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Uniform description of non-Arrhenius temperature dependence of reaction rates, and a heuristic criterion for quantum tunneling *vs* classical non-extensive distribution

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ABSTRACT

To account for frequently documented low-temperature deviations from Arrhenius rate law, the proposed expansion of inverse activation energy against inverse temperature is shown to yield a first order linearizing parameter which is formally correlated with Tsallis non-extensive classical statistical mechanics. Its sign provides a heuristic criterion, especially appealing in biochemistry, for assigning deviations as due either: (i) to quantum mechanical under-barrier tunneling, or (ii) to 'classical' collective phenomena. For (i), an explicit relationship is here derived in terms of barrier features. Case (ii) typically occurs in enzymatic or heterogeneous catalysis, in membrane mediated processes and in those controlled by diffusion or by transport in general.

1. Introduction

The rate constants k for most rate processes depend on absolute temperature T according to the Arrhenius law. When extended to low temperatures, deviations are observed even with no apparent changes in the chemical mechanism or in the physical nature of the moieties (e.g., their phase). The phenomenological description individuates convex or concave $\ln(k)$ *vs* $1/T$ plots, as Sub-Arrhenius or Super-Arrhenius regimes; they correspond, respectively, to higher or lower reactivity as temperature decreases, and therefore to a decrease or increase of the apparent activation energy, E_a [1,2]. Recent systematic investigations [2,3] lead to a simple formalism in terms of a single deformation parameter, d, which is inspired by Tsallis non-extensive statistical mechanics and exploits Euler's expression of the exponential function as the limit of a succession.

Formally, the d parameter accounts for positive or negative linear dependence of the inverse of activation energy against $1/T$ and reasonably covers uniformly both regimes. However, they are in general very different in nature, as discussed in Section 2. Evidence is being accumulated that in the vast majority of cases Sub-Arrhenius behavior arises because of quantum mechanical under-barrier tunnel, while Super-Arrhenius often manifests because of collective phenomena, such as those amenable of treatment by the non-extensive thermodynamics of Tsallis, and covers on ample set of phenomena (e.g., transport, diffusion, such as those playing roles in catalysis, both enzymatic and heterogeneous). We emphasize the contrast with quantum mechanical tunnel by referring to the Super-Arrhenius case as basically amenable of a 'classical' description, as indeed often documented by successful classical molecular dynamics simulations.

In Section 3 we describe a phenomenological formula, which uniformly covers both regimes. The present study accounts for the suitability of the deformation parameter d in the classical case, and shows also that an explicit relationship can be given to first order between d and height and width of the barrier, therefore interpreting the Sub-Arrhenius case according with the venerable quantum mechanical models of Eckart [4], Wigner [5] and Bell [6–8]. A summary and concluding remarks end the Letter in Section 4. The Appendix collects some mathematical details.

2. The two regimes

This selected account of relevant research includes mostly recent developments, amplifies and updates the scope of the discussion already given previously [1,3].

Due to the importance of understanding the mechanisms involved in physico-chemical transformations, studies have being carried out of reaction rate constant dependence with temperature for a large number of processes, not restricted to elementary chemical reactions [9–12], involving particle diffusion in supercooled liquids and glasses [13–15], electrical conductivity in ionic liquids [16–18], enzymatic catalysis [19–24], food preservation processes [25–27]. The Arrhenius rate law has been shown to be a fairly

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robust option in the description of the rate constant k, for most cases. However, several experimental results have arisen that show a significant deficiency on account of the non-linearity of the Arrhenius plot at low temperatures.

The deviations from linearity in Arrhenius plot leads to two quite distinct regimes (Figure 1) denoted Sub-Arrhenius and Super-Arrhenius. When the experimental data represented in the form of the Arrhenius plot (ln (k) *vs* $1/T$) feature a concave deviation they are referred to as Sub-Arrhenius, otherwise they are referred to as Super-Arrhenius. In a general way, there is a consensus in the literature that processes that exhibit Sub-Arrhenius behavior are intimately related to the quantum tunneling effect of penetration of an energy barrier in the reaction path along the potential energy surface, while Super-Arrhenius behavior is a typical manifestation of contributions from classical collectives phenomena, where transport (e.g., diffusion, membrane permeability) of particles play a role, see also below.

