Temperature dependence of chemical and biophysical rate processes: Phenomenological approach to deviations from Arrhenius law

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ABSTRACT

Arrhenius plots, which are used to represent the effects of temperature on the rates of chemical and biophysical processes and on various transport phenomena in materials science, may exhibit deviations from linearity. Account of curvature is provided here by a formula which involves a deformation of the exponential function, of the kind recently encountered in treatments of non-extensivity in statistical mechanics. We present here examples on diverse topics – respiration rates of plants, speed of gliding of bacteria, quantum mechanical tunneling in a chemical reaction – illustrating the variety of possible applications and the additional insight that can be gained.

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1. Introduction

Increasing evidence from a variety of studies of the temperature dependence of rate processes points out at the need of accounting for deviations from the Arrhenius law to accurately model situations occurring in modern applications of chemical kinetics to a wide range of phenomena. See Ref. [1], where it is outlined how such deviations manifest as concave or convex Arrhenius plots and can be referred to as sub- and super-Arrhenius behavior, respectively. A formulation (see Section 2.1) can be given in terms of a power series Taylor-like expansion of the logarithm of the reaction rate as a function of the inverse of the absolute temperature. In the present letter we point out an approach, denominated here as *deformed-Arrhenius (d-Arrhenius)* based on a non-Boltzmann distribution law occurring in non-extensive thermodynamics (Section 2.2). The aim is to provide possible insight on the observed deviations and a tool for extrapolating observations beyond the experimentally accessible range. Three examples are given in Section 3 and concluding remarks follow in Section 4.

2. Deviations from Arrhenius law

2.1. Quadratic Arrhenius plots

In an Arrhenius plot (see Fig. 1), the logarithm of an observed reaction rate k against the reciprocal of the absolute temperature

T sometimes turns out to be a curve, rather than the straight line expected according to the Arrhenius law

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right); \tag{1}$$

or

$$\ln k(T) = \ln A - \frac{E_a}{RT}; \tag{2}$$

where A is known as the pre-exponential factor and E_a as the activation energy. E_a is assumed to be independent of temperature in Eqs. (1 and 2), but in general it is given by [2]

$$E_a = -\frac{\mathrm{d}\ln k}{\mathrm{d}(1/RT)}. \tag{3}$$

In empirical Arrhenius plots, linearity (Eq. (2)), can be enforced, because number and accuracy of experimental data points are often not too high. Also, in most situations of biochemical and solution chemistry interest, the accessible range of the $1/T$ variable is small.

In Refs. [1] and [3], deviations from linearity in Arrhenius plots are accounted for by an additional *quadratic* term in $1/RT$ according to

$$\ln k(T) = \ln A + \frac{B}{RT} + \frac{C}{(RT)^2}, \tag{4}$$

where the sign of C dictates whether the plot is 'concave' or 'convex' (see Ref. [3]): correspondingly, we say that the reaction abides by a sub- or super-Arrhenius dependence. Accordingly, the activation energy E_a, being connected to the slope of the Arrhenius plot, as Eq. (3) shows, is no longer a constant but depends linearly on $1/T$:
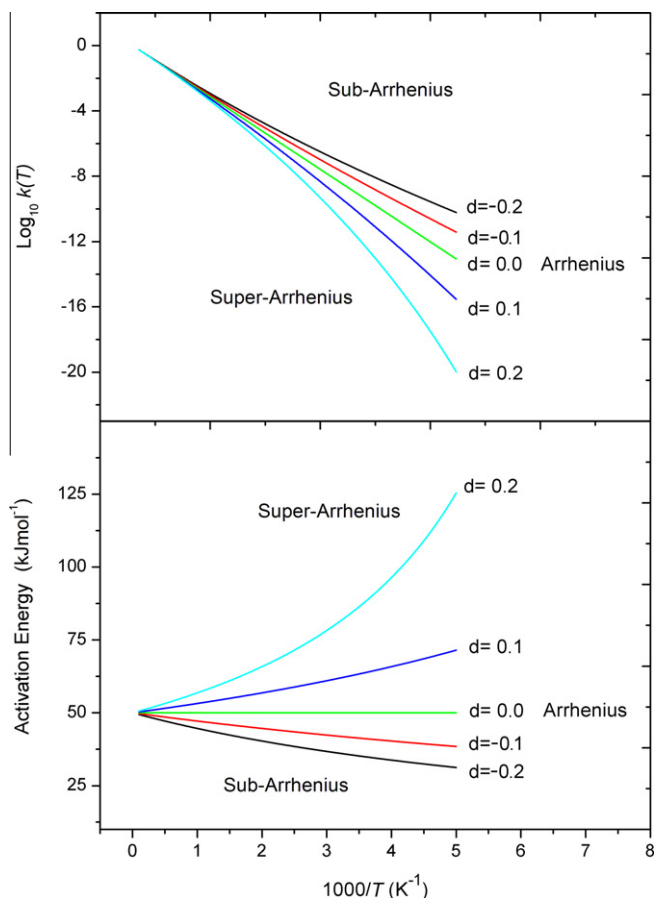
Figure 1. Arrhenius plot for a typical value the activation energy of 50 kJ/mol, and deviations described by the d parameter. In the graph we show the dependence of the function log $k(T)$ (upper panel) and the activation energy (lower panel), in terms of the inverse absolute temperature and of the d parameter. The super-Arrhenius processes are seen to be more sensitive to variations of the d parameter. Small changes in d produce large variations in the curvature of the logarithm of reaction rate. This figure has to be compared with Figure 2 in Ref. [1] and Figure 1 in Ref. [3].

