As first clearly stated by Schrödinger “a living organism tends to approach the dangerous state of maximum entropy, which is death. It can only keep aloof from it, i.e., alive, by continually drawing from its environment negative entropy. What an organism fed upon is negative entropy”.\[1\] Is it possible for an organism immersed in a thermal bath to be insulated, and thus avoid thermalization, and still be able to reduce its entropy? Unfortunately, the above scenario contradicts one of the most cherished laws of physics, that is the Second Law of Thermodynamics, which has victoriously resisted all the attempts aimed at finding a particular case where it could be violated. However, one has to consider that the Second Law has been formulated in the context of macroscopic physics and it is in this context that it has been successfully applied and verified. While the Second Law, being inherently statistical in its nature, cannot carry over to microscopic cases where the number of involved particles is too small, its limits of validity are not well understood in the region bridging the macroscopic to the microscopic world. In particular, the intermediate mesoscopic regime, which includes part of the biological realm, is still terra incognita and open to possible surprises. Recent years have actually witnessed a growing interest in the thermodynamics of small-scale non-equilibrium devices, especially in connection with the operation and efficiency of Brownian motors.\[2\] We believe that we have been able to devise a particular case in which an isolated object, placed in a thermal-equilibrium environment, is nevertheless capable of reducing its entropy or, equivalently, to extract work from the thermal bath surrounding it. We have identified this object with a mesoscopic system, typically of the size of a few microns, consisting of two isolated cavities, filled with a common number of molecules, separated by a movable adiabatic impermeable partition (see Fig.1). Its macroscopic equivalent is the so-called adiabatic piston, sometimes referred to as “enigmatic” because the description of its dynamical evolution toward equilibrium is far from being trivial, the problem being actually undetermined from the point of view of elementary thermodynamics.\[3\] A careful analysis of the problem, which has been tackled a few years ago by an approach based on gas kinetic theory,\[4\] shows that thermodynamic fluctuations cannot be neglected at the mesoscopic level and that they actually play a major role in determining the dynamic evolution of this isolated system. As shown in this paper, its behavior implies that the system fails to settle down to a well-defined equilibrium state and undergoes negative entropy fluctuations whose ensemble average over many replicas of the system can be quite large. Thus, on the average, the system is able to feed on negative entropy. It is also possible to show how the system can function as an engine and turn the entropy extracted from the surrounding thermal bath into work. These remarkable results are derived in the frame of a model which does not contain any ad hoc parameters and appears to possess some simple universal feature which makes it a potential candidate for supporting some still unknown ubiquitous biological process.

Our system consists of two isolated cavities A and B, filled with a common number of moles of the same gas, separated by a movable impermeable partition which is assumed to be initially at rest in a position corresponding to equal volumes and temperatures (and thus pressures) in the two cavities. Under these conditions, one would expect the wall to remain at rest, apart from microscopic random oscillations around the equilibrium position.

This is obviously the case in most ordinary situations,
where the wall thermal conductivity is large enough to maintain a common temperature in the two cavities, so that any small random displacement of the wall is immediately reversed by the induced pressure change. Conversely, if thermal conductivity is negligible, it will be shown below that the wall can actually undergo sizeable random displacements, during which the pressures on the two sides remain the same. In each realization, the system evolves and the total entropy variation, from the initial state in which both cavities have the same volume $V_0/2$ and temperature $T_0$ to a generic one $(V_A, T_A; V_B, T_B)$, is

$$\Delta S = \Delta S_A + \Delta S_B = n c_p \ln \frac{T_A}{T_0} + n c_p \ln \frac{T_B}{T_0}$$

$$= n c_p \left[ 1 - \left( \frac{\Delta V}{V_0/2} \right)^2 \right], \quad (1)$$

where $\Delta V = V_A - V_0/2$, $c_p$ being the molar heat at constant pressure and $n$ the common number of gas moles on each side. The ensemble average $\Delta S$ of this intrinsically negative entropy change can assume large values in specific mesoscopic situations, as it will be proved in this paper. Note that in deriving Eq. (1), we have exploited the relation $T_A + T_B = 2T_0$, which corresponds to neglecting the kinetic energy of the wall. In fact, under the adiabatic hypothesis, it can be regarded as a body possessing a single (translational) degree of freedom. As a consequence, its energy and entropy are of the order $kT_0/2$ and $k$, respectively, and can be neglected.

In order to corroborate the above considerations, we investigate the so-called “adiabatic-piston problem”, dealing with a system which, in the language of classical thermodynamics, consists of an isolated cylinder divided into two parts by means of a frictionless adiabatic piston, each section containing the same number $n$ of moles of the same perfect gas (see Fig. (1)). Initially, the piston is held in the fixed position corresponding to equal volumes and pressures in the two sections. Once the piston is released, the system evolves in a labile quasi-equilibrium state, driven by the random motion of the wall induced by the elastic molecular collisions, while the gas pressure on both sides remains equal to the initial one. We describe the dynamics of the system in terms of the random variable $X(t)$, that is the instantaneous position of the piston, whose ensemble-average value $\langle X(t) \rangle$ remains equal to $L/2$ for obvious symmetry reasons. The normalized mean-square value $\langle (X(t) - L/2)^2 \rangle/(L/2)^2$ represents the ensemble-average of the quantity $(\Delta V)^2/(V_0/2)^2$ appearing in Eq. (1) and determines the corresponding entropy decrease undergone by the system.