There are several examples being provided of systems that illustrate the two regimes. The reaction of a fluorine atom with molecular hydrogen has been recently representing the prototypical case of Sub-Arrhenius behavior. For this system a series of theoretical and experimental kinetic data provide to validate theoretical models for rate constants. This is perhaps the first and only reaction for which exact quantum mechanical results for various potential energy surfaces are available [3,9] providing a benchmark for rate constants for a wide range of temperatures. A demonstration is given of the clear Sub-Arrhenius behavior, which shows up at low temperatures, as a manifestation of the quantum mechanical under-barrier tunnel effect. See Section 4 for a very recent striking experimental test and similar results now available for HD as a reactant, of interest for discussing also the kinetic isotope branching ratio.

A few years ago, in an entirely different context, Ref. [11] has also presented a series of kinetic data related to transfer of hydrogen between heavy atoms, according to the present nomenclature showing strong Sub-Arrhenius behavior. Experimentally, rate constants are obtained by means of Nuclear Magnetic Resonance in liquids and solids. One of the systems studied in Ref. [11] is

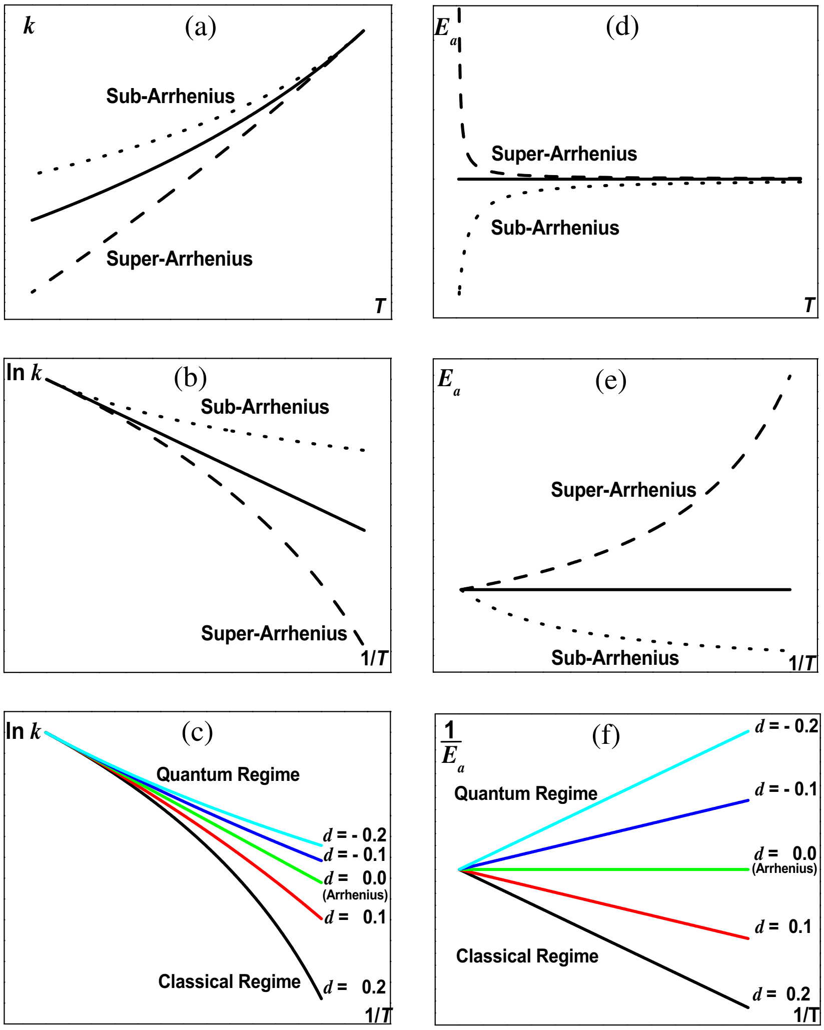

Figure 1. Panel (a) illustrates the typical exponential growth of reaction rates $k(T)$ as absolute temperature T increases. Experimental, theoretical and simulation data are universally analyzed, panel (b), by an Arrhenius plot, where ln (k) is reported against $1/T$. Deviations from linearity at low temperatures can be observed in the plot as showing either (i) a 'concave' behavior, i.e., higher than expected rates as temperature decreases, or (ii) a 'convex' curve, i.e., lower than expected rates as temperature decreases. We denote (i) as Sub-Arrhenius behavior, discussed here as a manifestation of quantum mechanical tunneling through a potential energy barrier, and (ii) as Super-Arrhenius behavior, often arising for collective phenomena, amenable of a classical mechanics interpretation. Panel (c) shows that the proposed d-Arrhenius formula (Eq. (2)) for the rates allows to uniformly describe both regimes in terms of the deformation parameter d, the Sub- and Super-Arrhenius cases corresponding to $d < 0$ and $d > 0$, respectively. The right hand side panels (d) and (e) show that deviations from constancy of the apparent activation energy, expected from the Arrhenius law, for a Sub-Arrhenius (Super-Arrhenius) behavior the apparent activation energy decreases (increases) with decreasing temperature. Panel (f) finally exhibits the linear relationship of the inverse activation energy with inverse temperature, basic to our derivation of the d-Arrhenius formula.

e.g., tautomerism in porphyrins [28], where there is interconversion between the structures by means of successive transfers of protons, which therefore represent another group of reactions that can show Sub-Arrhenius behavior, most likely to be attributed to cases where quantum mechanical tunneling is operative. Refs. [23,30] give further examples.