$$E_a(T) = -\frac{d \ln k}{d(1/RT)} = -B - \frac{2C}{RT};$$ (5)

here the C coefficient, which is given by

$$C = -\frac{d^2 \ln k}{d(1/RT)^2},$$ (6)

is positive or negative for the sub- or super-Arrhenius cases, respectively.

As illustrated in the upper panel of Figure 1, the sub-Arrhenius case, where higher than expected rates are observed as temperature decreases, corresponds to a 'concave' curve (this occurs as e.g. for quantum mechanical tunneling or for the emergency of competing mechanisms). In cases of higher than expected rates as temperature increases, we have super-Arrhenius behavior, according to a materials science nomenclature [1]: this is associated to a 'convex' curve in the upper panel of Figure 1.

2.2. Deformed Arrhenius plots

In the scientific literature there are a variety of deformed algebras with applications in different areas of science [4–6]. In the present letter we adopt a generalization of the Arrhenius law based on algebraic deformations.

We define a *deformed* exponential function as follows,

$$\exp_d(x) \equiv [1 + dx]^{\frac{1}{d}}.$$ (7)

In the limit of the deformation parameter $d \to 0$, the d-exponential function (Eq. (7)) coincides with the usual exponential function according to the well known limit due to Euler

$$\exp(x) \equiv \lim_{n \to \infty} \left(1 + \frac{x}{n}\right)^n$$ (8)

by identifying the deformation parameter d as a continuous generalization of $1/n$.

Such a deformation of the exponential function occurs in the non-Boltzmann distribution of non-extensive Statistical Mechanics [4,7,8] and has been used in recent work on Eyring's transition state theory [9–11] and in other applications [12–17]. Our deformation parameter d corresponds to 1-q of Ref. [7] and [4], and to v-1 of Ref. [9]. Borges [4] provides basic mathematical background information.

Considering the d-exponential function (Eq. (7)) we introduce the reaction rate in the following way,

$$k(T) = A \exp_d\left(\frac{-\varepsilon}{RT}\right) = A \left[1 - d\frac{\varepsilon}{RT}\right]^{\frac{1}{d}},$$ (9)

and in the limit $d \to 0$, $\varepsilon \to E_a$ (a constant) and the usual Arrhenius reaction rate law is recovered. In applications, A, ε and d are three phenomenological parameters. Taking the logarithm of the reaction rate (Eq. (9)) we obtain the following expression for the Arrhenius plot,

$$\ln k(T) = \ln A + \frac{1}{d} \ln \left(1 - d\frac{\varepsilon}{RT}\right)$$ (10)

The logarithm of the reaction rate found in this way against reciprocal temperature shows a curvature, rather than the straight line behavior described by the Arrhenius law. Figure 1, to be compared with Figure 2 in Ref. [1] and Figure 1 in Ref. [3], shows that the curvature of sub- and super-Arrhenius processes can be described by changing the d parameter.