The system evolution from an initial configuration of macroscopic equilibrium, that is equal pressures and temperatures on both sides and piston at rest, is described by the stochastic equation

$$\frac{d^2X}{dt^2} + \sqrt{\frac{16NkT_0}{\pi \mu ML}} \left( \frac{1}{\sqrt{X}} + \frac{1}{\sqrt{L-X}} \right) \frac{dX}{dt} + \frac{2}{\mu} \left( \frac{X - L/2}{X(L-X)} \right) \left( \frac{dX}{dt} \right)^2 = a(t), \quad (2)$$

where $k$ is Boltzmann’s constant, $N$ the common number of molecules on each side, and $\mu = M/M_g$, $M$ and $M_g$ being respectively the mass of the piston and the common value of the gas mass in each side. Determining the correct expression of $a(t)$ is a delicate task, since the standard Langevin approach does not in general carry over to nonlinear dynamical systems \cite{3}, as the one described by Eq. (2). In order to take advantage of the Langevin method, we linearize the above equation: a) by considering small displacements around the starting position, that is $\langle (X - L/2) \rangle/(L/2) \ll 1$, and b) by approximating the square of the piston velocity $(dX/dt)^2$ with its mean-square velocity $kT_0/M$ (both hypotheses will be proved consistent \textit{a posteriori}). Proceeding in this way, a straightforward application of the dissipation-fluctuation theorem yields $\langle a(t)a(t') \rangle = 8(2mK/\pi)^{1/2}PS/M^2\delta(t-t')$, where $m$ is the mass of the individual molecule, $P$ the common pressure on the two sides of the piston and $S$ its area. After introducing the variable $x = X - L/2$, the linearized form of Eq. (2) reads

$$\frac{d^2x}{dt^2} + 8\sqrt{\frac{2NkT_0}{\pi \mu ML^2}} \frac{dx}{dt} + \frac{8kT_0}{\mu ML^2} x = a(t). \quad (3)$$

We now observe that the above equation is formally identical to the one describing the Brownian motion of a harmonically-bound particle of mass $M$, that is

$$\ddot{x} + \beta \dot{x} + \omega^2 x = A(t), \quad (4)$$

where $A(t)$ is the Langevin acceleration, a problem which has been thoroughly described in the literature.
By comparing Eqs. (3) and (4), we can obviously apply the results of [7] to our case by identifying $\beta$ with $8(2NkT_0/\pi \mu ML)^{1/2}$ and $\omega$ with $8kT_0/\mu ML^2$. Whenever $\beta \gg \omega$ (“overdamped” case), which in our situation is equivalent to the obviously satisfied relation $\sqrt{N} \gg 1$, the analysis carried out in [7] naturally highlights the existence of two significant time scales $t_{th} = 1/2\beta$ and $t_{as} = \beta/2\omega^2 = (t_{as} \gg t_{th})$. They represent the thermalization time $t_{th}$, i.e., the time over which the mean-square velocity $\langle (dx/dt)^2 \rangle$ attains its equipartition value $kT_0/M$, and the much longer time $t_{as}$ over which the mean-square displacement reaches its asymptotic value $\langle x^2 \rangle = kT_0/M\omega^2$. For our system $t_{as} = (NL/w)(M/M_2)\rangle/\pi^{1/2}$ and $t_{as}/t_{th} = 16N/\pi$, where $w = (2kT_0/m)^{1/2}$ is the most probable velocity of the gas Maxwellian distribution function. Therefore, since $N \gg 1$, $t_{th}$ is much smaller than $t_{as}$, a circumstance which justifies a posteriori the replacement of $(dx/dt)^2$ in Eq. (2) by its average value $kT_0/M$. The asymptotic expression of the mean-square displacement of the piston from its central position reads

$$\langle x^2 \rangle = \frac{kT_0}{m \omega^2} = \frac{\mu \cdot L}{2 \cdot 2^2},$$

so that, in the limit $\mu \ll 1$ (that is, small piston mass with respect to gas mass), the above assumptions a) and b) allowing us to linearize Eq. (2) are both satisfied.