Super-Arrhenius behavior is amply documented in a variety of collective processes, which are often satisfactorily simulated by classical molecular dynamics (see e.g., Ref. [29] and the references therein). It is important to stress that there is a marked difference between the two physically distinct situations, for the description of which we can often be misled by using the same keywords (proton, hydrogen or hydride tunneling), while one of them most likely involves genuine quantum mechanical penetration through a barrier in the potential energy surface, while the other one presumably involves collectivity or transport, for example transfer through the sieve of a molecular membrane (as e.g., in Ref. [1]), or diffusion to the active site of a catalyzer, or even the macroscopic sliding of bacteria described in Ref. [30] and discussed in Ref. [2]. For these reasons, we affirm that the Sub-Arrhenius case explicitly requires a quantum mechanical treatment, while for the Super-Arrhenius case a classical molecular dynamics approach can be sufficient to generate often useful simulations.

Several investigations have revealed Super-Arrhenius behavior for rates of enzymatic catalysis promoted processes [22,23,32], such as those most likely involved in the plant respiration experiments of Refs. [1,31]. The authors in Ref. [20] have observed Super-Arrhenius behavior in the reaction of thermophilic alcohol dehydrogenase (ADH) suggesting that hydrogen tunneling makes a significant contribution. However, according to the present view of processes of enzymatic catalysis involving convex curvature, they are to be taken as circumstantial evidence of collective phenomena, involving for example classical diffusion or otherwise controlled transfer, with quantum tunneling effect presumably not playing a major role.

It has also to be noted that there is a considerable continuing interest in basic features of the dynamics of complex or glass-forming liquids and solids, particular attention being devoted to the temperature dependence. The latter has been the subject of intense research, which, for our purpose, can be described as follows [13]. In the vicinity of the glass transition temperature the viscosity and diffusion coefficients of polymers and other glass forming liquids are strong functions of temperature, and it is a frequently occurring observation that materials exhibit deviation from Arrhenius behavior. Non-Arrhenius relaxation rates in glassy materials can be associated with thermally activated rearrangements of increasing numbers of molecules as temperature decreases. In particular, Garrahan and Chandler [32] conclude that relaxation times should obey the Arrhenius like formula only at low temperatures rather than, as is more commonly supposed, changing from Arrhenius to Super-Arrhenius as the temperature decreases.