The activation energy is now

$$E_a = -\frac{d \ln k}{d(1/RT)} = \varepsilon \left(1 - \frac{d\varepsilon}{RT}\right)^{-1}.$$ (11)

Comparing with the quadratic expression, (Eq. (4)), the correspondence holds for small deformations, since when $d\varepsilon/RT \ll 1$, Eq. (11) can be expanded as

$$E_a \cong \varepsilon + d\frac{\varepsilon^2}{RT} + \cdots$$ (12)

and in this limit (see Eq. (5)),

$$\varepsilon = -B \quad \text{and} \quad d\varepsilon^2 = -2C.$$ (13)

According to Eq. (10), we can use the logarithm of the reaction rate (Eq. (9)) to describe experimental data where curved (sub- or super-Arrhenius) plots are observed. It is important to point out that the success of this fitting procedure is, in part, due to the d-exponential function's flexibility. Also, Eq. (10) uses only three parameters to fit the experimental data, while formulations based on Eyring's transition state theory [10,11] appear to need more parameters, like all treatments employing piecewise linear fits matched at an Arrhenius break temperature (see [1]).

3. Results and discussion

In the following, we discuss the significance of the deformed Arrhenius approach, placing it in a broader context by considering three different processes. The first case is related to a study of the temperature dependence of the – respiration rates of leaves [18]. The next case study considers the leg-substrate interaction mechanism to explain the observed temperature dependence of *Myco-*
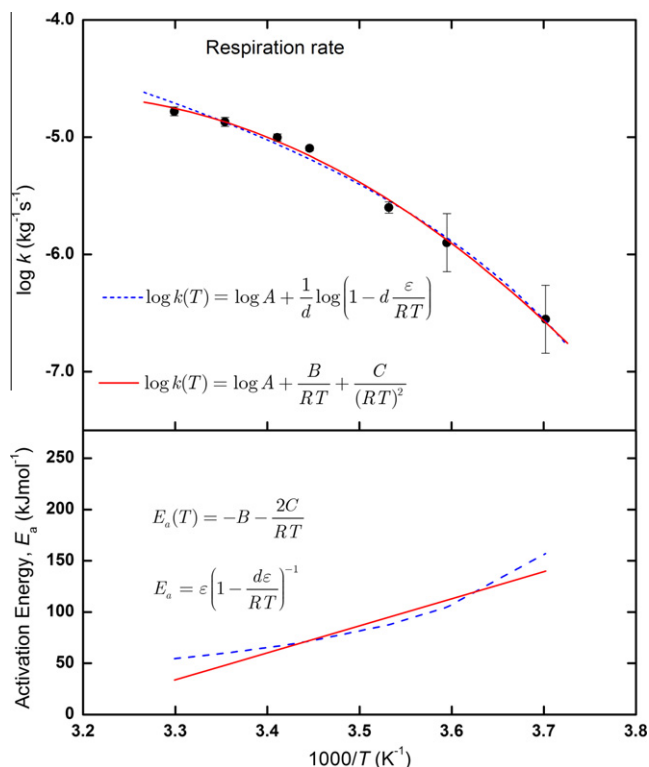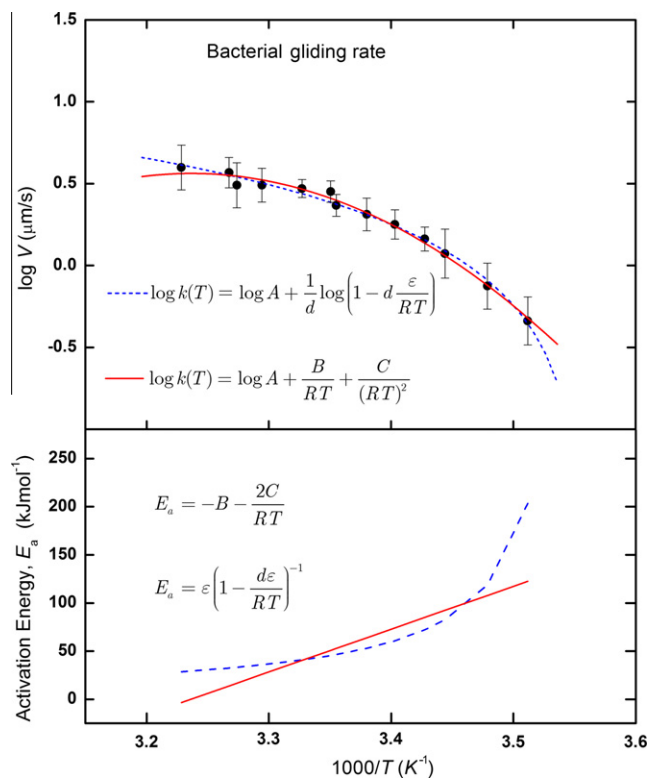
Figure 2. Arrhenius and activation energy plots for the respiration rate of *Camellia Japonica* leaves. The upper panel is semi-logarithmic plot of the reaction rate data from the experiment (dots), *d*-Arrhenius (dashed line) and quadratic fit (solid line) versus $1/T$. The lower panel shows the corresponding $1/T$ dependence of the activation energy (E_a) given in kJ/mol using both approaches. The $\log_{10} A$, *B*, and *C* parameters of quadratic approach are -74.634, 3.667×10^5 (kJ/mol) and -4.802×10^8 (kJ^2/mol^2), respectively. This fit is consistent with that of Ref. [1], apart from the higher number of significant digits presented here. In the case of the *d*-Arrhenius approach $\log_{10} A = -1.456$, $\varepsilon = 8593$ (kJ/mol) and $d = 0.247$ is dimensionless. The reaction rates $k(T)$ are given in kg^{-1} s^{-1}, Ref. [1].