We can now evaluate the entropy change $\langle \Delta S \rangle$ averaged over many realizations of our system, starting from the initial state corresponding to $X(t = 0) = L/2$. Since in our case $\langle (\Delta V)^2 \rangle/(V_0/2)^2 = \langle x^2 \rangle/(L/2)^2 = \mu/2 \ll 1$, Eq. (4) approximately yields

$$\frac{\langle \Delta S \rangle}{k} = -\frac{\epsilon_p}{2R}N\mu,$$

which corresponds to a large entropy decrease whenever $\mu N \gg 1$. The question naturally arises: what are the spatial and temporal scales over which this violation of the second law of thermodynamics can actually occur? Before answering this question, the conceptual meaning of the result implied by Eq. (6) has to be clarified. To this aim, we note that, according to standard thermodynamics, any closed system in an equilibrium state, once an internal constraint is removed, eventually reaches a new equilibrium state characterized by a larger value of the entropy. The case considered in this paper represents a remarkable exception to this statement. More precisely, our closed system is made up of the two gases and the initial internal constraint is provided by the piston held in the central position. After the piston is released, our analysis shows that no final equilibrium state is eventually reached, since the piston keeps wandering, performing random oscillations around $X=L/2$, with mean-square amplitude $\langle x^2 \rangle = (L/2)^2\mu/2$.

The system behaves as a perpetuum mobile of the second kind. If embedded in a thermal bath at temperature $T_0$ and pressure $P_0$, one can devise a process through which work can be extracted from this environment. To this end, let us assume our system to be capable of splitting into the two separate cavities $A$ and $B$ if a large fluctuation $\Delta V$ occurs (see Fig. 2). The two cavities can then undergo a reversible adiabatic process which drives them back to the initial temperature $T_0$. If, at this point, the wall of the cavities becomes thermally conductive for a finite amount of time, the two cavities can be brought back to the initial volume $V_0/2$ through a reversible isothermal process at the bath temperature $T_0$. Let us now assume that the wall recovers its insulating nature and that the two cavities are reunited again: the total work extracted in this cyclic process is precisely $W = T_0\Delta S \equiv kT_0N\mu$, where $\Delta S$ is the negative entropy variation associated with $\Delta V$.

We now return to the question of the spatial and temporal scales over which our results apply. To this end, let us consider the specific case of a gas under standard conditions of temperature and pressure, for which, expressing hereafter $L$ in microns, $N \equiv 3 \cdot 10^7 L^3$. According to Eq. (6), if we refer as an example to a biatomic gas, we have $\langle \Delta S \rangle/k \equiv -5 \cdot 10^7 L^3\mu$ and, recalling the expression of $t_{as}$, that is $t_{as} = NL/\mu \sqrt{\pi}$, we obtain $t_{as} \equiv 5 \cdot 10^{-2} \mu L^2$ sec (having assumed $w \equiv 4 \cdot 10^8$ microns/sec, molecular oxygen). This extremely sensitive dependence of $t_{as}$ on the linear dimension of the cylinder ($t_{as} \propto L^4$) appears to limit the applicability of our model to values of $L$ up to a few microns. In fact, beyond this mesoscopic scale, $t_{as}$ becomes so large as to render unrealistic the adiabatic piston assumption over this time interval. As an example, for $\mu = 10^{-2}$ and $L = 1$ cm, we obtain $t_{as} \equiv 5 \cdot 10^{12}$ sec, that is about 1000 centuries! Conversely, by taking $L = 1$ micron, we get the reasonable value $t_{as} \equiv 5 \cdot 10^{-4}$ sec and $\langle \Delta S \rangle/k \equiv -5 \cdot 10^5$. This corresponds to a violation of the second law of the mesoscopic realm.

The above approach has allowed us to deal with the situation $\mu \ll 1$. In order to have an insight into the behavior of our process in the more general case $\mu \lesssim 1$, we assume Langevin’s approach to be approximately valid also in this moderately nonlinear regime, and use the nonlinear Eq. (2), with the same stochastic acceleration $a(t)$ worked out in the linear case. After introducing the dimensionless units $\xi = X/L$ and $\tau = t/t_o$, where
The two-particle correlation function of the gas near the piston, while the single-particle correlation functions are independent from the sign of $v_x$ and $v_x'$. This prevents the two-particle correlation distribution to factorize into the product of the one-particle distribution functions and, thus, the molecular-chaos assumption does not apply.

Finally, the validity of our conclusions appears to be corroborated by suitable molecular dynamic simulations of the evolution of our system. These typically involve a considerable number of point particles, which model the gas inside the cylinder, separated by a frictionless piston against which they undergo perfect elastic collisions. In particular, a microscopic model consisting of $N = 500$ hard disks furnishes a relaxation time $\tau$ (corresponding to our $t_{as}$) in good qualitative and quantitative agreement with our results. [11]

Besides, numerical investigations of a system consisting of a number of particles of the order of $10^3$, indicates that the difference between the temperatures on the two sides undergoes relevant oscillations, so that the system does not reach equilibrium, as predicted by our model. [12]

Further recent molecular dynamic simulations describing the time evolution of the piston position around $X \approx L/2$ are in fairly good agreement with our results, both qualitatively and quantitatively. [13]

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