Shorter Communication

$q$-Exponential Structure of Arbitrary-Order Reaction Kinetics

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Abstract

The rate equation for an arbitrary $m$th order growth or decay reaction can be expressed in terms of the $q$-exponential function $\exp_q f = [1 + (1 - q)f]^{1/(1-q)}$, with $q$ equal to $m$. The analysis suggests that a wide variety of reaction rate (kinetic) processes and models, in chemistry, biology/ecology, unit operations and contaminant transport, are amenable to analysis by Tsallis’ non-extensive statistical mechanics. A number of $q$-analogues of common kinetic mathematical models are proposed, and illustrated by several examples.

Keywords: Tsallis entropy, $q$-exponential, reaction rate, chemical kinetics, population dynamics, logistic model, non-linear advection-dispersion-reaction.
1. Introduction

In recent years, a major advance has taken place in theoretical physics of great importance to engineers, with the development of so-called “non-extensive” statistical mechanics based on the Tsallis (1988) entropy function:

\[ S_q = -k_B \sum_{i=1}^{s} p_i^q \ln_q p_i = \frac{k_B}{q-1} \left(1 - \sum_{i=1}^{s} p_i^q\right), \quad (1) \]

where \( S_q \) is the Tsallis entropy, \( k_B \) is the Boltzmann (or any other applicable) constant, \( p_i \) is the probability of occurrence of the \( i \)th state, \( s \) is the number of possible states, \( q \in \mathbb{R} \) is the Tsallis parameter, and \( \ln_q f = (1 - q)^{-1}(f^{1-q} - 1), f > 0 \) is the \( q \)-logarithmic function (Tsallis, 1994). Note \( S_q \) is here defined in the units of \( k_B \), i.e. \( J \, K^{-1} \) molecule\(^{-1} \). In the limit as \( q \to 1 \), \( \ln_q f \to \ln f \) and \( S_q \) reduces to the well-known Boltzmann (1877)-Planck (1914) and Shannon (1948) definitions of entropy:

\[ S = -k_B \sum_{i=1}^{s} p_i \ln p_i. \quad (2) \]

Using the Tsallis entropy, a new theory of statistical mechanics (including thermodynamics and information theory) has been built up over the past decade (e.g. Tsallis, 2001; Plastino, 2004) - forming a superset of “traditional” or Maxwell-Boltzmann statistical mechanics - for the analysis of systems which exhibit some form of “correlated” structure between individual entities or elements within the system. Examples include systems with long-range interactions, long-range memory effects and/or multi-fractal (power-law) space-time structures, encompassing a rich assortment of physical, chemical, astronomical, fluid mechanics, engineering and financial systems (Tsallis, 2001; Tsallis et al. 2002; Beck, 2000).

The purpose of this communication is to extend the work of several workers (e.g. Tsallis, 2001; Tsallis et al., 1999; Plastino et al., 2000), to delineate another class of systems with \( q \)-exponential structure, involving rate processes of arbitrary reaction order. Such
systems extend over the breadth of physical chemistry and biochemistry; mathematical biology and ecology; chemical, environmental and process engineering; and the migration of constituents (contaminants) within natural or constructed media.

2. Theoretical Analysis

Consider the reaction of a single chemical, biological, radioactive or other species A:

\[ A \rightarrow \text{products or reactants} \rightarrow A, \]  

(3)

for which the reaction rate is expressed by the simple arbitrary-order kinetic equation (e.g., Moore, 1972; Levenspiel, 1972; Jordan, 1979; Moore & Pearson, 1981; Atkins, 1982):

\[ \frac{d\chi_A}{dt} = k\chi_A^m, \]  