Figure 3. Arrhenius and activation energy plots on the bacterial gliding application. The upper panel is semi-logarithmic plot of the reaction rate data from the experiment (dots), *d*-Arrhenius (dashed line) and quadratic fit (solid line) versus $1/T$. The lower panel shows the corresponding $1/T$ dependence of the activation energy (E_a) given in kJ/mol using both approaches. The $\log_{10} A$, *B*, and *C* parameters of the quadratic approach are -121.11, 6.252×10^5 (kJ/mol) and -8.031×10^8 (kJ^2/mol^2), respectively. In the case of the *d*-Arrhenius approach, $\log_{10} A = 1.787$, $\varepsilon = 2654$ (kJ/mol) and $d = 0.881$ is dimensionless. The reaction rates $k(T)$ are given in μm/s, Ref. [19].

plasma mobile bacteria [19]: the recently published findings on this subject establish an important bridge with disciplines – chemical kinetics, materials science – for which similar behavior has been studied in a variety of rate processes. The enhanced increase in reaction rates with temperature corresponds to an apparent decrease of the activation energy and is the reason for referring to such curvature as 'super-Arrhenius' temperature dependence (Fig. 1). Data found when plotting both the respiration rates of *Camellia Japonica* leaves [1,18], as when plotting 'peel-off' rates of *M. mobile*, show a 'convex' curved shape. As a third prototypical case, we consider the reaction of fluorine atoms with hydrogen molecules, where quantum effects play a crucial role at the investigated temperatures and the reactivity is essentially under barrier, leading to the 'concave' curved shape of sub-Arrhenius behavior.

3.1. Plant – respiration rates

In Refs. [1] and [20], we have studied the respiration of *Camellia Japonica* leaves stored under atmospheric pressure in temperature controlled, light sealed vessels, by sampling the oxygen/carbon dioxide ratio in the volume after specific time intervals. The rate of oxygen consumption and carbon dioxide production gives an insight into the mechanism of the enzymatic reactions that take place inside the mitochondrion. Ref. [1] reports oxygen-18 measurements and correlates super-Arrhenius behavior to increase of catalytic activity as temperatures increases. Figure 2 reports the Arrhenius and activation energy plots on the respiration of *C. Japonica* leaves.

