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Technology Report

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From Discrete to Continuous Process Simulation in Classical Thermodynamics: Irreversible Expansions of Ideal Monatomic Gases

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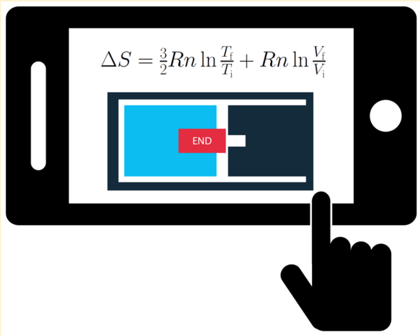
Supporting Information

ABSTRACT: Thermodynamic processes are complex phenomena that can be understood as a set of successive stages. When treating processes, classical thermodynamics (and most particularly, the Gibbsian formulation, predominantly used in chemistry) only pays attention to initial and final states. However, reintroducing the notion of process is absolutely necessary to get to know the final state from the initial state conditions. In general, complex concepts can be better understood through visualization. Nowadays, computer graphics can be used to simulate processes, from initial to final states, including interactivity and time progression. This technology report attempts to illustrate the benefits that the use of computer graphics may provide in learning classical thermodynamics. Our work shows how interactive graphic animations may be used to dynamically study thermodynamic processes. This report illustrates how key concepts in thermodynamic process, such as reversibility and irreversibility, can be easily introduced to students through visualization and interactivity. For this goal, we have tested a programming environment called Processing, widely used in the context of the visual arts to create images, animations, and interactions. The Processing software development environment has four major advantages: it is free of charge and open source, easy to use, multiplatform, and oriented to get immediate visual feedback while programming.



KEYWORDS: *First-Year Undergraduate/General, Second-Year Undergraduate, Physical Chemistry, Computer-Based Learning, Internet/Web-Based Learning, Thermodynamics*

INTRODUCTION

It is indisputable that the language of science is mathematics, as Galileo claimed in the 17th century. And it is equally true that becoming familiar with mathematics is not a simple task due to its inherent abstraction. Accordingly, mathematics often imposes a high toll to make a rigorous approach to science. This is commonly the main cause, as argued by many students, to reject scientific activity. Mathematicians were always aware of the difficulty exhibited by their equations. Among the solutions they propose, there is a very prominent one: graphical representation. This idea was implemented, for example, in classical thermodynamics, by B. P. E. Clapeyron and W. J. M. Rankine when they developed the indicator diagrams.[1] J. W. Gibbs reached the summit of this trend, within the same discipline, when he included in the titles of two of his most famous works[2] the idea of graphical representation.

SIMULATION OF PROCESSES

Visualizing Equations

Obviously, none of these scientists had computers at their disposal. The birth, and subsequent proliferation, of computers made the visualization of equations easier. Initially, the graphical capabilities of computers were nonexistent or severely limited. Their main task was to quickly generate tables of values that, subsequently, were manually plotted on graph paper. As the graphical capabilities were increased, displaying graphics directly on a screen became a reality. Software had to evolve accordingly, and the tortuous process of generating numerical values using programming languages such as FORTRAN[3] to transfer them to graphing utilities, like GNUPLOT,[4] was superseded by powerful and modern tools as MATLAB[5] or MATHEMATICA.[6] Nowadays there is no difficulty in drawing any equation on a computer (excepting those derived from very complex research problems).

Discrete Simulation

In general, relatively simple physical processes can be depicted through a set of points (contiguous or not) of the curve or surface that represent the physical magnitudes (if the processes

