



Irreversible thermodynamic analysis and application for molecular heat engines



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ABSTRACT

Is there a link between the macroscopic approach to irreversibility and microscopic behaviour of the systems? Consumption of free energy keeps the system away from a stable equilibrium. Entropy generation results from the redistribution of energy, momentum, mass and charge. This concept represents the essence of the thermodynamic approach to irreversibility. Irreversibility is the result of the interaction between systems and their environment. The aim of this paper is to determine lost works in a molecular engine and compare results with macro (classical) heat engines. Firstly, irreversible thermodynamics are reviewed for macro and molecular cycles. Secondly, irreversible thermodynamics approaches are applied for a quantum heat engine with $-1/2$ spin system. Finally, lost works are determined for considered system and results show that macro and molecular heat engines obey same limitations. Moreover, a quantum thermodynamic approach is suggested in order to explain the results previously obtained from an atomic viewpoint.

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1. Introduction

Applications of thermodynamics range from the thermo-economic evaluation of the energy resources, to the relationships among properties of matter, living matter included. Energy is a thermodynamic property, and it is always constant in the universe; it doesn't destroy, but only changes form a form to another one [1]. The useful work is obtained by evaluating the variations of the energy, which means that any change in a system is always related to a transition between, at least, two different system states.

Energy changes, no more than a conversion form one form of energy to another one, and interactions with environment are fully explained by the laws of thermodynamics. The first law of thermodynamics expresses the conservation of energy, while the second law states that entropy continuously increases for the system and its environment [2]. The second law gives us information about the quality of the energy and the evolution path of the system, as well as it allows us to evaluate the irreversibility of any real system [1]. Scientists and engineers have always been trying to obtain the maximum useful work and to decrease losses or irreversibility to the minimum level related to the specific constraints [3–26].

During the last decades, a continuous interest on micro- and nano-thermodynamic cycles is growing, with developments in nano-technology and nano-medicine. Thermodynamic assessments for quantum- and nano-systems, hence quantum thermodynamics, has been focused on [27–75]. In recent years, thermodynamic developments in the field of nanotechnology have raised novel questions about thermodynamics away from the thermodynamic limit. Indeed, quantum heat engines are devices that convert heat into work described by the laws of quantum and statistical thermodynamics. They have been a subject of intense research due to their great practical applications, as, for example:

1. Different thermometry approach, with the aim to reduce the dimensions of the probe and in pushing away from the thermalisation timescale to obtain a temperature measurement response in the emergence of small thermometers for nano-scale use;
2. The use in opto-mechanical systems, for the realization of nano-scale quantum thermal machines with particular interest for nano-mechanical resonators and quantum opto-mechanical engines, which should convert incoherent thermal energy into coherent mechanical work for power applications in photovoltaic systems;
3. The bacteria conversion of light energy into bio-fuels;

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and many others. Unlike a classical heat engine, in quantum heat engines, the energy exchanged between the system and the thermal reservoirs occurs in quantized fashion. Therefore the quantum heat engines are modelled as sets having discrete energy levels unlike classical engines. But, one of the open problems of this topic is the link between classical and quantum thermodynamics for the analysis and designing of the quantum heat engines.

In 1803, Lazare Carnot developed a mathematical analysis of the efficiency of pulleys and inclined planes [76] in a general discussion on the conservation of mechanical energy. He highlighted that, in any movement, there always exists a loss of “moment of activity”. In 1824, his son Sadi Carnot [3] introduced the concept of the ideal engine. It is a system which operates on a completely reversible cycle without any dissipation. But, this result seems nonsensical because, apparently, this system has no irreversibility and, consequently, it could convert all the absorbed heat into work, without any energy loss. On the contrary, Carnot proved that [3,4]:

1. All ideal engines operating between the same two thermal baths of temperature T_1 and T_2 , with $T_1 > T_2$, has the same efficiency $\eta_C = 1 - T_1/T_2$;
2. Any other engine has an efficiency η such that always $\eta < \eta_C$.

Consequently, the efficiency of a reversible Carnot cycle is the upper bound of thermal efficiency for any heat engine working between the same temperature limits [3,4,17,76]. Carnot's general conclusion on heat engines is no more than the proof of the existence of natural limit for the conversion rate of the heat into the mechanical energy [4].

A great number of attempts have been developed to improve the calculation of the efficiency of the real machine [5,17,77–85] because all the thermodynamic processes occur in finite-size devices and in finite-time, in presence of irreversibility. The Carnot's limit is inevitable for any natural system [4], and it has always been experimentally verified.

In this paper, it is aimed to determine irreversibility in a quantum heat engine. Irreversibility is classified external, internal and total irreversibility that is sum of internal and external irreversibility. A method is presented to describe irreversibility for a quantum heat engine operating -1/2 spin system and also some numerical result are summarized.

2. Irreversibility from a quantum point of view

In This Section we consider the continuous interaction between atomic electrons and the environment photons. For simplicity, but without any loss of generality, we consider the Hydrogen-like atoms in interaction with the electromagnetic waves present in their environment.

The electromagnetic wave is a flow of photons, which incomes into the atoms, are absorbed by the atomic electrons if the electromagnetic wave frequency is resonant, and outcomes from them. At atomic level, the photons can be absorbed by the electrons of the atoms, and an electronic energy transition occurs between energy levels of two atomic stationary states. Then, the photons are emitted by the excited electrons, when they jump down into the energy level of the original stationary state.