3.2. Bacterial gliding

A recent paper [19] reports deviation from Arrhenius temperature dependence of motility of the bacterium *M. mobile* (regarding mechanism of gliding on solid surfaces, see Ref. [20]). *M. mobile* glides on solid substrates, a motility attributed to the interaction between the substrate and many single protein 'legs' protruding the membrane of the bacteria. Cells of *M. mobile* were deposited on a glass slide under an optical microscope with a temperature controlled stage. As had been reported previously [21], the gliding velocity was measured with a video camera and was observed to increase with temperature. The authors of Ref. [19] model the motor function of the leg proteins that goes through several separate steps in a single cycle. The 'foot' reaches down to contact and stick to a surface, subsequently dragging the leg along. It only 'peels off' the surface when it is being dragged forward by the leg (in Figure 2B of Ref. [19]). The temperature dependence of the individual foot-substrate interaction is reflected in similar temperature dependence for the velocity, generated by all the bacteria's legs as an ensemble. In Figure 3B of Ref. [19], data are displayed in an Arrhenius plot, where the logarithm of the rate *k* at which a protein foot peels off is reported as a function of $1/T$. See also Refs. [22,23]. When the data from Ref. [19] are fitted either using the quadratic polynomial of Eq. (4) or by the present *d*-deformed Arrhenius formula, the fits are found to follow the data points excellently, as shown in the upper panel of Figure 3. The corresponding activation energy of the process as a function of reciprocal temperature is plotted in the lower panel of Figure 3. Note that the authors of

Ref. [19] call sub-Arrhenius behavior the observed curved appearance of the plot. This is in contrast with the materials science literature, adopted here and recently discussed in the two papers [1] and [18] on – respiration rates of leaves. Another matter of nomenclature involves what Chen et al. [19] refer to as an Arrhenius factor, which is given in units of $k_B T$ and is evidently to be identified with an activation energy. The reported finding that this quantity turns out to be a decreasing function of temperature (Fig. 3) is indeed consistent with super-Arrhenius behavior, resulting in higher than expected rates when temperature increases. One of the purposes of this letter is therefore also that of reconciling the nomenclature used by the authors of Ref. [19] with the one that has become customary in the kinetics of a variety of phenomena, adopted here and in part accounted for in papers [1] and [18].

3.3. Tunneling in the F + H₂ reaction

As a third example we consider the reaction of a fluorine atom with hydrogen molecules from the d-Arrhenius point of view. In Ref. [24] benchmark quantum mechanical rate constants have been obtained using various potential energy surfaces differing in details of the approach to the transition state. In view of the central importance of rate constants in chemical kinetics, extensive experimental and theoretical investigations have been devoted to their determination for this prototypical reaction and to the study of their temperature dependence, in an effort to provide insight into the microscopic mechanism of chemical processes, and also in or-

der to test theoretical models of reaction rates. As discussed in Ref. [24], the rate constants that have been calculated in a broad range of temperatures, lead to the finding that reaction rates have an Arrhenius-like behavior (exponential fall-off with inverse temperature),interpreted as a manifestation of the fact that typically reactivity proceeds overcoming a natural energy barrier giving rise to an effective "activation energy". Statistical theories satisfactorily reproduce these features, but under cold and very cold conditions this picture breaks down, and full quantum mechanical calculations are needed. Figure 4 reports exact quantum mechanical results [24], showing that the effect is small but definitely in the sense of a 'concave' curvature, and therefore of a sub-Arrhenius behavior. Here deviation from the Arrhenius law is small, and both the quadratic and the d-deformed approaches give essentially the same results.

4. Conclusion and further remarks

As a conclusion to this letter, we note that the three cases are just illustrations of how to cope with a phenomenological description of deviations from Arrhenius's law. Experimental and other evidence is increasing rapidly. Both the quadratic expansion and the d-deformed formula have merits, the latter providing somewhat higher flexibility and enabling extrapolation to more extended ranges of temperature. This is particularly evident in Figure 2 and especially Figure 3, where the decrease with temperature of the activation energy, according to the quadratic fit, appears to unphysically tend to negative values, while an asymptotically correct behavior is described by the d-deformation approach.

The previous papers [1 and 18] discuss and provide documentation of observed super-Arrhenius behavior in a variety of rate processes (for an additional reference in materials science, see Ref. [25]). To those reference lists, we add here other papers from materials science where sub-Arrhenius behavior is explicitly mentioned, described and illustrated: Ref. [26], see Figure 1, Ref. [27], see Figures 11 and 12, Ref. [28] see Figure 2b. All these latter examples involve concavity, in Arrhenius plot, to be contrasted with the 'convex' case of Figure 2. Indeed, while the figures illustrate the suitability of the d-deformation formula for the phenomenological description of the observed deviation of linearity in Arrhenius plots, a detailed mechanistic interpretation of parameters evidently varies according to the diversity of the contexts. It is expected that the established relationship with a distribution law occurring in non-extensive statistical mechanics can provide further insight with respect to the quadratic polynomial approach and the underlying (microscopic and thermodynamic) interpretations discussed in Ref. [1].