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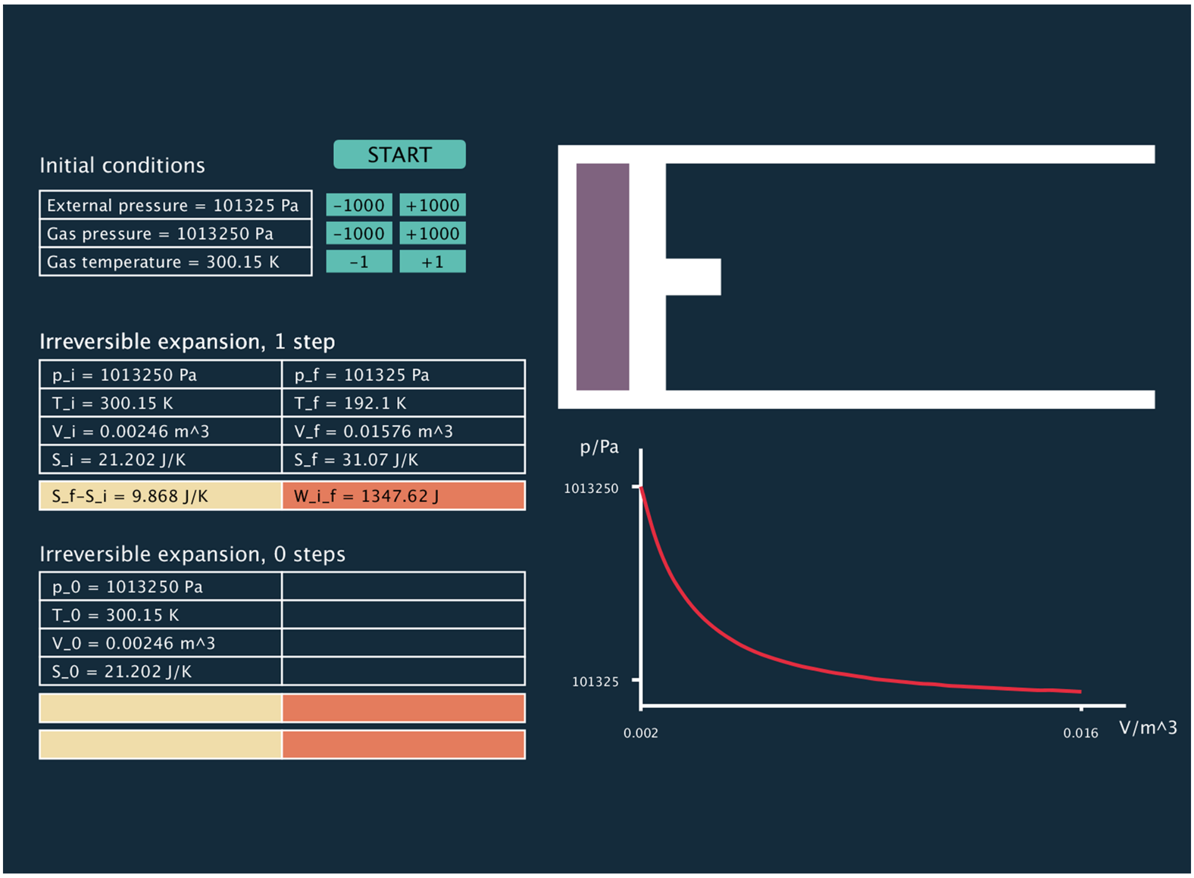

Figure 1. Screenshot of the sketch in the initial situation.

are more complex, a single equation will not be enough to get a full description of them). Although the graphical representation of an equation is more intuitive than its symbolic expression, the reader still has to imagine the physical situation corresponding to each point in the graph. Therefore, to facilitate the understanding of the processes, graphs typically include schemes that symbolize some of the most significant physical situations (the initial, the final, and a few of the intermediate states). This discrete representation, although useful, lacks dynamism.

Continuous Simulation

Nowadays, a number of software solutions (e.g., Adobe Animate CC[7]) and language programs (e.g., Javascript) exist that allow modeling and viewing processes, in a very simple way and, simultaneously, couple them with the mathematical equations that govern their behavior. It is worth noting the substantial change with respect to traditional software. Formerly, the graphical representation of the equations was the first step, and then, some schemes were included to represent some special physical situations. Currently, the working scheme is just the reverse: first the process, and finally the equations that control it. New technology allows, in addition, a high degree of interactivity through touchscreen devices (a nonexistent advantage in the traditional software mentioned above). A very simple example is moving a piston (and, therefore, altering the volume of a cylinder), dragging it only with a finger. If the volume change can be parametrized in terms of the movement of the finger, numerical calculations can be performed using that volume change. New technologies endow the teacher with powerful tools to facilitate the learning of processes occurring in nature. For all of these reasons, interactive simulations have acquired a very significant role in science education.[8−10]

The current offer of existing programming and visual creation tools is ample. Among them we have decided to test the Processing[11,12] platform as a tool for creating interactive simulations. Processing is an open source programming language and integrated development environment, which began to be used in 2001 in the MIT Media Lab as an educational tool to introduce design and art students in the world of visual programming. The advantage of this tool, compared to other options, is its ease of use. It allows the user to focus on graphics and creative aspects rather than on programming issues. In this paper, Processing has been used to create a small individual program (called a "sketch" in this working environment), that generates a graphic application that allows one to simulate and visualize a thermodynamic process.

