Supplementary Materials for

dQ_{d10}GSA Fitting code

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Materials and Methods

In this tutorial, unless otherwise noted, "dQ_{10}GSA " will refer to computational code.
dQ_{10}GSA is a multi-platform application and is written in Python, it is a free open-source code compatible with Windows, Linux, and MacOS platforms.

The novelty of this code is its general scope and particular exploit of Q_{d10} formulations to cope with Arrhenius and non-Arrhenius behavior at different temperatures, a topic which is the focus of recent intense investigations in biological processes. It presents a very intuitive graphical interface which we believe to provide an excellent working tool for researchers and as courseware to teach rates versus temperature. The code is referred to as "dQ_{10}GSA " (see Figure 1), that works with concepts relates to the diffusion process or rates (Eq.4), activation energy (Eq.5) and Q_{10} coefficient (Eq.6). It offers the possibility of estimating phenomenological parameters from Arrhenius and d-Arrhenius plots using the stochastic optimization method, Generalized Simulated Annealing (GSA)(*1–3*).
We expect that this code serve as a quick and practical tool for data characterization from experimental data and different proposed models. It presents a very intuitive graphical interface which we believe to provide an excellent working tool for emphasize the need to generalize the usual Q_{10} approach.

In the main window of the code, the user can choose between two main options of rate constants: (i) Usual Arrhenius plot and (ii) deformed Arrhenius and its Q_{10} definitions.

Steps to run the code

1. First of all, open the file containing the experimental data or type on the screen, for example a table $T \times \ln(k)$, or others options of input. The open file button appears in the high side of the main window.

2. Select the model to adjust the experimental data (see 

). In this step the code automatically initialize with the appropriate model parameters. We suggest to use, at first, the usual Arrhenius model because it has just two parameters.

3. To initialize the fitting process click on the button 

. The fitting time depend on the number of GSA loop. To get better fitting just click again or increase the number of "Number of GSA loop".

4. After the fitting procedure it is possible to plot different kind of graphics as shown in the window "Plot" (Fig.2) or save the fitted parameters toa text file by pressing the button Save.

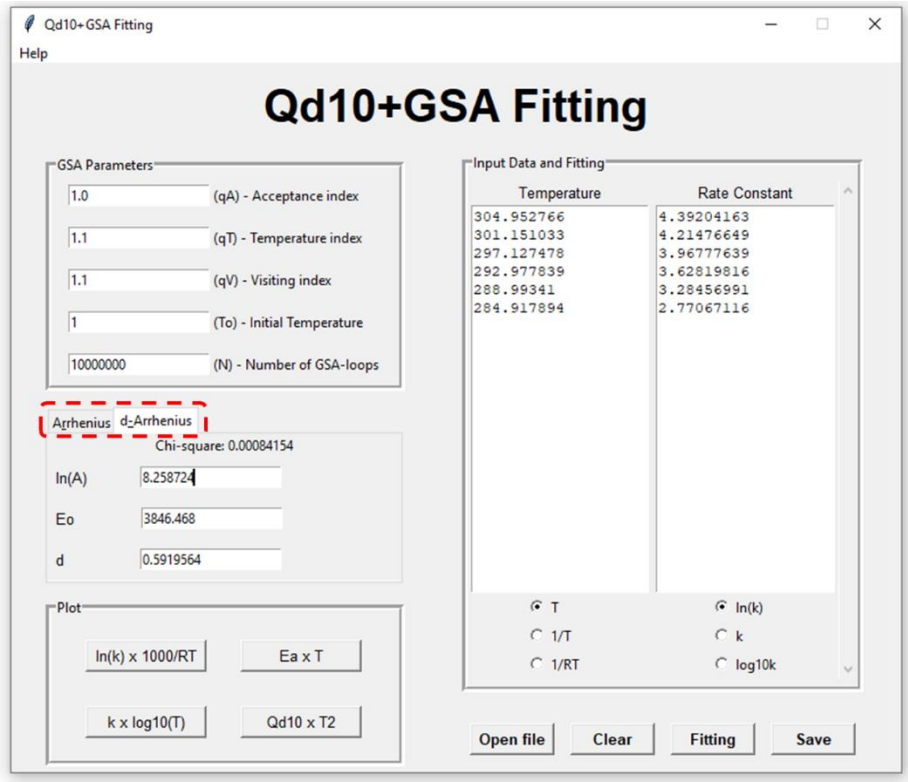

Fig. 1: Main window of the computational code.

The raw data and the fitted curve are plotted on the Fit Curve window (Fig.2).