(4)

where \( \chi_A(t) = C_A(t) / C_{Aref} \) is the normalised concentration (more accurately, the normalised activity or fugacity) of species A, such that the activity \( C_A(t) \) of species A is expressed relative to some reference activity \( C_{Aref} \); \( k \) is the rate constant; \( t \) is time; and \( m \) is the reaction order. The normalisation of \( C_A(t) \) is necessary to avoid expressing \( m \) in awkward units; also in general \( 0 \leq \chi_A(t) \leq 1 \) (if \( \chi_A(t) \) is a mole or population fraction, then \( 0 \leq \chi_A(t) \leq 1 \)). Eq. (4) with \( m=1 \) and \( k>0 \) (or \( k<0 \)) gives the familiar first order growth (decay) process, common in chemical and biological reactions and always evident in radioactive decay phenomena. Other well-known examples from chemical kinetics include \( m=0 \) (zeroth order) and \( m=2 \) (second order) reactions. In general \( m>0 \) and \( k>0 \) (\( k<0 \)) indicates a growth (decay) relationship of arbitrary \( m \)th order.

Solution of eq. (4) with the initial condition \( \chi_A(0) = \chi_{A0} \) yields (Atkins, 1982; Levenspiel, 1972; Moore & Pearson, 1981; Tsallis et al., 1999):

\[ \chi_A(t) = \left[ \chi_{A0}^{1-m} + kt(1-m) \right]^{1/(1-m)}. \]  

(5)

This can be expressed in terms of the \( q \)-exponential function \( \exp_q f = [1 + (1-q)f]^{1/(1-q)} \), the
inverse of the $q$-logarithm function (Tsallis, 1994):

$$\chi_A(t) = \chi_{A_0} \exp_m (\chi_{A_0}^{1/(1-m)} k t).$$

(6)

In other words, an arbitrary $m$th order growth or decay process exhibits a $q$-exponential mathematical structure, with $q=m$. If for some reason we had chosen the reference activity $C_{A_{ref}}$ equal to the initial activity $C_{A_0}$, whence $\chi_{A_0} = 1$, then eq. (6) reduces to:

$$\chi_A(t) \bigg|_{C_{A_{ref}}=C_{A_0}} = \exp_m (k t).$$

(7)

In general, the parameters $k$ and $\chi_{A_0}$ in eqs. (6)-(7) can be calculated from reaction rate data by the use of various $m$-logarithmic plots of $\ln_m C_A(t)$ against $t$, for different values of $m$.

3. Applications

The above rate expressions have obvious implications for the application of Tsallis (power law) statistics to a variety of reaction rate processes of arbitrary order. There are myriad applications in many fields, for example:

- **Chemical kinetics:** $q$-formulations of chemical reaction kinetics, e.g. for the generalised reaction:

$$aA + bB \rightleftharpoons cC + dD,$$

(8)

where $A$, $B$, $C$, $D$ are chemical species and $a$, $b$, $c$, $d$ their respective stoichiometric coefficients, we write the rate equation (Moore, 1972; Levenspiel, 1972; Jordan, 1979; Moore & Pearson, 1981; Atkins, 1982):

$$\frac{d\xi}{dt} = \frac{1}{a} \frac{d\chi_A}{dt} = \frac{1}{b} \frac{d\chi_B}{dt} = \frac{1}{c} \frac{d\chi_C}{dt} = \frac{1}{d} \frac{d\chi_D}{dt} = k \chi_A^\alpha \chi_B^\beta \chi_C^\gamma \chi_D^\delta,$$

(9)

where $\xi$ is a measure of the extent of reaction; $\chi_A$, $\chi_B$, $\chi_C$, $\chi_D$ are the normalised activities of each species and $\alpha$, $\beta$, $\gamma$, $\delta$ are the reaction orders with respect to each species as measured by experiment, in general unequal to unity and not necessarily
related to \(a, b, c, d\) or each other. By stoichiometry, eqs. (8)-(9) give:

\[
\frac{d\zeta}{dt} = k(\chi_{A0} - a\zeta)^a(\chi_{B0} - b\zeta)^b(\chi_{C0} + c\zeta)^c(\chi_{D0} + d\zeta)^d.
\] (10)

where \(\chi_{A0}, \chi_{B0}, \chi_{C0}, \chi_{D0}\) are the initial activities of each species. Eqs. (8)-(10) can be further generalised to more complicated multi-reaction chemical systems, for example with opposing, consecutive and/or parallel reactions, as well as multiple or oscillating equilibria (Moore, 1972; Levenspiel, 1972; Jordan, 1979; Moore & Pearson, 1981; Atkins, 1982).