■ PROCESSING SKETCH

The difference between irreversible and reversible processes is one of the cornerstones of classical thermodynamics. Its quantification is possible by the quintessential thermodynamic quantity: the entropy. The adiabatic expansion of a monatomic ideal gas, enclosed in a cylinder equipped with a movable frictionless piston, against a constant external pressure, is a very simple example (and therefore one that is commonly used) to

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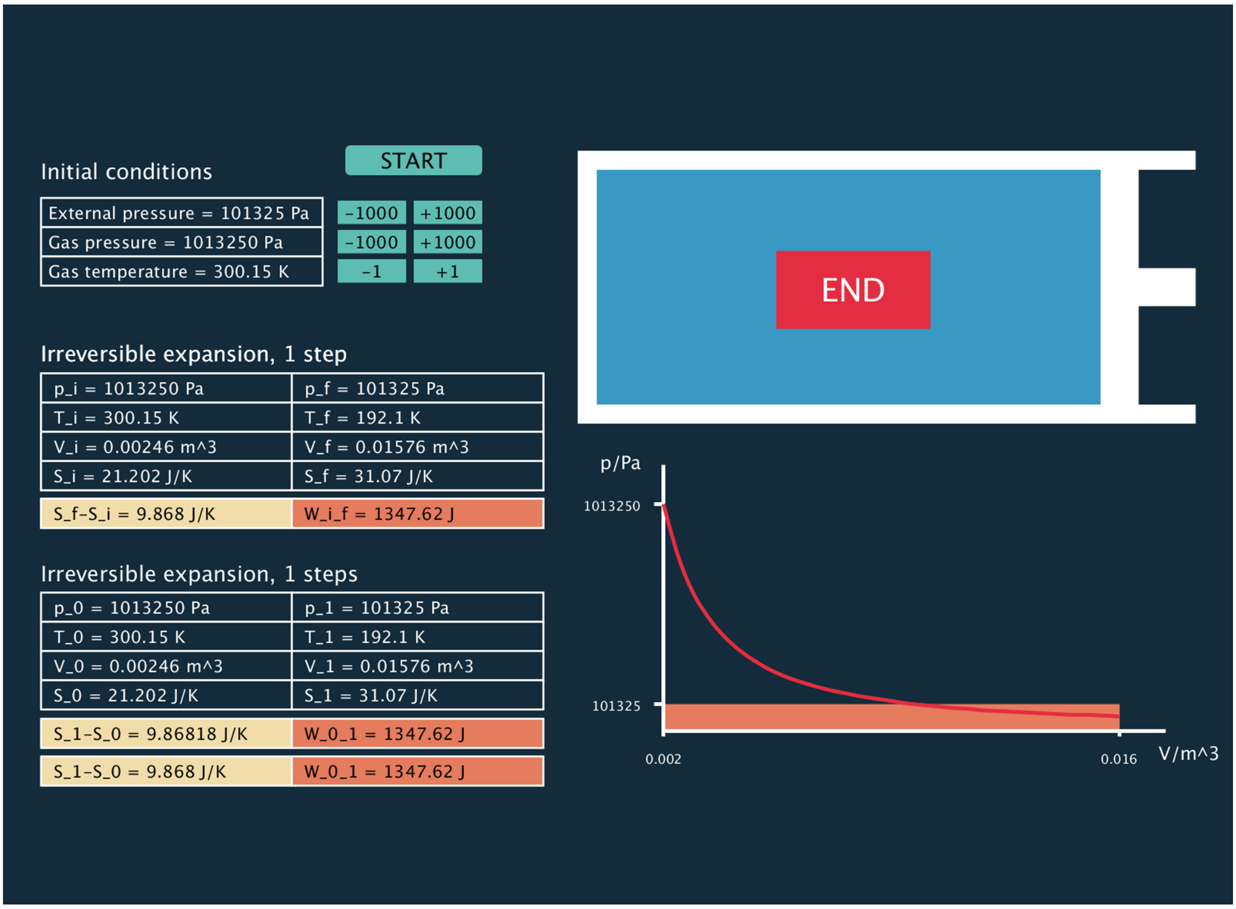

