AN INTRODUCTION TO THE BOLTZMANN FACTOR BY USING INFORMATION TECHNOLOGY TOOLS

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Abstract
We present an experiment and simulations aimed at introducing the Boltzmann factor mathematical expression and at illustrating the fundamental concepts on which it is grounded. The experiment uses an easily available Microcomputer Based Laboratory apparatus. Simulations are developed in the Net-Logo environment that, besides having a friendly user-interface, allows an easy interaction with the algorithm. The approach supplies a pedagogical support for the introduction of the Boltzmann factor at undergraduate level to students without a background in statistical mechanics.

1. Introduction
One of the main objectives of Science is to supply an unifying framework for the description and interpretation of phenomena developing in different fields. In physics, the Boltzmann factor (B-factor), $e^{-\frac{E_i}{kT}}$, is at the basis of the description of a great amount of systems, both classical and quantum. For a system of particles at a given temperature, T, it represents the fraction F_i of particles with energy E_i.

To understand why the B-factor has its specific form involves a mathematical analysis whose flow of logic is hard to see and that is not always at the level of high school or college students' preparation. Books for undergraduate students use different approaches and arguments for its derivation: most of them, following Feynman (Feynman et al., 1963), justify it heuristically by referring to the "exponential atmosphere", others analyse the quasi-continuous states of the heat bath (Feynman, 1974; Reif, 1965) or use the method of the most probable distribution (Schrödinger, 1967).

Some pedagogical experiments directly related to the B-factor have been published, as that suggested by Einstein and first performed by Perrin: the sedimentation equilibrium of colloidal suspensions. The experiment analyses the behaviour of small plastic spheres suspended in a liquid slightly denser than water representing a miniature atmosphere (Horne, 1973). The measure of the sphere concentration at different heights shows to obey the Boltzmann distribution.

MBL can supply ways to use the same approach in design experiments belonging at different scientific fields. In a previous paper (Battaglia et al., 2009) we described experiments analysing thermodynamic and electric phenomena and introduced an analogical mechanical model able to interpret the experimental results in different fields of physics, highlighting the physical meaning of the B-factor. In this paper, we present an alternative experiment, based on the study of the speed of a chemical reaction as a function of the reactant temperature and propose a working model able to make sense of the experimental results and its implementation. The conclusion section outlines the main features of the approach and its pedagogical relevance.

2. The experiment
The chemical reaction we use here to study the temperature dependence of its speed occurs between two solutions: solution A consisting of sodium disulfite ($Na_2S_2O_5$) and sodium sulfite (Na_2SO_3) dissolved in water [1]; solution B, consisting of methanal or formaldehyde (HCHO) and phenolphthalein ($C_{20}H_{14}O_4$), also made up with water [2].
The main reaction develops between the bisulfite ion (HSO_3^-) and methanal (HCHO):

$$HCHO + HSO_3^- = CH_2OHSO_3^- \qquad (1)$$

Two other interesting clock reactions can be taken into account. Sulfite ions (SO_3^{2-}) react with the methanal and water in a slow reaction, where OH^- ions are produced:

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[1] 5g of $Na_2S_2O_5$ and 1g of Na_2SO_3 in 1 litre of water.
[2] 10 cm^3 of HCHO and 20 cm^3 of $C_{20}H_{14}O_4$ in 1 litre of water.

$$H_2O + HCHO + SO_3^{2-} = CH_2OHSO_3^- + OH^- \qquad (2)$$
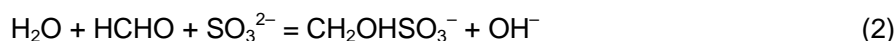
The OH^- ions would turn the phenolphthalein pink but they are captured by bisulfite ions, much faster that they are generated, in the quick reaction:

$$OH^- + HSO_3^- = SO_3^{2-} + H_2O \qquad (3)$$

Once all the bisulfite ions have been exhausted by the main reaction, OH^- ions can no longer be removed via reaction (3) and the phenolphthalein turns pink to indicate the conclusion of the main reaction.

In our measurements, we study the temperature dependence of the speed of reaction (1), i.e. the speed of production (during reaction (2)) of the quantity of OH^- ions that is to react with the disulfite ions. As the end of reaction (1) is marked by the solution mixture colour change, we measure its light absorbance, by using a microcomputer based spectrometer, in order to detect the exact instant in which the phenolphthalein starts turning pink[3].