- **Biological and ecological population dynamics:** \(q\)-variants of the many biological population dynamics models (c.f. Jones & Sleeman, 1983; Krebs, 1985; Banks, 1994; Kapur & Kesevan 1992), for example:

  - simple \(q\)-exponential growth and decay models, of similar form to eqs. (3)-(4);
  - \(q\)-logistic models, reflecting some physical limitation to growth, such as (c.f. Jones & Sleeman, 1983; Krebs, 1985; Banks, 1994):
    \[
    \frac{d\chi_A}{dt} = \frac{k_{\text{max}}}{K_A} \left( 1 - \frac{\chi_A}{K_A} \right) \chi_A^\alpha,
    \] (11)
    where \(k_{\text{max}}\) is the maximum rate constant, \(K_A\) is the normalised carrying capacity (the maximum attainable \(\chi_A\)) and \(\alpha, \kappa\) are power law exponents;
  - \(q\)-Monod models, reflecting limitations to growth due to scarcity of some critical substrate (nutrient or resource), e.g. (c.f. Banks, 1994):
    \[
    \frac{d\chi_A}{dt} = \frac{k_{\text{max}} S}{K_{sA} + S} \chi_A^\alpha,
    \] (12)
    where \(S\) is the substrate concentration, \(K_{sA}\) is the half-saturation coefficient and \(\alpha, \sigma\) are power law exponents;
  - \(q\)-interacting species models, including:
(i) $q$-predator-prey models, e.g. for population counts $N$ of prey and $P$ of predator (c.f. Jones & Sleeman, 1983; Krebs, 1985):

\[
\frac{dN}{dt} = k_N N^\nu \left(1 - \frac{N}{K}\right)^\kappa - P^\pi F(N, P), \\
\frac{dP}{dt} = -k_P P^\pi + N^\nu G(N, P)
\]  

(13)

where $k_N, k_P$ are the rate constants for predator and prey; $K$ is the carrying capacity of the prey; $F(N, P), G(N, P)$ are specified functions of $N$ and $P$; and $\nu, \kappa$ and $\pi$ are power law exponents; and

(ii) $q$-competing species models, e.g. for population counts $M, N$ (c.f. Jones & Sleeman, 1983; Krebs, 1985):

\[
\frac{dM}{dt} = k_M M^\mu \left(1 - \frac{M + aN}{K_M}\right)^\kappa, \\
\frac{dN}{dt} = k_N N^\nu \left(1 - \frac{N + bM}{K_N}\right)^\lambda
\]  

(14)

where $k_M, k_N$ are rate constants; $K_M, K_N$ are carrying capacities; $a, b$ are model parameters and $\mu, \nu, \kappa, \lambda$ are power law exponents;

- a wide range of other variants of the above, for example with time lag effects, memory effects, age structure or stochastic variables (c.f. Jones & Sleeman, 1983; Krebs, 1985; Banks, 1994).