Figure 2. Screenshot of the sketch at the end of the irreversible expansion carried out in a single step.

illustrate an irreversible process that creates entropy. Once students are presented with the concept of irreversibility, the majority of the textbooks go on to explain how the same adiabatic expansion could be done in a reversible way. The solution is known to everyone: just move the piston infinitely slowly. The slower the movement, the lower the irreversibility. In the limit, a reversible process would be reached, and entropy would not be created.

A Processing sketch, called IrrevExpansion, has been developed to facilitate the understanding of these processes.[13] The initial situation of the sketch is shown in Figure 1.

The cylinder contains 1 mol of a monatomic ideal gas, at 300.15 K and 1,013,250 Pa. These initial conditions appear in the upper left corner of the screen and can be altered using the corresponding adjacent green buttons (pressure intervals are ±1000 Pa and temperature intervals are ±1 K). The gas will undergo an irreversible process: an adiabatic expansion against an external pressure (101,325 Pa), that also appears in the screen (and which may also be suitably modified; in steps of ±1000 Pa). With this situation as a starting point, the Second Law of Thermodynamics (see details of the calculation in the Supporting Information) predicts the final temperature of the gas (192.1 K), and with application of the ideal gas law (the final pressure is known since it is identical to the external pressure and the amount of substance remains constant), the final volume is obtained (0.01576 m^3). Likewise, it is possible to calculate the increase of entropy of the gas for this process (9.868 J/K). The amount of useful work done by the gas during this expansion is $p_f(V_f - V_i)$ = 1347.62 J. All of these results appear on the screen, in a table entitled "Irreversible expansion, 1 step". In order to simulate this irreversible process, the student must press the START button and, next, place one finger at the end of the cylinder. The piston will be automatically dragged to the position corresponding to the final volume. The result is shown in Figure 2.

In the lower left corner, the results for the process just executed appear. Obviously, they are coincident with the above-mentioned description.[14] Note that the color of the gas changes with temperature (red for high temperatures, blue for low temperatures). In the lower right corner appears an indicator diagram. Let us forget, for the moment, the red curve shown in the diagram. The orange area corresponds to the amount of useful work done by the gas during the expansion (the area is exactly the useful work if the origin of the vertical axis is set to zero). With the START button pressed again, the sketch returns to the initial situation.

Suppose now that the irreversible expansion ending at 101,325 Pa had happened in three stages: to a random pressure, p_1, less than 1,013,250 Pa but greater than 101,325 Pa; to a pressure p_2, less than p_1 but greater than 101,325 Pa; and finally, to 101,325 Pa. To illustrate this process, it is simply necessary to place the finger or click in three different positions of the cylinder: the first one, close to the starting position; the second one, toward the center; and the last one, to the right