Finally, on the general question of caution needed in attributing deviations from linear Arrhenius dependence to abrupt changes in mechanism or to phase-like transitions at a 'break temperature', our discussion in Ref. [1] finds interesting correspondence in biophysical contexts. Such a word of caution appears that needs to be applied for example to early work by Anson [29], who also quotes Refs. [30–32], and to the more recent one by Boehm et al. [33], who propose non-Arrhenius fits with a break temperature: see discussions in Refs. [34,35]. In general, these approaches imply one parameter more than those discussed here, which are therefore to be recommended from the viewpoint of economy of a phenomenological description.

Current work involves extension to a variety of other cases, and (more importantly) to the interpretation of deformations in terms of non-extensive statistical mechanics, in view of getting further insight with respect to the microscopic and 'thermodynamic' views sketched in Ref. [1].
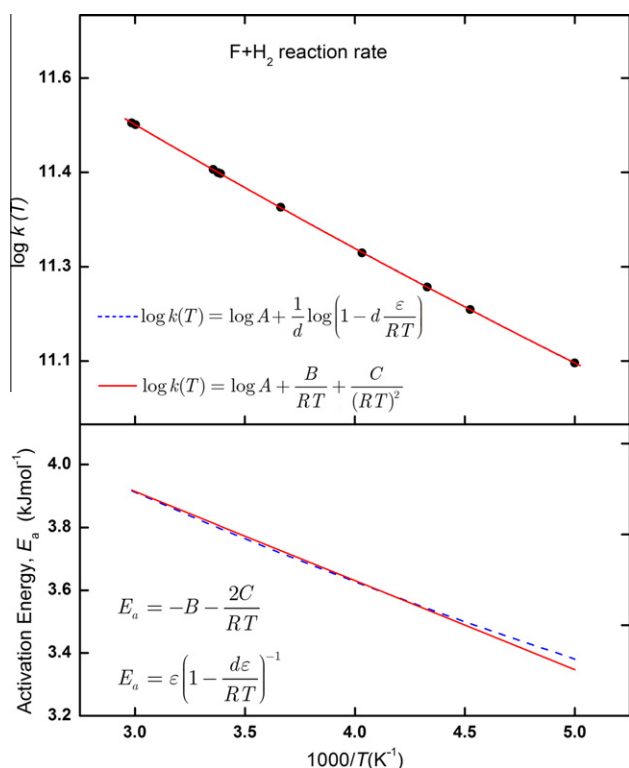
Figure 4. Arrhenius and activation energy plots on the F + H₂ reaction. The upper panel is semi-logarithmic plot of the reaction rate data from the d-Arrhenius (dashed line) and quadratic fit (solid line) versus $1/T$. The lower panel shows the corresponding $1/T$ dependence of the activation energy (E_a) given in kJ/mol using both quadratic and deformed Arrhenius approaches. The results emphasize that the non-Arrhenius tunneling behavior of the F + H₂ quantum mechanics calculated rate constants, at low temperature, is equally well described by both approaches. The $\log_{10} A$, B, and C parameters of quadratic approach are 12.156, −2069.0 (kJ/mol) and 5.119×10^5 (kJ²/mol²), respectively. For the d-Arrhenius approach, $\log_{10} A = 12.175$, $\varepsilon = 5119$ (kJ/mol) and $d = -0.167$ is dimensionless. It can be checked that Eq. (13) approximately hold. The reaction rates $k(T)$ are given in cm³/molecule·s, Ref. [24].