- **Unit operations**: $q$-formulations of the conservation of mass of each constituent within a control volume in chemical, environmental or process engineering, as given by (Levenspiel, 1972; Mihelcic et al. 1999; Felder & Rousseau, 2000):

\[
\frac{\partial M_i}{\partial t} = \frac{\partial M_{i,\text{in}}}{\partial t} - \frac{\partial M_{i,\text{out}}}{\partial t} + \frac{\partial M_{i,\text{react}}}{\partial t}, \quad i = 1, \ldots, w
\]  

(15)

where $\partial M_i / \partial t$ is the net rate of change of mass of constituent $i$ (from a total of $w$
constituents) within a control volume; and $\frac{\partial M_{i,\text{in}}}{\partial t}$, $\frac{\partial M_{i,\text{out}}}{\partial t}$ and $\frac{\partial M_{i,\text{react}}}{\partial t}$ are respectively the total rates of flow of mass of $i$ into, out of and production (by reaction) within the control volume. For a constant volume process:

$$\frac{\partial M_{i}}{\partial t} = V \frac{\partial C_{i}}{\partial t}, \quad \frac{\partial M_{i,\text{react}}}{\partial t} = V \frac{\partial C_{i,\text{react}}}{\partial t}$$

(16)

where $V$ is the control volume, and $\frac{\partial C_{i}}{\partial t}$ and $\frac{\partial C_{i,\text{react}}}{\partial t}$ are respectively the net and reactive rates of change of concentration (in mass/volume units) of $i$ in the control volume. For an arbitrary order reaction process, eq. (4) gives (ignoring activity effects):

$$\frac{\partial C_{i,\text{react}}}{\partial t} = kC_{\text{ref}} \left( \frac{C(t)}{C_{\text{ref}}} \right)^{m}$$

(17)

Eqs. (15)-(17) can be readily applied to typical unit operation problems involving batch, well-mixed or plug flow reactors.

The above equations reduce to their first-order counterparts when the power law exponents approach unity. Some of the above power law models have been presented previously (e.g. Kapur & Kesavan, 1992; Banks, 1994), but apart from a few instances (e.g. Plastino et al., 2000) have not been examined from the perspective of a Tsallisian or “correlated” statistical framework. Furthermore, whilst many of the above models cannot at present be solved analytically, or are of complicated mathematical form, analysis in light of the $q$-exponential structure may reveal superior numerical reduction techniques and/or more concise analytical solutions.

In the above systems, any observed Tsallis-like mathematical structure is not the result of some anomalous (long-range correlated) configuration in geometric space, but rather is brought about by the reaction mechanism; i.e. by the structure of reactions within and between individual entities in the system. It is interesting that first order ($m=1$) processes -
widely adopted as the default case throughout science and engineering - reflect the “no feedback” scenario; i.e. the probability of reaction of a given entity (individual molecule or organism) is unaffected by the presence of other entities. A non-first order \((m \neq 1)\) reaction rate reveals the existence of some interaction mechanism, such that the reaction rate is modified (decelerated or accelerated) by other entities.

4. **Examples**

Several examples will now be considered. Firstly, consider a simple \(q\)-exponential decay relationship (eqs. (5)-(6)) for a reactive species \(A\), with \(C_{A0}=100\) mg L\(^{-1}\) (or any other appropriate units), \(C_{A,ref}=1\) mg L\(^{-1}\) and \(k=-220\) min\(^{-1}\) (recall \(k < 0\) indicates a decay relationship). Plots of \(\ln \chi_A(t)\) against time are illustrated in Figure 1 for various values of \(m\). As expected, \(\ln \chi_A(t)\) for \(m=1\) follows a straight line decay relationship with time. For \(m<1\) \((m>1)\) the reaction proceeds less (more) rapidly, producing a curve of increasing (decreasing) negative gradient with time on a natural logarithm plot.