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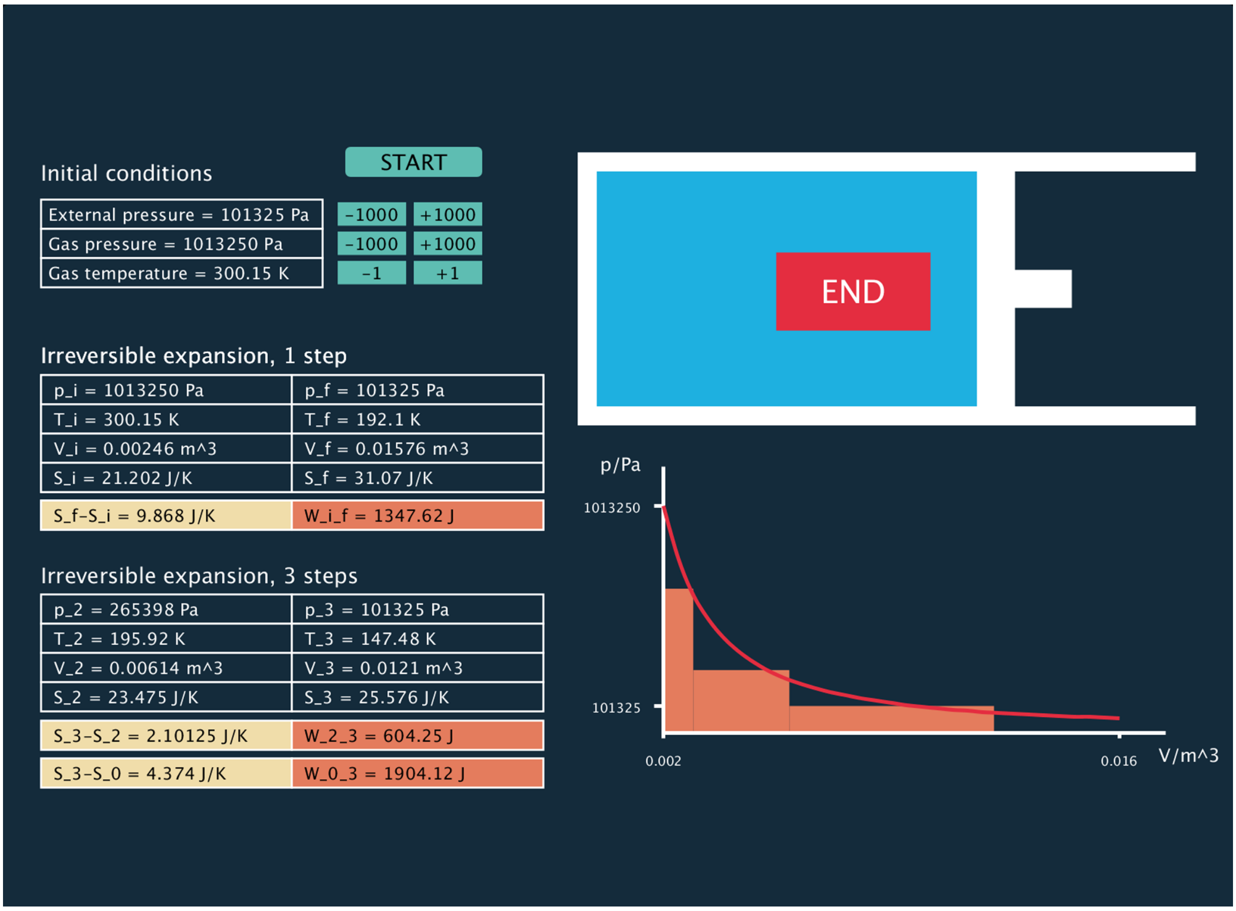

Figure 3. Screenshot of the sketch at the end of the irreversible expansion carried out in three steps.

end of the cylinder. In each step, the values of the corresponding thermodynamic variables are displayed in the lower left corner of the graphical area. The final result is shown in Figure 3 (see details of the calculation in the Supporting Information).

Although the final pressure is the same (101,325 Pa), the final volume and temperature have changed, and therefore, the entropy change of the gas is different (4.374 J/K): lower than the value obtained in the expansion in one step. Note also that the amount of useful work has increased (1904.12 J). This value is the sum of the areas of the three rectangles (one for each expansion step) that appear in the indicator diagram. Changes in all these amounts show that the first and the second processes carried out are different (the initial state is always the same, but the end state is different). As previously indicated, the second process is less irreversible than the first one.

In the light of this last result, an obvious question arises: What would happen if we increase the number of stages? The sketch provides the solution without difficulty. Pressing again the START button, the initial situation is restored. If the finger is placed on the piston and is slowly slid to the right, a process is achieved in multiple stages (the END title appears when pressure is 101,325 Pa). Figure 4 shows a process in 316 steps.

Note the small value of the entropy change (0.052 J/K) and the big value of the useful work (2249.35 J) obtained in the expansion. Note also that, in this process, the gas goes to a final state that is at a lower volume and lower temperature than in the preceding cases. The indicator diagram shows that the orange area matches (to the naked eye) now with the area under the red curve. This curve represents the adiabatic and reversible expansion of the gas from identical initial conditions to a final pressure of 101,325 Pa. The final temperature in the reversible expansion is 119.5 K; the final volume is 0.00981 m^3, and the useful work is 2251.1 J (see details of the calculation in the Supporting Information). Note the extremely small differences between these values and those obtained in the irreversible expansion carried out in 316 steps. It is easy to infer that the reversible process is a limit situation obtained when the number of expansion steps approaches infinity.