3. The uniform formula

Recently, several studies [33–35] have been devoted to describe the non-Arrhenius behavior in chemical kinetics by classical continuous probability distributions inspired by Tsallis non-extensive statistical mechanics [36,37]. The Figure 2 gives an illustration of the probability distribution function.

$$P(E) = \left(1 - d\frac{E}{RT}\right)^{\frac{1}{d}}, \tag{1}$$

which tends to a Boltzmann-like distribution when d tends to zero, according to the celebrated limit by Euler: in our formulation we exploit the suitability of the parameter d to provide the degree of deformation of the exponential function. See some elementary mathematical details in the Appendix. The distribution (1) is a corollary of the Tsallis Thermodynamics, which he postulates as generalization of the entropy to cover cases of non-extensivity. In the Ref. [2,3] we proposed and tested the formula:

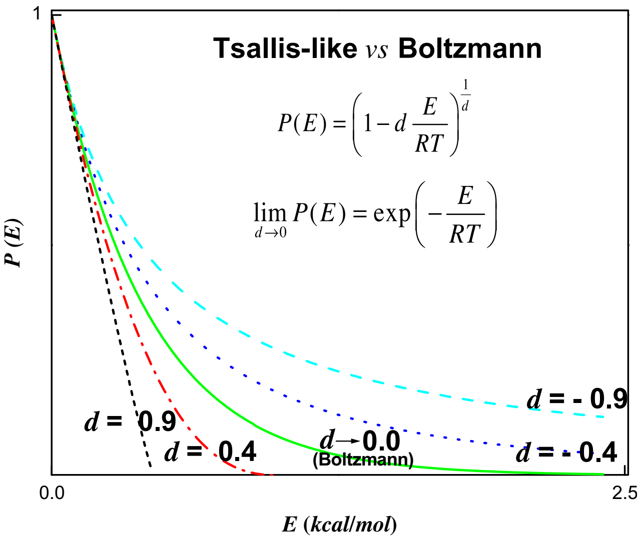

Figure 2. Tsallis-like probability distribution function (Eq. (1)) for several values of the deformation parameters d. When the parameter d tends towards zero, the Boltzmann distribution is recovered thanks to the Euler limit. Both distributions are normalized to 1 for $T \to \infty$. Note that, for $d > 0$, the Tsallis-like distribution may not be well defined above some specific energy values, as shown for $d = 0.4$ and $d = 0.9$.

$$k(T) = A\left[1 - d\frac{E_0}{RT}\right]^{\frac{1}{d}} \tag{2}$$

for rate constants deviating from Arrhenius behavior, and referred to (2) as the 'deformed Arrhenius' (d-Arrhenius) equation. Eq. (2) containing only three phenomenological parameters, A, E_0 (see Section 3.2) and d, only the latter appearing besides the familiar two of the Arrhenius equation, to which Eq. (2) tends when d tends to zero. The application to several kinetic problems with non-Arrhenius behavior supports our suggestion that the parameter d could cover both regimes of previous Section, discriminating them by its sign. The value of d can, in principle, be determined by the microscopic dynamics of the system, which is frequently unknown, so that d has to be in general considered as phenomenological, except for simple tunneling processes, as we will show below in Section 3.2. From Figure 1(c), we can see that for $d > 0$ and $d < 0$, the d-Arrhenius formula shows the typical deviation from linearity for the Super- and Sub-Arrhenius cases, respectively.

Once shown that the formula provides a good option for the description of non-Arrhenius behavior, it becomes a task of great interest to establish the connection between the phenomenological nature of the formula and the different physical origin of processes exhibiting the Sub-Arrhenius and Super-Arrhenius behaviors. The previous section discussed how 'classical' effects related to collectivity and transport of particles seem to be at the origin of most Super-Arrhenius cases ($d > 0$), substantiating the consistency of our formulation based on the Tsallis statistical mechanics of non-extensive processes. However, the Tsallis-like probability distribution of molecular velocities is essentially classical – like that of Boltzmann – and has to be analytically continued in order to provide a physical model covering phenomena associated to quantum mechanical effects [Sub-Arrhenius cases ($d < 0$)]. Remarkably however, we will succeed below to establish an explicit connection to first order between the present formula for the Sub-Arrhenius case and the approach by Bell [8] for quantum mechanical tunneling.