Now consider a well-mixed tank problem, in which a reactor of constant volume \(V=500\) L and steady flow throughput \(Q=Q_{in}=Q_{out}=50\) L min\(^{-1}\) (hence a mean residence time of \(\theta=V/Q=10\) min) initially contains a steady state concentration \(C_{A0}=100\) mg L\(^{-1}\) of a reactive constituent \(A\), again with a \(q\)-exponential rate constant of \(k=-220\) min\(^{-1}\). The incoming concentration is suddenly changed to \(C_{in}=0\) at \(t=0\), whilst the flow rate \(Q\) is kept constant. How will the concentration change with time? We again use a reference concentration of \(C_{A,ref}=1\) mg L\(^{-1}\), and ignore activity effects. From eqs. (15)-(17), the governing differential equation is:

\[
\theta \frac{d\chi_A(t)}{dt} = -\chi_A(t) + k \theta [\chi_A(t)]^m
\]  

(18)

Solution with the initial condition \(\chi_A(0) = \chi_{A0}\) yields:
\[
\chi_A(t) = \left[ k \theta \left( 1 - (e^{-t/\theta})^{1-m} \right) + \left( \chi_{A0} e^{-t/\theta} \right)^{1/(1-m)} \right]^{1/(1-m)},
\]  

(19)

This is of somewhat similar form to the \(q\)-exponential function (compare eq. (5)), and clearly belongs to the same mathematical family. Eq. (19) is plotted for the above parameter values and various values of \(m\) in Figure 2. Once again, \(\chi_A(t)\) for \(m=1\) exhibits an exponential decay relationship with time. The curves for \(m<1\) (\(m>1\)) follow broadly similar patterns of curvature to those in Figure 1. (A second branch of the \(m=\frac{1}{2}\) curve is evident for \(t>34.2596\) min.; this is mathematically valid but physically spurious.) In this case, however, the decay curves for a reactive species are bounded by the normalised concentration of a non-reactive (conservative) species \(\chi_A(t) = \chi_{A0} e^{-t/\theta}\), shown as a dotted line, which is removed solely by dilution.

Now consider a biological species \(A\) which exhibits \(q\)-logistic growth (eq. (11)). With the initial condition \(\chi_A(0) = \chi_{A0}\), the (implicit) analytical solution is:

\[
t = \frac{\chi_A^{1-m} F([\kappa,1-m],[2-m],[\chi_A/K_A]) - \chi_{A0}^{1-m} F([\kappa,1-m],[2-m],[\chi_{A0}/K_A])}{k_{max} (1-m)}
\]

(20)

where \(F([..],[..],[..])\) is the generalised hypergeometric function (Waterloo Maple Inc., 1981-2004). For \(\kappa=m=1\), this reduces to the familiar solution:

\[
t = \frac{1}{k_{max}} \ln \left( \frac{\chi_A(K_A - \chi_{A0})}{\chi_{A0}(K_A - \chi_A)} \right)
\]

(21)

For a specific example with \(\chi_{A0}=1/2500\) units, \(K_A=1\) units and \(k_{max}=1\) min\(^{-1}\), plots of \(\chi_A(t)\) obtained using eqs. (20)-(21) are shown in Figures 3a-b - respectively for \(\kappa=1\) and \(m=1\) - for convenience using a logarithmic time scale. As evident, parameter \(m\) (Fig. 3a) modifies the steepness of the sigmoidal curve, producing a delayed but more rapid (earlier but less rapid) reaction for \(m>1\) (\(m<1\)). On the other hand, parameter \(\kappa\) (Fig. 3b) modifies the rate at which \(\chi_A\) approaches its asymptotic limit \(K_A\), such that it takes much longer as \(\kappa>>1\) (but \(\chi_A\) flies off...
to infinity as $\kappa \to 0$). Both $m \neq 1$ and $\kappa \neq 1$ therefore reflect processes in which the reproduction of species A is modified by the presence of other members of that species, in two different ways.