The sketch allows one to introduce a game-based approach element in the learning process. The object of the game is to get an expansion process as close as possible to a reversible one. To this end, the student must complete the process using the greatest possible number of stages (until the label END appears). The higher the number of steps is, the lower the entropy change of the gas is, and the maximum useful work is obtained; therefore, there is a greater approximation to a reversible process.

To conclude this section, we would like to recall that entropy is a state function. Starting from the final state obtained in the irreversible expansion carried out in one step (green box in Scheme 1), a new process is executed. It involves cooling the gas, at constant pressure, until its temperature reaches the value obtained in the reversible expansion (blue box in Scheme 1).

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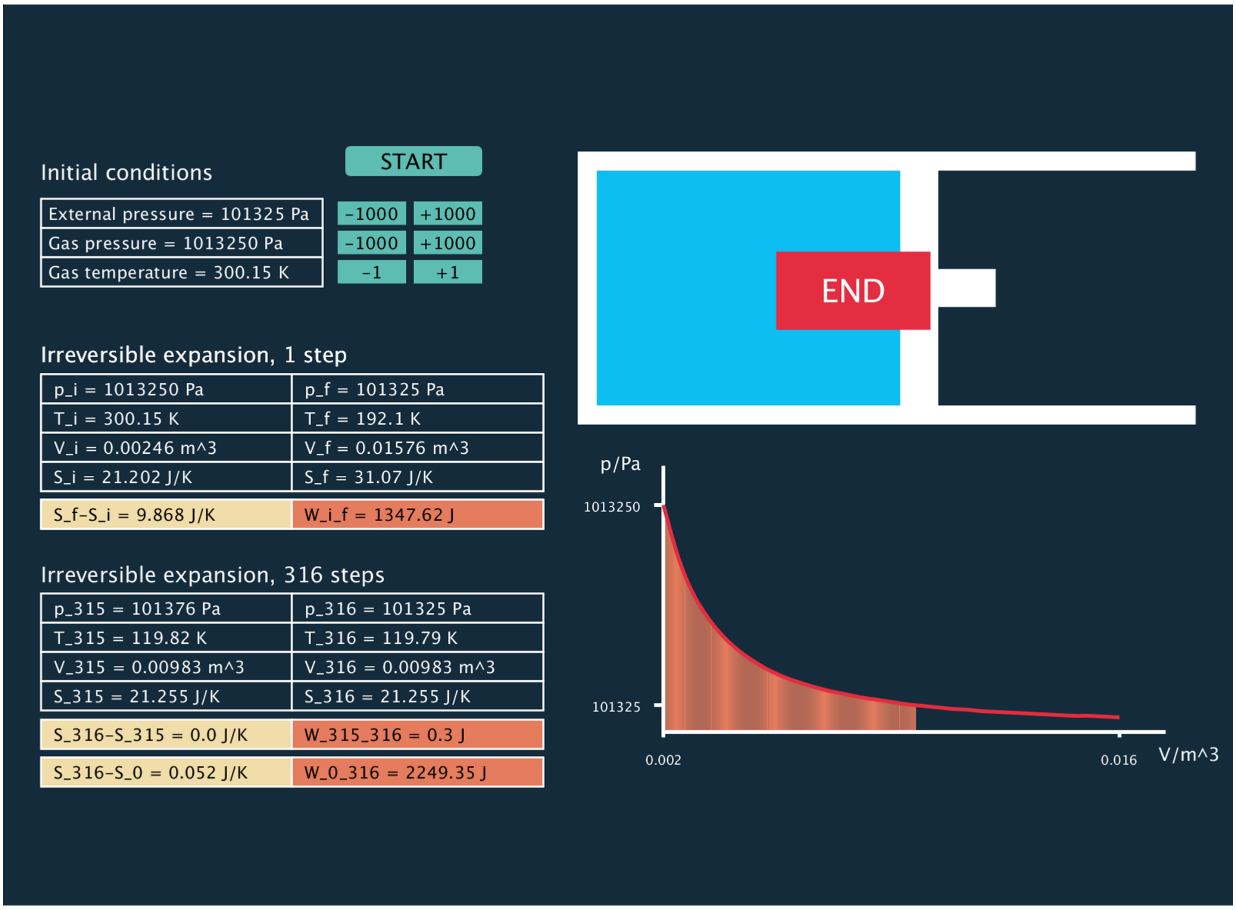
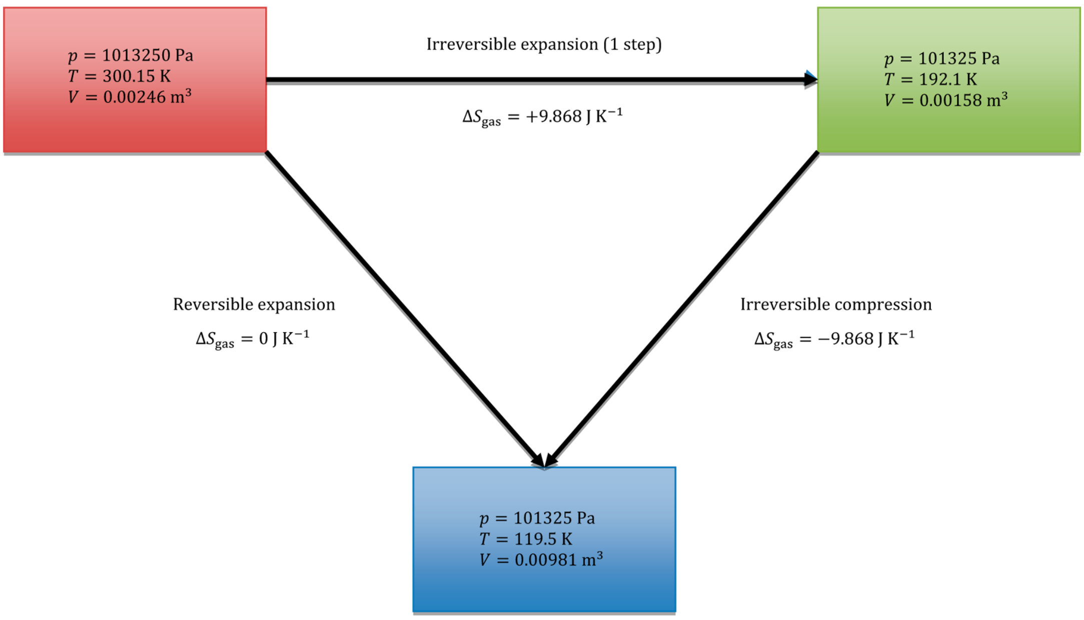