Apparently, there are no changes in the energy of the atom, but only in the electronic transition. But, in reality there exists a change in the kinetic energy of the center of mass of the atom, which is usually negligible in relation to the to the energy change in electronic transition. Moreover, the time of occurrence of the energy variation of the atomic center of mass (10^{-13} s) is greater than the time of electronic transition (10^{-15} s).

Here, we stress that an energy variation of the atomic center of mass exists and it cannot be neglected if we consider a great number of interaction as it happens at macroscopic level [86].

Any atomic stationary state has a well defined energy level, identified by the principal quantum number n [87–94]. An electronic transition between two energy levels can occur following the quantum selection rule $\Delta n = n_f - n_i = \pm 1$ [87–94], where the subscript f means final state and the subscript i means initial state. The atom has an atomic number Z and only one electron in the last orbital. This electron moves in its orbital, for which, following the approach used in spectroscopy [92–95], we can introduced [86]:

1. The apparent atomic radius:

$$r_n = \frac{4\pi\epsilon_0\hbar^2}{m_e Z e^2} n^2 \quad (1)$$

2. The energy of the atomic level:

$$E_n = \frac{m_e Z^2 e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \frac{1}{n^2} \quad (2)$$

3. the Sommerfeld-Wilson rule states that [38–41]:

$$\oint p_e dr_n = p_e r_n = m_e v_e r = n\hbar \quad (3)$$

where p_e r is the angular momentum of the electron, being r_n defined by the relation (1), $n = 1, 2, 3, \dots$ is the principal quantum number, always integer, and \hbar is the Dirac constant, $p_e = m_e v_e$ is the electronic momentum, where m_e is the mass of the electron and v_e its velocity inside the atom, e is the elementary charge, and ϵ_0 is the electric permittivity. Considering an Hydrogen-like atom, at initial state, the geometric reference system can be fixed in the center of mass of the nucleus, so that the atom is at rest with null momentum \mathbf{p}_{atm} . Its Schrödinger's equation is [87–95]:

$$\left[-\frac{\hbar^2}{2m_N} \nabla_{\mathbf{r}_N}^2 - \frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}_e}^2 + V(\mathbf{r}_e - \mathbf{r}_N) \right] \psi(\mathbf{r}_N, \mathbf{r}_e) = E_{tot} \psi(\mathbf{r}_N, \mathbf{r}_e) \quad (4)$$

where \hbar is the Dirac constant, m_N is the mass of the nucleus, m_e is the mass of the electron, \mathbf{r}_N is the nucleus coordinate, \mathbf{r}_e is the electron coordinate, $V(\mathbf{r}_e - \mathbf{r}_N)$ is the electrostatic potential, E_{tot} is the total energy, and $\psi(\mathbf{r}_N, \mathbf{r}_e)$ is the wave function. Now, by using the relative coordinates $\mathbf{r} = \mathbf{r}_N - \mathbf{r}_e$, the coordinates of the center of mass $\mathbf{R} = (m_N \mathbf{r}_N + m_e \mathbf{r}_e)/(m_N + m_e)$, the total mass $M = m_N + m_e$, the reduced mass $\mu = (m_N^{-1} + m_e^{-1})^{-1}$, the momentum of the center of mass $\mathbf{P} = M \dot{\mathbf{R}} = -i\hbar \nabla_{\mathbf{R}}$, and momentum of the reduced mass particle $\mathbf{p} = \mu \dot{\mathbf{r}} = -i\hbar \nabla_{\mathbf{r}}$, the Eq. (4) becomes [87–95]:

$$\left[\left(-\frac{\hbar^2}{2\mu} \nabla_{\mathbf{r}}^2 + V(\mathbf{r}) \right) - \frac{\hbar^2}{2M} \nabla_{\mathbf{R}}^2 \right] \psi(\mathbf{r}, \mathbf{R}) = E_{tot} \psi(\mathbf{r}, \mathbf{R}) \quad (5)$$

The wave function $\psi(\mathbf{r}, \mathbf{R}) = \phi(\mathbf{r})\vartheta(\mathbf{R})$ is usually introduced to separate the Eq. (5) in the following two equations:

$$\begin{aligned} -\frac{\hbar^2}{2M} \nabla_{\mathbf{R}}^2 \vartheta(\mathbf{R}) &= E_{CM} \vartheta(\mathbf{R}) \\ \left(-\frac{\hbar^2}{2\mu} \nabla_{\mathbf{r}}^2 + V(\mathbf{r}) \right) \phi(\mathbf{r}) &= E_{\mu} \phi(\mathbf{r}) \end{aligned} \quad (6)$$

where $E_{CM} = \mathbf{P}^2/2M$ is the energy of the free particle *center of mass*, and E_{μ} is the energy of the bound particle of *reduced mass*, such that $E_{tot} = E_{CM} + E_{\mu}$, and $V(\mathbf{r}) = -Ze^2/r$.

Now, we consider the Hydrogen-like atom in interaction with external electromagnetic waves. The electromagnetic radiation is a flux of photons, with [95,96]:

1. The energy E_{γ} :

$$E_{\gamma} = h\nu \quad (7)$$

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