The experimental apparatus is shown in Fig. 1 and consists of a transparent glass cylinder, containing solution A, placed in a large Plexiglas container filled with water, whose temperature can be controlled by a thermoregulator. An optic fibre is placed inside the cylinder, together with a MBL probe that monitors the solution's temperature. A white light source is placed near the Plexiglas container, as shown in Fig. 1. Solution B is simply placed in another cylinder and made reach an equilibrium temperature with the thermal bath. By means of the spectrometer, we study the light absorbance of the mixture obtained when solution B is poured into solution A cylinder.
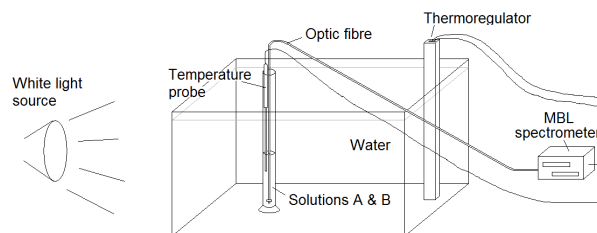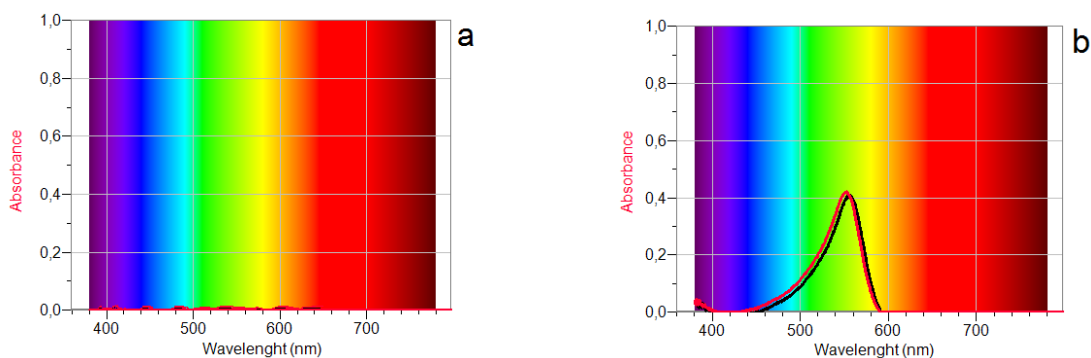

Figure 1: The experimental apparatus.

In order to determine the exact wavelength of light at which to conduct the absorbance measurement, we first studied the solution A & B absorbance as a function of light wavelength. This is represented by Fig. 2a and 2b, that report the absorbance spectra before and after the end of reaction (1).

Figures 2a and 2 b. Spectra of light absorbance of solutions A & B before (a) and after (b) the main reaction (1) has ended.

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[3] It is possible to simply use a chronograph to measure the time interval during which the main reaction develops. Yet this method is affected by a relevant uncertainty, as the exact instant at which the phenolphthalein actually starts turning pink has to be visually determined before pushing the chronograph stop button.

As it easy to see, the spectrum is almost flat during the development of reaction (1) (i.e., no light is absorbed), while it shows a marked peak at a given wavelength (about 552 nm) when the main reaction has ended and the phenolphthalein reacts with OH^- ions, turning pink.

We, then study the absorbance of solutions A & B at 552 nm and monitor the speed of the main reaction between the two solution reactants by measuring the time delay between solution B pouring into solution A and the first detection of the absorbance signal at 552 nm. Fig. 3 shows some of the obtained results, from which it is evident that at a given temperature (294 K) the main reaction lasts more than in the case of a higher temperature (315 K). The exact duration of the reaction, at each temperature value, is calculated by taking the time interval between the signal onset and the instant at which the abrupt increase of the absorbance at 552 nm is detected by the sensor, marking the instant at which the two solution mixture starts to turn pink.
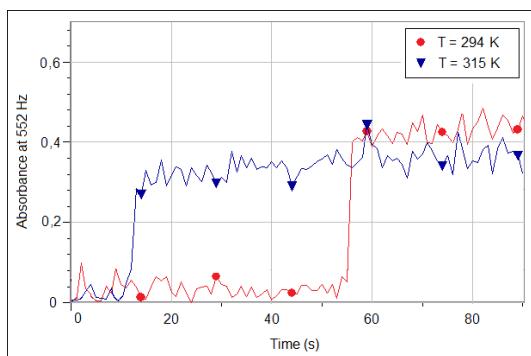

Figure 3. Absorbance of solutions A & B at 552 nm versus time at two different temperature values.
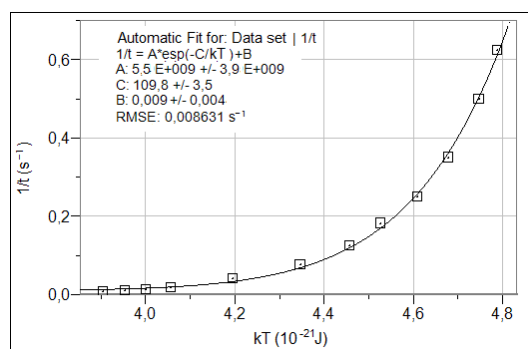

Figure 4. Speed of reaction versus kT with fitting curve.