5. Further Discussion

Although not the object of this discussion, it is worth reporting that a $q$-variant of the Arrhenius (1889) expression for the rate constant of a chemical reaction has recently been presented (Andricioaei & Straub, 2001; Lenzi et al., 2001):

$$k_q = A \frac{\exp\left(-E^\ddagger/k_B T\right)}{\exp\left(-E_0/k_B T\right)}$$

where $A$ is a normalising ("pre-$q$-exponential") factor, $T$ is absolute temperature, $E^\ddagger$ is the energy of the transition state and $E_0$ is that of the ground state. As $q \to 1$, $k_q$ approaches the familiar Arrhenius (1889) form $k = A \exp\left(-\frac{E^\ddagger - E_0}{k_B T}\right)$, where $\Delta E = E^\ddagger - E_0$ is the activation energy. It is important that the two different Tsallisian influences on chemical reactions be clearly distinguished: the $q$ in eq. (22) reflects a reaction with a Tsallisian (correlated) thermodynamic structure, whilst the power law exponent in the rate expression itself (eqs. (4) or (9)-(14)) reflects a Tsallisian (non-first order) reaction mechanism. Conceivably, there are four possible combinations of these two quite different effects.

The foregoing rate equations can be further incorporated into a generalised nonlinear advection-dispersion-reaction equation (equivalent to a nonlinear Fokker-Planck equation with reaction) of the following type (c.f. Tsallis & Bukman, 1996; Plastino et al., 2000; Lenzi et al., 2001; Plastino, 2001; Frank, 2002):

$$\frac{\partial \chi_i}{\partial t} = -\nabla \cdot (v \chi_i^{\nu_i}) + \nabla \cdot (D \cdot \nabla \chi_i^\delta) + J_i, \quad i = 1, \ldots, w$$

(23)
where $\chi_i = \chi_i(x,y,z,t)$ is the normalised activity of species $i$ (entities of type $i$) in cartesian coordinates, from a total set of $\nu$ species; $\mathbf{v}$ is the velocity (transport) vector; $\mathbf{D}$ is the dispersion or diffusion coefficient (diffusivity) tensor; $\nabla$ is the grad operator; $\nabla \cdot$ is the div operator; $\upsilon$ and $\delta$ are power law exponents (in general $\upsilon \neq \delta$); and $J_i$ is a generalised non-linear reaction rate equation for species $i$, e.g. of the form given in eqs. (4) or (9)-(14). Eq. (23) provides a $q$-generalised model for the anomalous transport, anomalous (non-Fickian, correlated) dispersion or diffusion, and non-first-order (power-law) growth or decay of any set of physical, chemical and/or biological species. Additional source-sink terms for the creation or destruction (or entry or exit) of entities, if required, can be added to eq. (23). Furthermore, if the advection or dispersion terms for the $i$th species are influenced by the activities of species $j \neq i$, time lag effects or other complications, further extensions to eq. (23) are possible.

Conclusions

It is shown that the rate equation for an arbitrary $m$th order growth or decay reaction can be expressed in terms of the $q$-exponential function, with $q$ equal to $m$. Arbitrary order reactions therefore fall within the framework of Tsallis (correlated) statistical mechanics. The analysis has application in many fields, e.g. physical chemistry and biochemistry; mathematical biology and ecology; chemical, environmental and process engineering; and the migration of constituents (contaminants) within natural or constructed media. Arbitrary order chemical reaction mechanisms are well known; it will be interesting to see if analogous power law kinetic models could be relevant in biological/ecological, process engineering or contaminant transport modelling applications.
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**Figure Captions**

Figure 1: Plots of $\ln x_A(t)$ against time for $m$th order decay of reactive species $A$, for various values of $m$ (eqs. (5)-(6); for parameter values see text).

Figure 2: Plots of $\ln x_A(t)$ against time in a well-mixed reactor containing $m$th order reactive species $A$, for various values of $m$ (eq. (19); for parameter values see text). The dilution of a conservative species is shown by a dashed line.

Figure 3: Plots of $x_A(t)$ against $\ln(t)$ for $\varphi$-logistic growth of biological species $A$ (eqs. (20)-(21)), for (a) $\varphi=1$ and various $m$; and (b) $m=1$ and various $\varphi$ (for parameter values see text).
FIGURE 1

FIGURE 2
FIGURE 3a

FIGURE 3b