Figure 4. Screenshot of the sketch at the end of the irreversible expansion carried out in 316 steps.

Scheme 1. Entropy Is a State Function, Independent of the Path Followed by the System; Hence, If a System Undergoes a Cyclic Process, the Entropy Change Must Be Null



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The entropy change associated with this process is −9.868 J/K (see details of the calculation in the Supporting Information). This result is entirely logical, since the final state of the gas after the cooling is identical to that achieved in the reversible expansion.

This sketch has been used during this academic year, in the first course of the Degree in Chemical Engineering delivered at the Universidad de Oviedo (Spain), to interpret reversible processes as limit situations. In previous years, the methodology used in the classes to illustrate these concepts was to implement in a spreadsheet the formulas corresponding to the irreversible adiabatic expansion of a monatomic ideal gas against a constant pressure that appear in the Supporting Information. Then, students used the spreadsheet to calculate the thermodynamic variables (T_f, V_f, S_f) associated with the final states of several irreversible expansions (always starting from the same initial conditions and against the same external pressure, but differing in the number of applied steps). Gathering all the results, a table was constructed (each row representing the results of an expansion). The next step was to analyze the observed trends in the final thermodynamic variables as the number of steps in the expansion increased. The results of these observations allow the teacher to introduce effortlessly the reversibility concept (and its associated mathematical equations). Using this procedure, students could not interact with the process; they had to infer the difference between the two concepts just by looking at numbers. However, this year, using the sketch, students learned immediately that the numerical results were heavily dependent on the speed of the movement of the finger over the piston. Of course, once students had understood the concepts through the use of the sketch, the next step was to perform some calculations (using the old spreadsheet) of those executed with the sketch, but now concepts were clearer because students had experienced them previously. The key point in this new methodology is that the concepts are introduced before the calculations in a much more appealing way. Students do not forget the effort they had to do to approach a reversible process because they did it with their own fingers. The game-based approach element adds an extra plus that helps to fix, on a permanent basis, the concepts. An objective measure of the benefits produced by using the new sketch is a significant savings (compared to the old method of the spreadsheet) in lecture time. It takes 1 h, approximately, to generate, iteratively using the spreadsheet, the results of an irreversible expansion carried out in multiple steps that are comparable with those of a reversible expansion. However, in less than a minute, the sketch produces Figure 4 (316 steps).