3.1. The activation energy

As remarked previously [3], the expression for the activation energy E_a [8] implied in the *d*-Arrhenius Eq. (2) can be written in the concise form

$$\frac{1}{E_a} = \frac{1}{E_0} - d\frac{1}{RT}. \tag{3}$$

This Equation can be obtained by Eq. (2) directly applying the current definition of the IUPAC for the apparent activation energy [38] as the negative of the logarithmic derivative of the rate constant with respect to $1/RT$:

$$E_a(T) = -\frac{\mathrm{d}\ln k(T)}{\mathrm{d}\left(\frac{1}{RT}\right)} = \frac{E_0}{\left(1 - d\frac{E_0}{RT}\right)}, \tag{4}$$

giving by rearrangement Eq. (3), which is a linear relationship between inverse activation energy and inverse temperature illustrated in Figure 1(f). When regarded as the power expansion in inverse temperature, basic in statistical thermodynamics, and truncated to the second term, the *d* parameter is interestingly seen as playing the role of the linearization parameter.

Further insight on the relationship (3) is gained by taking an alternative route and inserting it in the first equality in Eq. (4), considered as a differential equation for $k(T)$ when $E_a\,(T)$ is assumed to be the known function of T given by 3. Eq. (4) is first order in the variable $1/RT$ and is easily integrated specifying the lower limit of the integration range at a standard-state temperature T_0, as shown below:

$$\begin{aligned}\ln k(T) &= \int_{1/RT_0}^{1/RT} \frac{-E_0}{\left(1 - d\frac{E_0}{RT}\right)}\mathrm{d}\left(\frac{1}{RT}\right) \\ &= -\frac{1}{d}\ln\left(1 - d\frac{E_0}{RT}\right) + \frac{1}{d}\ln\left(1 - d\frac{E_0}{RT_0}\right)\end{aligned} \tag{5}$$

or

$$\ln k(T) + \ln\left(1 - d\frac{E_0}{RT_0}\right)^{\frac{1}{d}} = \ln\left(1 - d\frac{E_0}{RT}\right)^{\frac{1}{d}}. \tag{6}$$

when $d \to 0$, the term $\ln\left(1 - d\frac{E_0}{RT_0}\right)^{\frac{1}{d}}$ can be identified with the Arrhenius pre-factor A, and the apparent activation energy E_a becomes a constant and identified with E_0, recovering Arrhenius Equation, $k = A\exp\left(-\frac{E_0}{RT}\right)$. In general, when *d* differs from zero, we obtain the Tsallis-type of formula for the rate constant, Eq. (2).

3.2. The d parameter from features of the barrier

In order to establish an important connection with well known tunneling models, the following will treat in detail the model of Bell, which incorporates, at least regarding salient features, those of Eckart [4] and Wigner [5], which have been generalized in various way through advanced semiclassical WKB and instanton methods.

In his book in 1980 Bell [8] presented his approach [6,7] to attempt to incorporate the effect of tunneling in kinetics. He proposes a function for the energy dependence barrier permeability, $G(E)$, that was in accordance with the physical behavior revealed from solvable quantum mechanical models, explicitly Eckart's [4]. The function proposed by Bell is given below:

$$G(E) = \left[1 + e^{\zeta\left(1 - \frac{E}{E_0}\right)}\right]^{-1}, \tag{7}$$

where, $\zeta = \frac{2\pi^2 l\sqrt{2mE_0}}{h}$ and $2l$ is the width of the barrier (see also below). From this model of a quantum mechanical permeable barrier, it was possible to calculate the tunneling correction as power series:

$$\begin{aligned}Q_{\mathrm{Bell}} = &\frac{\left(\frac{\pi E_0\beta}{\zeta}\right)}{\sin\left(\frac{\pi E_0\beta}{\zeta}\right)} \\ &- \frac{E_0\beta e^{(E_0\beta - \zeta)}}{(\zeta - E_0\beta)}\left[1 - \frac{\zeta - E_0\beta}{(2\zeta - E_0\beta)}e^{-\zeta} + \frac{\zeta - E_0\beta}{(3\zeta - E_0\beta)}e^{-2\zeta} - \ldots\right],\end{aligned} \tag{8}$$

where $\beta = \frac{1}{RT}$.