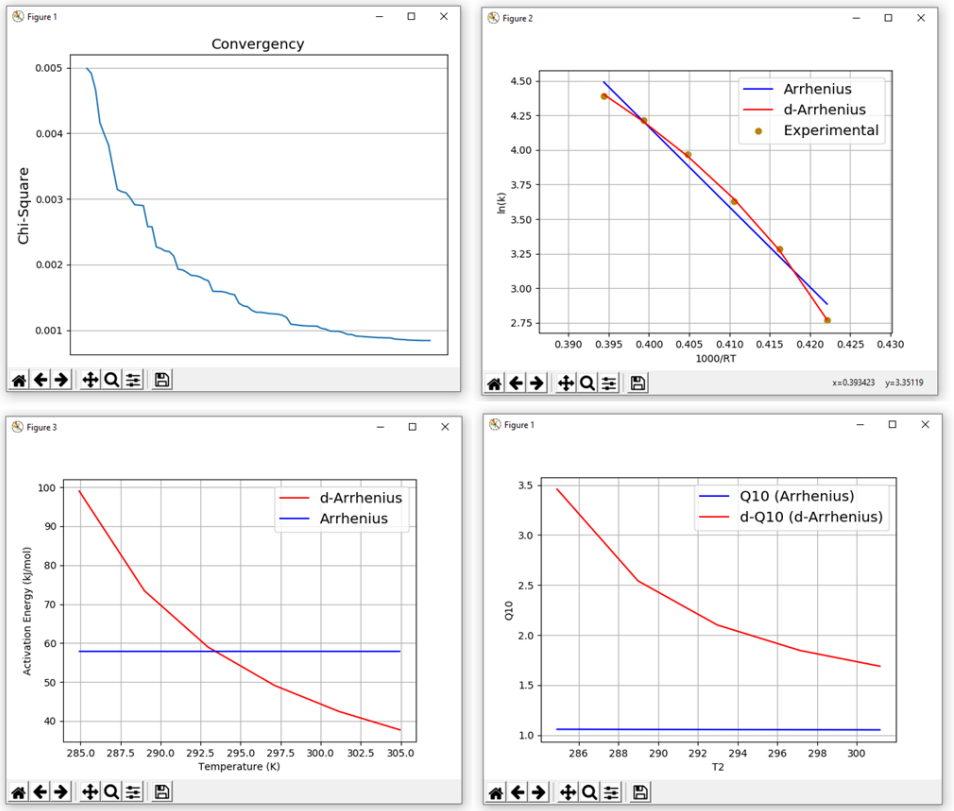

Fig. 2: Some example of fitting graphics

The stochastic fitting procedure is based on the minimization of the simple χ^2 method, defined as

$$\chi^2 = \sum_{i=1}^{N} \left(f_{exp_i} - f_{the_i}\right)^2$$

Where N is the number of experimental data, f_{exp_i} is the i-th experimental point and f_{the_i} is the i-th theoretical value of the Arrhenius or *d*-Arrhenius model, as described in Eq. 2 and Eq. 4, respectively.

Mathematical Approaches:

Q_{10} Usual Model

The usual model for the Q_{10} coefficient is expressed by the following equation:

$$Q_{10} = \left[\frac{k(T_2)}{k(T_2)}\right]^{10/(T_2 - T_1)} . \quad (1)$$

Where T is the temperature in Celsius degrees or Kelvin and k is the rate constant expressed as exponential decay with temperature, commonly expressed by the Arrhenius equation, as follows:

$$k = Ae^{-E_o/(T_2-T_1)} \tag{2}$$

where A, E_o and R are the frequency factor, activation energy of a reaction, and ideal gas constant, respectively.

Deformed Arrhenius Model

The proposed mathematical model is based on the theory of deformed exponential functions(*4*, *5*). Deformed exponential functions are derived from the definition of Euler's exponential function (*6*), where $e^x = \lim_{n\to\infty}\left(1+\frac{x}{n}\right)^n$, using the following equation:

$$e_d^{\pm ax} = \left(1 \pm dax\right)^{1/d}, \tag{3}$$

where $d = 1/n$ (deformation parameter) and a are real numbers that satisfy the equation $e^{-ax} = \lim_{d\to 0} e_d^{-ax}$. This class of exponential functions was used for the first time in statistical physics by Landau, in the book Statistical Physics(*7*).

For a diffusion process the rate equation, is defined as following:

$$k_d\left(T\right) = A\left(1 - d\,\frac{E_o}{RT}\right)^{1/d}, \tag{4}$$

whose activation energy, according to the IUPAC definition, is given by:

$$E_a = -\frac{\partial \ln\left(k_d\right)}{\partial \frac{1}{RT}} = \frac{1}{f}\frac{\partial \mathrm{l}\, f}{\partial \frac{1}{RT}} = E_o\left(1 - d\,\frac{E_o}{RT}\right)^{-1} = -E_o f^{-d}, \tag{5}$$

where $k_d(T) = Af(T)$ is a rate or coefficient of diffusivity and $f(T)$ is the contribution of temperature variation. Using Eq. (5), the new Q_{d10} coefficient is given by:

$$Q_{d10} = \left[\frac{k_d(T_2)}{k_d(T_1)}\right]^{\frac{10}{T_2 - T_1}} \tag{6}$$

$k(T) = \lim_{d\to 0} k_d(T)$ and $Q_{10} = \lim_{d\to 0} Q_{d10}$, which render a possible generalisation of rates and Q_{10} coefficients. The algebraic sign of the *d*-parameter controls the functional behaviour of the generalized Arrhenius law; d < 0 gives rise to a concave or ´sub-Arrhenius´ behaviour, $d > 0$ to a convex or 'super-Arrhenius', and at $d = 0$ the conventional linear Arrhenius form is attained.