CONCLUSIONS

A Processing sketch has been developed to simulate continuous thermodynamic processes. In particular, the sketch tries to foster the learning of two quite complicated concepts: reversibility and irreversibility. Users may interact with the sketch at any time through touchscreen devices. Since it is possible to execute the sketch on smartphones and tablets, we believe it is a very useful tool to promote and ease teaching and learning of classical thermodynamics.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.6b00226.

Processing sketch (IrrevExpansion.pde) for computers, tablets, and smartphones (Android devices); installation instructions; brief summary of thermodynamic formulas (ZIP)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Maxwell, J. C. *The Theory of Heat*; Dover Publications, Inc.: Mineola, NY, 2001; p 102.

(2) *The Scientific Papers of J. Willard Gibbs. Vol. One. Thermodynamics*; Bumstead, H. A., van Name, R. G., Ed.; Ox Bow Press: Woodbridge, CT, 1993; pp 1−54.

(3) Backus, J. W.; Beeber, R. J.; Best, S.; Goldberg, R.; Haibt, L. M.; Herrick, H. L.; Nelson, R. A.; Sayre, D.; Sheridan, P. B.; Stern, H. J.; Ziller, I.; Hughes, R. A.; Nutt, R. In *Proceedings Western Joint Computer Conference*; Los Angeles, California, 1957; pp 188−198.

(4) *GNUPLOT*. http://www.gnuplot.info (accessed Sep 26, 2016).

(5) *MATHWORKS*. http://www.mathworks.com/products/matlab (accessed Sep 26, 2016).

(6) *WOLFRAM*. http://www.wolfram.com/mathematica (accessed Sep 26, 2016).

(7) Adobe Systems Incorporated. *Adobe Animate CC*. http://www.adobe.com/s/animate.html (accessed Sep 26, 2016).

(8) Seery, M. K.; McDonnell, C. The application of technology to enhance chemistry education. *Chem. Educ. Res. Pract.* **2013**, *14*, 227−228.

(9) Moore, E. B.; Chamberlain, J. M.; Parson, R.; Perkins, K. K. PhET Interactive Simulations: Transformative Tools for Teaching Chemistry. *J. Chem. Educ.* **2014**, *91*, 1191−1197.

(10) Belford, R.; Moore, E. B. ConfChem Conference on Interactive Visualizations for Chemistry Teaching and Learning: An Introduction. *J. Chem. Educ.* **2016**, *93*, 1140−1141.

(11) *Processing*. https://processing.org (accessed Sep 26, 2016).

(12) Reas, C.; Fry, B. *Processing: A Programming Handbook for Visual Designers*, 2nd ed.; The MIT Press: Cambridge, MA, 2014.

(13) The sketch can be launched directly from the following web page: http://www.unioviedo.es/jborge/materiales-didacticos/recursos-didacticos-para-la-ensenanza-de-la-termodinamica-clasica/la-expansion-irreversible-de-un-gas-ideal-monoatomico (accessed Sep 26, 2016). It is also included in the Supporting Information.

(14) In Processing, numbers have to be converted to strings before being displayed in graphical screens. That affects the way in which significant figures can be displayed. For the sake of compatibility with different operating systems and regional formatting settings, we have decided to use default numerical notation options as implemented in the Processing environment in the distributed source code. As Processing is a Java-based programming language, experienced Java programmers may easily modify the local code by making use of Java classes (such as String and Locale classes). In the example discussed in Figure 2, the entropy variation showed in the bottom left corner table is displayed by using a different number of decimal figures. This is to guarantee that, in less irreversible simulations, when the entropy difference between expansion steps is very small, the corresponding

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variation is not rounded to 0, leading to the wrong conclusion that the entropy remains unchanged.

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