For the case where, $\zeta > E_0\beta$ (the case of more general interest of kinetic problems of chemistry) the first order term need be retained:

$$Q_{\mathrm{Bell}} = \frac{\left(\frac{\pi E_0\beta}{\zeta}\right)}{\sin\left(\frac{\pi E_0\beta}{\zeta}\right)}. \tag{9}$$

The model of Bell for the rate constant will be:

$$k_{\mathrm{Bell}}(T) = A\frac{\left(\frac{\pi E_0\beta}{\zeta}\right)}{\sin\left(\frac{\pi E_0\beta}{\zeta}\right)}\exp(-E_0\beta), \tag{10}$$

where A is the pre-exponential factor.

Using the definition for activation energy (Eq. (4)), the following equation is obtained [7]:

$$E_{a\mathrm{Bell}} = E_0 - \frac{1}{\beta} + \frac{\pi E_0}{\zeta}\mathrm{cotg}\left(\frac{\pi E_0\beta}{\zeta}\right). \tag{11}$$

To make a comparison between the Eqs. (11) and (3), it is convenient to express the inverse energy of activation for the Eq. (11) in a power series:

$$\frac{1}{E_{a\mathrm{Bell}}} = \frac{1}{E_0} + \frac{1}{3}\left(\frac{\pi}{\zeta}\right)^2\beta + \frac{1}{9}\left(\frac{\pi}{\zeta}\right)^2 E_0\beta^2 + \ldots \tag{12}$$

Disregarding the terms of order higher than one for Eq. (12) and comparing with Eq. (3), we arrive at the required correlation for the deformation parameter:

$$d = -\frac{1}{3}\left(\frac{\pi}{\zeta}\right)^2. \tag{13}$$

The term $\frac{\pi}{\zeta}$ can be rewritten as a function of the penetration frequency (ν^*) for crossing the barrier [8,39], $\frac{\pi}{\zeta} = \frac{h\nu^*}{2E_0}$, obtaining:

$$d = -\frac{1}{3}\left(\frac{h\nu^*}{2E_0}\right)^2. \tag{14}$$

This model provides a description of the deformation parameter through the tunneling parameters: barrier height and frequency for crossing the barrier at potential energy surface, as can be seen in the Figure 3. The greater the barrier height and lower the frequency to traverse the barrier this deformation parameter tends to zero neglecting the effect of tunneling and retrieving the Arrhenius model (the Boltzmann distribution). See [40] for an extension of a Tsallis-type Transition State Theory to cover the tunneling regime.