Fig. 4 reports the reciprocal of the measured time intervals (that is proportional to the speed of reaction) as a function of kT for the whole range of temperatures (282 K – 346 K) we studied. An exponential function is fitted to data and the fitting parameters are reported in figure.

Our experimental results and the data fitting show a clear exponential dependence of the speed of reaction on the temperature. This is in accordance with the well known Arrhenius equation, that expresses the dependence of the reaction speed, V, on the reactant temperature, T, expressed in kelvins, and on the activation energy, E_a :

$$V = Ae^{-\frac{E_a}{kT}}$$
(4)

Here, A is a reaction-specific constant and k is the Boltzmann constant. V has the units s^{-1} and so it is often called the reaction *frequency factor*. When the activation energy is given in molar units instead of molecular units, e.g. joules per mole instead of joules per molecule, the universal gas constant, R, , is used instead of the Boltzmann constant.

Fig. 4 fitting parameters show our estimate of the activation energy, E_a, of reaction (1), equal to $(1.10 \pm 0.03) \, 10^{-19}$ J per molecule, a value in good accordance with values reported in literature (Weast, 1974).

3. Model and simulations

The experiment deals with a situation where equilibrium conditions can be described on the basis of a simple two-level system (reactant mean kinetic energy less or more than reaction (1) activation energy), in which the B-factor appears in the evaluation of the temperature effect on the speed at which the two-levels are populated. A chemical reaction can develop only when the reactant molecules collide and, in order that the collision between two molecules, A and B, be effective for the reaction development, two conditions have to be fulfilled:

- A and B must possess a sufficient average energy (energy factor)
- A and B must collide with the appropriate reciprocal orientation (steric factor)

If the reactant concentration is constant, the reaction speed only depends on the fraction of effective collisions per time unit, i.e., neglecting the steric factor, on the fraction of reactant

molecules per time unit having an average kinetic energy higher that the activation energy, E_a, typical of the specific reaction. At an absolute temperature T, the fraction of molecules that have a kinetic energy greater than E_a can be calculated from the Maxwell-Boltzmann distribution and turns out to be proportional to the Boltzmann factor, $e^{-\frac{E_a}{kT}}$.

In order to understand the role of thermal energy in the onset of the analysed process, a mechanical model of a two-level system has been developed and implemented through a simulation. It supplies a clear view of the dynamics of a mechanical two-level system and works by analogy with respect to the performed experiment.

The model system consists of a box containing some small hard spheres free of moving (see Fig. 5). The whole system friction is negligible and the spheres can interact among them and with the box walls through elastic collisions. The box floor consists of two equal parts at different levels, with a height difference h through a slope. Each sphere of mass m is free of moving from one level to the other one if its kinetic energy is enough to supply the necessary potential energy mgh.
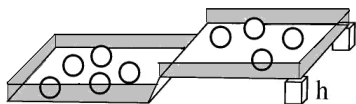

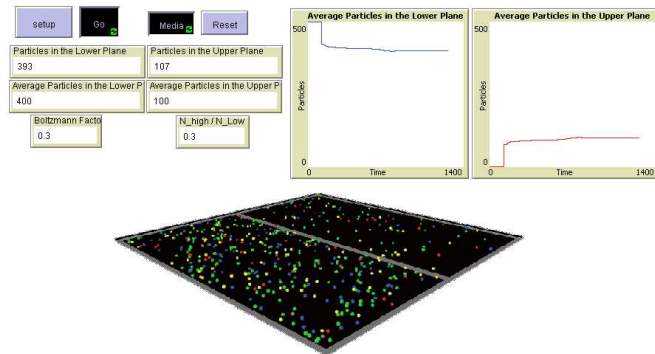Figure 5. Mechanical model of a two-level system.

Figure 6. Net-Logo interface of the two-level mechanical system simulation.

The model implementation considers N spheres randomly distributed on the box floor, with the initial vector velocities equal in modulus and at random horizontal directions. Molecular dynamics is used for the numerical resolution of the equations of motion. After each collision, the new components of each sphere velocity are found by applying the laws of energy and momentum conservation. The program registers the number of particles for each level as a function of time.