GSA- Generalized Simulated Annealing Procedures

Simulated Annealing methods have been used successfully in the description of a variety of global extremization problems. Simulated Annealing methods have attracted significant attention due to their suitability for large scale optimization problems, especially for those in which a desired global minimum is hidden among many local minima. The basic aspect of the Simulated Annealing method is that it is analogous to thermodynamics, especially concerning the way that liquids freeze and crystallize, or that metals cool and anneal. The first nontrivial solution along this line was provided by Kirkpatrick et al(*8*)(*9*) for classical systems, and also extended by Ceperley et al(*10*) to quantum systems. It strictly follows the quasi-equilibrium Boltzmann-Gibbs statistics using a Gaussian visiting distribution, and is sometimes referred to as *Classical Simulated Annealing* (CSA) or *Boltzmann machine*. The next interesting step in this subject was Szu and Hartley proposal(*11*) to use a *Cauchy-Lorentz visiting distribution*, instead of a Gaussian distribution. This algorithm is referred to as *Fast Simulated Annealing* (FSA) or *Cauchy machine*. In 1996, Tsallis and Mundim(*1*) proposed a generalization approach referred to as *Generalized Simulated Annealing* (GSA)(*12–14*) used in this code.
Additional information and use of GSA visit the site:

Stochastic Dynamics Through Generalized Simulated Annealing

REFERENCES

1. K. C. Mundim, C. Tsallis, Geometry optimization and conformational analysis through generalized simulated annealing. *Int. J. Quantum Chem.* **58**, 373–381 (1996).
2. A. Dall'Igna Júnior, R. Silva, K. C. Mundim, L. E. Dardenne, Performance and parameterization of the algorithm Simplified Generalized Simulated Annealing. *Genet. Mol. Biol.* **27**, 616–622 (2004).

3. M. D. De Andrade, K. C. Mundim, L. A. C. Malbouisson, Convergence of the generalized simulated annealing method with independent parameters for the acceptance probability, visitation distribution, and temperature functions. *Int. J. Quantum Chem.* **108** (2008), doi:10.1002/qua.21736.

4. V. Aquilanti, K. C. Mundim, M. Elango, S. Kleijn, T. Kasai, Temperature dependence of chemical and biophysical rate processes: Phenomenological approach to deviations from Arrhenius law. *Chem. Phys. Lett.* **498** (2010), doi:10.1016/j.cplett.2010.08.035.

5. C. Wikipedia, Aquilanti–Mundim deformed Arrhenius model --- {Wikipedia}{,} The Free Encyclopedia (2019), (available at https://en.wikipedia.org/w/index.php?title=Aquilanti–Mundim_deformed_Arrhenius_model&oldid=888041699).

6. L. Euler, *Introductio in analysin infinitorum* (Apud Bernuset, Delamolliere, Falque & soc., Lugduni, 1797; file://catalog.hathitrust.org/Record/000168048).

7. L. D. Landau, E. M. Lifshitz, *Physique statistique; 2rd ed. BT - Physique théorique* (MIR, Moscow, 1967; http://cds.cern.ch/record/247923).

8. S. Kirkpatrick, C. D. Gelatt, M. P. Vecchi, *Science (80-.).*, in press, doi:10.1126/science.220.4598.671.

9. S. Kirkpatrick, Optimization by simulated annealing: Quantitative studies. *J. Stat. Phys.* **34**, 975–986 (1984).

10. D. CEPERLEY, B. ALDER, *Science (80-.).*, in press, doi:10.1126/science.231.4738.555.

11. H. Szu, R. Hartley, Fast simulated annealing. *Phys. Lett. A.* **122**, 157–162 (1987).

12. M. A. Moret, P. M. Bisch, K. C. Mundim, P. G. Pascutti, New stochastic strategy to analyze helix folding. *Biophys. J.* **82** (2002), doi:10.1016/S0006-3495(02)75471-4.

13. M. A. Moret, P. G. Pascutti, P. M. Bisch, K. C. Mundim, Stochastic molecular optimization using generalized simulated annealing. *J. Comput. Chem.* **19**, 647–657 (1998).

14. M. A. Moret, P. G. Pascutti, K. C. Mundim, P. M. Bisch, E. Nogueira Jr., Multifractality, Levinthal paradox, and energy hypersurface. *Phys. Rev. E - Stat. Nonlinear, Soft Matter Phys.* **63** (2001), doi:10.1103/PhysRevE.63.020901.