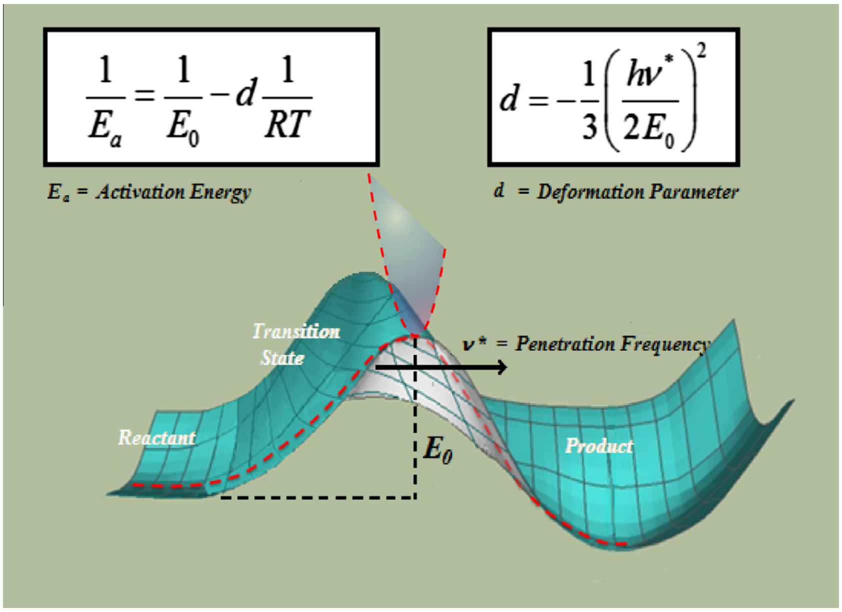

Figure 3. The figure illustrates schematically a chemical reaction as proceeding from reactants to products along a path on a generally multidimensional potential energy surface, here shown on a two dimensional cut. Zero point energies are neglected and E_0 is height of the barrier of the saddle point where the transition state is located, corresponding to the Arrhenius activation energy. The quantum mechanical tunneling occurs as penetration of the barrier, with a penetration frequency given to first order by ν^*. According to our treatment the activation energy varies with temperature according to the left hand formula, where the d parameter is related to ν^* and E_0 by the formula in the right hand side.

4. Summary and final remarks

A summary of results presented in the previous sections is displayed in Table 1. Nomenclature, definitions, physical and chemical implications, the use of the approach and exemplary aspects are listed. A few remarks follow.

An important word of caution involves the general validity of the distinctions of the two regimes, emphasized in this Letter. We would not be surprised that additional work will discover counter examples, but we believe that the classification will nonetheless bear a heuristic validity.

It is interesting to read what Bell wrote in its impressive 1980 [8] book summarizing more than 40 years of achievements on the main consequences of occurrence of quantum mechanical tunneling in chemistry (pp. 75–76, rearranged):

'The most useful results are obtained especially when experiments can be carried out over a wide range of temperature, preferably including low ones. There will be deviations from simple Arrhenius equation in the sense that the apparent activation energy will decrease with decreasing temperature, and at sufficiently low temperatures the reaction velocity will become independent of the temperature'.

Accordingly, encouraged by the first demonstration by exact quantum mechanical calculations for the F + H_2 reaction (Ref. [9]) and the just announced experimental confirmation [41], we have been careful to speak of tunneling in this spirit for the Sub-Arrhenius regime. However, the biochemical literature, at ever increasing frequency, includes tunneling in the terminology for Super-Arrhenius behavior, and its manifestation in convex Arrhenius plots, in which case we would prefer a nomenclature such as e.g., hydrogen transfer, transport across membranes and the like. This also in view of the fact that in most cases simulations are carried out by recourse to classical molecular dynamics.

Bell goes on saying (p. 76) '*the study of hydrogen isotopic effects provides much more useful experimental criteria of tunneling*'. Again, our exact quantum mechanical treatment of the F + HD reaction,

Table 1
Nomenclature and Confrontation of the two regimes.

	Sub-Arrhenius	Super-Arrhenius
Arrhenius plot, ln (k) vs 1/T (k = rate coefficient, T = Absolute temperature)	Concave plot	Convex plot
Temperature dependence of activation energy, E_a	E_a increases with T	E_a decreases with T
Heuristic criterion	Quantum phenomena (Tunneling)	Classical phenomena (Collective, transport, diffusion, enzymatic and heterogeneous catalysis)
Inverse E_a vs inverse T linear relationship[a], $\frac{1}{E_a} = \frac{1}{E_0} - d\frac{1}{RT}$.($E_0$ = barrier height, d = deformation parameter)	$d < 0$	$d > 0$
Connection of d with	Wigner[b] and Bell[c] tunneling models. $d = -\frac{1}{3}\left(\frac{h\nu^*}{2E_0}\right)^2$[d] $\nu^{\#}$ = penetration frequency).	Tsallis's non-extensivity parameter[e], $q = 1-d$ Truhlar–Kohen curvature parameter[f] $d = -\frac{2C}{E_0^2}$

[a] Ref. [2].
[b] Ref. [5].
[c] Ref. [34,35].
[d] This work.
[e] Ref. [36].
[f] Ref. [24].

yielding either DF + H or HF + D [42], as will be shown by additional results in the near future [43,44], substantiates these views.