Acknowledgements

References

[1] M. Nishiyama, S. Kleijn, V. Aquilanti, T. Kasai, Chem. Phys. Lett. 482 (2009) 325.
[2] D.G. Truhlar, J. Chem. Edu. 55 (1978) 309.
[3] D.G. Truhlar, A. Kohen, Proc. Natl Acad. Sci. USA 98 (2001) 848.
[4] E.P. Borges, Physica A-Statistical Mech Appl. 340 (2004) 95.
[5] R.L. Rubin, Aequationes Math. 59 (2000) 38.
[6] T.H. Koornwinder, Special functions and q-commuting variables, <http://Arxiv.org/PS_cache/Q-Alg/Pdf/9608/9608008v2.pdf>. (1996).
[7] C. Tsallis, J. Stat. Phys. 52 (1988) 479.
[8] E.P. Borges, J. Phys. A-Mathematical. Gen. 31 (1998) 5281.
[9] E.K. Lenzi, C. Anteneodo, L. Borland, Phys. Rev. E 63 (2001) 051109.
[10] W. Quapp, A. Zech, J. Comput. Chem. 31 (2010) 573.
[11] J.L. Zhao, J.D. Bao, Commun. Theor. Phys. 44 (2005) 752–756.
[12] H.C.B. de Oliveira, F.C. Rangel, C.S. Esteves, F.M.C. Vieira, K.C. Mundim, J. Phys. Chem. A 113 (2009) 14691–14698.
[13] C.S. Esteves, H.C.B. De Oliveira, L. Ribeiro, R. Gargano, K.C. Mundim, Chem. Phys. Lett. 427 (2006) 10–13.
[14] L.E.E. Lopez, R. Gargano, K.C. Mundim, J.J.S. Neto, Chem. Phys. Lett. 361 (2002) 271–276.
[15] M.A. Moret, P.G. Pascutti, K.C. Mundim, P.M. Bisch, E. Nogueira, Phys. Rev. E 63 (2001) 020901.
[16] M.A. Moret, P.G. Pascutti, P.M. Bisch, K.C. Mundim, J. Comput. Chem. 19 (1998) 647–657.
[17] K.C. Mundim, C. Tsallis, Int. J. Quantum Chem. 58 (1996) 373–381.
[18] M. Nishiyama, S. Kleijn, V. Aquilanti, T. Kasai, Chem. Phys. Lett. 470 (2009) 332–336.
[19] J. Chen, J. Neu, M. Miyata, G. Oster, Biophys. J. 97 (2009) 2930–2938.
[20] M. Miyata, Trends Microbiol. 16 (2008) 6–12.
[21] M. Miyata, W.S. Ryu, H.C. Berg, J. Bacteriol. 184 (2002) 1827–1831.
[22] T. Nonaka, J. Adan-Kubo, M. Miyata, J. Bacteriol. 192 (2010) 636–642.
[23] C. Lesoil, T. Nonaka, Sekiguchi, T. Osada, M. Miyata, R. Afrin, et al., Biochem. Biophys. Res. Commun. 391 (2010) 1312–1317.
[24] V. Aquilanti, S. Cavalli, D. De Fazio, A. Volpi, A. Aguilar, J.M. Lucas, Chem. Phys. 308 (2005) 237–253.
[25] P.P. Cortet, L. Vanel, S. Ciliberto, Europhys. Lett. 74 (2006) 602–608.
[26] U. Albrecht, H. Bässler, Chem. Phys. Lett. 235 (1995) 389–393.
[27] M.P. Kennett, C. Chamon, L.F. Cugliandolo, Phys. Rev. B 72 (2005) 024417.
[28] C. Lee, J.W. Oh, C.S. Choi, N.S. Lee, N. Kim, Bull. Korean Chem. Soc. 30 (2009) 97–101.
[29] M. Anson, J. Mol. Biol. 224 (1992) 1029–1038.
[30] J.A. Biosca, F. Travers, T.E. Barman, FEBS Lett. 153 (1983) 217–220.
[31] J.A. Biosca, F. Travers, D. Hillaire, T.E. Barman, Biochemistry 23 (1984) 1947–1955.
[32] K.W. Ranatunga, J. Physiol.-London 351 (1984) 517–529.
[33] K.J. Bohm, R. Stracke, M. Baum, M. Zieren, E. Unger, FEBS Lett. 466 (2000) 59–62.
[34] F.S. Soo, J.A. Theriot, Proc. Natl Acad. Sci. USA 102 (2005) 16233–16238.
[35] K. Kawaguchi, S. Ishiwata, Biochem. Biophys. Res. Commun. 272 (2000) 895–899.