Figure 6 shows the simulation interface implemented by using the Net-Logo environment (NetLogo, 2009). Different experiments with the model can be performed by varying the h values, the number of spheres and their initial velocity (and consequently the mean kinetic energy).

Some simulation results, obtained by varying the mean kinetic energy per particle $<E_{kin}>$, are shown in figures 7 and 8. The reported simulations have been performed with N= 500 hard spheres with mean kinetic energy per particle in the range $0< E_{kin} <4mgh$. For all the simulations, the program was run until the fluctuations of the two population ratio, n_{high}/n_{low}, were almost constant.
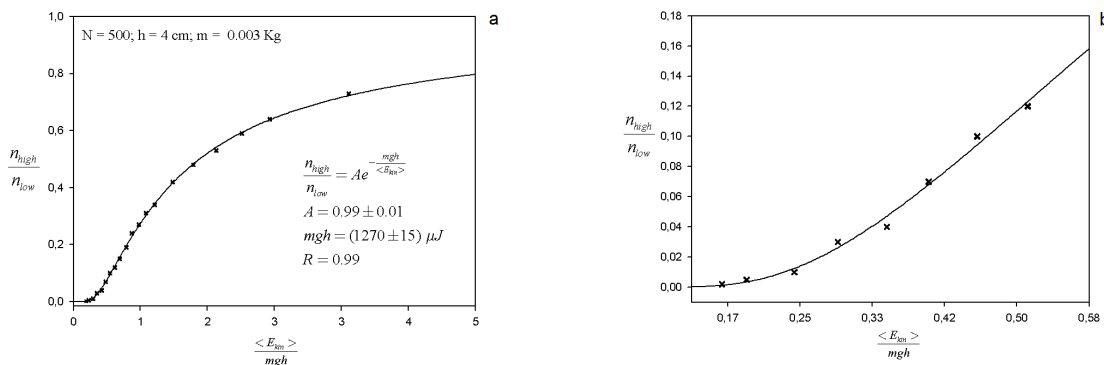
Figures 7a and 7b. a) Simulation results of population ratio, n_{high}/n_{low} as a function of the ratio $<E_{kin}>/mgh$. b) Enlargement of the initial part of figure 7

As shown in figures 7a and 7b, the dependence of n_{high}/n_{low} on the B-factor is evident, as well as its meaning. The ratio n_{high}/n_{low} varies from 0 to 1 as a function of the ratio $<E_{kin}>/mgh$: i.e. when this ratio is high (low h or high kinetic energy) the particles do not "see" the change of energy level; for low values of the ratio $<E_{kin}>/mgh$ (high h or low kinetic energy), the population ratio increases at a higher rate. This is the case reported in our experiments.

The modelling of our experimental systems by means of a two-level system supplies, in our opinion, a twofold advantage: it presents an enlightening illustration of the argument and allows students to become familiar with a model widely used in physics for the description of simple systems of non-interacting particles, as dissociation of particles in liquids, spins in magnetic fields, and many others. All are examples of activation processes, in which for something to happen particles have to acquire an activation energy greater than kT. The higher the temperature, the more likely this is to occur. However, a small fraction of particles acquires a much larger than average energy and activates the process. The two-level model makes evident that " the activation energy is like a hill over which the particle has to climb before getting down into the next valley" (Ogborn, 2008).

4. Conclusion

The present approach shows how the B-factor can describe the experimental results in a typical example of chemical reaction. Other experiments can be performed, since many natural systems exist in two different states characterised by a transition gap ΔE. Evaporation of a liquid, where the characteristic energy is the mean energy to supply a molecule to achieve the liquid-vapour transition, or semiconductors, where the characteristic energy is the energy gap, can supply other experimental fields of investigation. All such systems must borrow from their environment the necessary energy in order to change their state. The conceptual relevance of the dimensionless parameter $\Delta E/kT$, relies on the idea of the necessary balance between the energy needed for a process and the available energy.

The simulation illustrates a working model of a two-state atomic system. It can be improved by, for example, putting it in a temperature bath and requiring that the mean kinetic energy of both the two subsystems is maintained constant. It can be also extended to a multi-level system by allowing an easy visualization of the density distribution of atmosphere.

The reported experimental data were collected during the physics lab section activities of the Physics Program of the Graduate School of Pre-Service Physics Teacher Education at Palermo University. The same approach has been also used during the lab activities of a Introductory Course of Statistical Mechanics for undergraduate engineering students. In both cases we found that the lacking of a background in statistical mechanics did not prevented students understanding the argument. The experiments performed and the discussions about the simulation model, with its possible extensions, allow us to conclude that trainee teachers, as well as undergraduate students, have deepened their understanding of the physics content involved.

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