A very recent review examines how 'Hydrogen tunneling links protein dynamics to enzyme catalysis' [45], and the nomenclature sometimes appears to differ from ours and caution has to be taken with respect to the underlying physico-chemical interpretation. However, it shows how the scope of this research is being greatly amplified. This reference and several others therein discuss examples of varied relevance to the present Letter. However, a remark concerns occasional fits of data generically showing temperature breaks in Arrhenius plots, use often being made of two piecewise linear behaviors. Again, it is our opinion that one should distinguish the two regimes and use of our heuristic criterion may help. For the concave case, continuous curve fits according to the quantum mechanical tunnel formula are probably the right choice, also in view of the fact that the elementary principles of the chemical kinetics of mechanisms involving multiple processes enforce the concept of rate determining step: in the vast majority of conceivable situations, this excludes concave piecewise behavior of sequential Arrhenius segments. For appraisal of the convex plots fitted by two segments, see cautionary remarks in Ref. [1] regarding unwanted excessive use of parameters. Actually, often experimental data are not sufficiently accurate to distinguish between a piecewise segmented convex fit with temperature break point, and a continuous curve, possibly obeying our formula, which we recommended as to be preferred for testing.

Basic challenges for future theoretical work regard both regimes in a different way. A main result of this Letter is the correlation of the parameter d with parameters of the barrier in the potential energy surface penetrated by quantum mechanical tunneling.

Agreement with recently available exact quantum mechanical results and their experimental confirmation in a prototypical case is very satisfactory: it also propitiated extension to a recently tested Tsallis-type Transition State Theory [33] continued to include tunneling [40]. However, the complete characterization of the d parameter in the convex case still awaits to be put on a more solid ground beyond the argument that we provide, based on the formal analytical continuation from the correlation with the classical Tsallis non-extensive distribution.

This correlation, on the other hand, has to be regarded as phenomenological, work being needed to give d an interpretation providing its meaning regarding both the properties of the system and possibly the route to its quantitative appraisal, at least in simple model cases. In this effort, one might be helped by alternative (see e.g., Ref. [46]) approaches to thermodynamics and the associated non-Boltzmann distributions.

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Appendix A. Essentials of the deformed algebra of non-extensive statistical thermodynamics

In the main text, the formal relationship was noted between the present d-Arrhenius approach and the probability distribution function in Tsallis statistics. see Refs. [36,37], and further developments, e.g., Ref. [47]. Basic to the formalism is the remarkable discovery by Euler (see Ref. [48]) that the exponential function can be considered as the limit of a succession:

$$\exp(x) = \lim_{n\leftarrow\infty}\left(1+\frac{x}{n}\right) \tag{A1}$$

Identifying the deformation parameter d as the continuous generalization of $1/n$ and defining a d-exponential as follows:

$$\exp_d(x)\equiv(1+dx)^{\frac{1}{d}} \tag{A2}$$

(compare with Eq. (1)), a deformed algebra can be constructed, see Ref. [49] and references therein. In short, a d- logarithm can be defined analogously:

$$\ln_d(x)\equiv\frac{x^d-1}{d} \tag{A3}$$

and interesting properties can be established, such as the following:

$$\exp_d(x)\exp_d(y) = \exp_d(x+y+dxy) \tag{A4}$$

$$\ln_d(xy) = \ln_d(x)+\ln_d(y)+d\ln_d(x)\ln_d(y) \tag{A5}$$

$$\ln_d(x/y) = \frac{\ln_d(x)-\ln_d(y)}{1+d\ln_d(y)} \tag{A6}$$

$$\frac{d}{dx}[\exp_d(x)] = [\exp_d(x)]^{1-d} \tag{A7}$$

$$\int \exp_d(ax)dx = \frac{1}{(1+d)a}[\exp_d(ax)]^{1+d} \tag{A8}$$

Note a change in notation here, needed in order to avoid ambiguities with alternative usages of the q symbol in modern mathematical analysis and algebras, see for example Ref. [50]: in terms of Tsallis' q, we have $d = 1-q$. It is important to remark also that in most applications of Tsallis statistics the range of q is restricted between 0 and 1, while the extension to negative d is crucial to our treatment of the quantum tunneling regime.

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