a measure of sequence complexity. The higher the value of \( c(0)t_{1/2} \), the more complex is the DNA.

The Cot method which was developed in the 1960’s and widely used in the 70’ was then nearly abandoned. It made a comeback recently [37] as a much cheaper method because of its ability to concentrate on the low copy sequences, the highly repeated sequences being irrelevant as far as the genetic information is concerned.
Due to the complexity of the DNA structure, it would be surprising if there would be no short time memory effects in the reassociation process, since it involves quite complex biomolecules. Indeed, fingerprints of fractality and nonextensivity in DNA fragment distribution has been reported recently [38]. The ideas and formalism developed in this paper might be of interest also in that field of primary importance.

5 Discussion

Using ideas and theoretical tools borrowed from recent works on the theory of relaxation, we have derived a universal function for the kinetics of complex systems characterized by stretched exponential and/or power-law behaviors. This kinetic function unifies and generalizes previous theoretical attempts to describe what has been called "fractal kinetic". The concentration evolutionary equation (12) is formally similar to the Burr_{XII} relaxation function obtained in the theory of relaxation, with two exponents $\alpha$ and $n$. The first one is due to memory effects and short-range correlations and the second one finds its origin in the long-range correlations and geometrical frustrations which give rise to ageing behavior. As in the theory of relaxation, these effects can be formally handled by introducing adequate probability distributions for the rate coefficient. We have shown that the distribution of rate coefficients is the consequence of local variations of the free energy appearing in the exponent of the Arrhenius formula. The scaling (power-law) behavior of the kinetic is therefore another example of what has been called "exponential conspiracy" [21]. The two macroscopic observables $n$ and $\alpha$ are formally related to the energy landscape of the complex system which varies if physical, chemical or biological external factors are modified.

The fractal $(n, \alpha)$ kinetic has been applied to a few problems of fundamental and practical importance [32][33][39], examples of which have been presented in section 4.

In references [9] we have shown how a universal relaxation function can be derived if we use distributions of macroscopic waiting times maximizing the nonextensive Tsallis entropy. Similar conclusions can be drawn in the present problem, if we introduce local reaction waiting time in a probabilistic derivation of the universal kinetic function.

The relation between the $(n, \alpha)$ kinetic and nonextensive thermostatistics will be the subject of further studies.
6 Captions of Figures

Fig.1 \((n, \alpha)\) kinetic of adsorption of melanoidine in aqueous solution on activated carbon with \(n = 1.5\) and \(\alpha = 0.56\).

Fig.2 \((n, \alpha)\) kinetic (eq.49) of the conversion of protochlorophyllide into chlorophyllide (transformation of 647 nm pigment by 630 nm photons). The smaller points for \(t > 0.4\) sec. are results of the two first order model (eq.48).

Fig.3 Log-Log plot (eq.47) applied to data of Fig.2.

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Fig. 1 Kinetic of adsorption of melanoïdine in aqueous solution on activated carbon.
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