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Entropy production and generation: clarity from nanosystems considerations

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Abstract

The interest in designing of nanosystems is continuously growing. In engineering many optimization approaches exist to design macroscopic machines. If these methods could be introduced in the nanosystems designing, a great improvement would be obtained in nanotechnologies. But, it is necessary to obtain a link between classical thermodynamics and nanosystems. The aim of this paper is to obtain a first step towards this link. Some considerations on the role of power, time and non equilibrium temperature are discussed and a link between non equilibrium temperature and macroscopic thermodynamic quantities is suggested. This last result opens to new questions.

Keywords: nano-systems efficiency; entropy; fluctuations, irreversibility; molecular machines; non-equilibrium temperature.

Introduction

Interest in engineering applications of composite materials, molecular machines, reacting systems, drug delivery and chemical storage is continuously increasing [1-3]. Consequently, nano-thermodynamics represents a fundamental topic of investigation.

Since the 19th century, thermodynamics has been developed to study processes of macroscopic systems, which means that the number of particles is, at least, on the order of Avogadro's number [4,5]. Since 1930s, scientists and engineers have been trying to understand how to extend thermodynamic approach and methods as well as related fundamental quantities to small systems [5,6,7]: yet, today, this remains an open problem. Indeed, in general, the laws of thermodynamics operate at all scales, but at the small scale some phenomena, non visible at the macroscopic scale, must be taken into account; i.e. interfacial energy and the thermal fluctuations [8-12]. As results of these studies, many new approaches have been developed and improved, e.g. non equilibrium statistical thermodynamics, quantum thermodynamics, non equilibrium fluids, molecular dynamics, etc. [13-23].

In this context, surface energies have been highlighted to modify the physical and chemical properties of the small systems, which is taken into account by introducing a contribution to the total Gibbs free energy of the system [24-26]. The consequences of the progress in the small systems designing and synthesis have pointed out the scale-related properties, often different from the macroscopic ones [2]. Many approaches have been developed [25], but in relation to some of them, some criticisms [26-28] have been counterpoised. Consequently, in this paper, following the original aim of Hill and Tsallis, we will consider only the approaches based on the well known classical thermodynamics [4, 29-40] in order to obtain results starting from an acknowledged theory as the classical thermodynamic laws and their consequences. Indeed, applied and engineering thermodynamics is the science which studies both energy and its best use in relation to the available energy resources: energy and energy transformations, including power production, refrigeration and relationships among the properties of matter, including also living matter. The first law of

thermodynamics expresses the conservation of the total energy, while the second law states that entropy continuously increases for the system and its environment [28,29]. The analysis of irreversibility in applied thermodynamics is a fundamental science for the analysis of open systems when energy transfers and energy transformations occur. In this context, it has been highlighted that any effect in Nature is always the consequence of the dynamic balances of the interactions between the real systems and their environment and the real systems evolution is always related to the decrease of their free energy, in the least time [41-51]. Time is a quantity which doesn't usually appear explicitly in thermodynamics, but, when real systems are considered, it must be introduced [52].

This considerations allows us to introduce power balances in order to obtain a classical thermodynamic approach to irreversibility in nanosystems and to highlight the differences between entropy production and entropy generation.

The approach suggested

In relation to the small systems, the concept of variance of the distribution and fluctuations are fundamental to develop a thermodynamic approach. Indeed, the energy of any system fluctuates around its average value, without representing the begin of a process or a transition, but only the dynamical character of any thermodynamic configuration [53,54]. In the macroscopic limit

$$\frac{N}{V} \underset{\substack{N \to \infty \\ V \to \infty}}{\to} n \tag{1}$$

where N is the number of particles of the system, V is the volume of the system and n is its number density, considered fixed and constant for any defined system, fluctuations can be neglected, while in nanoscale systems they must be taken into account because a lot of nanoscale thermal properties and the transport phenomena can be evaluated [14-24] just by using also the fluctuation theory.

Fluctuation of a physical quantity ξ can be mathematically defined as the deviation $\delta\xi$ of any single measurement of ξ from its average value $\langle \xi \rangle$:

$$\delta\xi = \xi - \langle\xi\rangle \tag{2}$$

and the relevance of the fluctuation can be evaluated considering its fractional deviation

$$\sigma_{\xi r} = \frac{\sigma_\xi}{\langle\xi\rangle} \tag{3}$$

where σ_ξ is the standard deviation of ξ.

In relation to fluctuation it must be considered the Ehrenfest's fundamental question on the existence of a functional which achieves its extreme value, as entropy does for the stationary states in equilibrium thermodynamics. So, many fluctuation theorems have been developed to obtain this general principle of analysis and designing of the stationary systems for complex, and in this context also small systems [55-59]. Strictly related to this topic, it is the analysis of the self-organization systems introduced by Mayer, Boltzmann, Schrödinger and Prigogine. The basis of their approach is the fundamental role of the exchanges between the system and the surrounding. Related to this topic, it must be consider also the development of non-equilibrium or irreversible thermodynamics, begun by Joseph John Thomson (1856-1940), John William Strutt Rayleigh (1842-1919), Pierre Maurice Marie Duhem (1861-1916), Władysław Natanson (1864–1937), Gustav Jaumann (1863–1924) and formalized by Louis Georges Gouy (1854-1926), Aurel Stodola (1859-1942), Lars Onsager (1903-1976), Carl Henry Eckart (1902-1973), Josef Meixner (1908-1994), Hendrik Casimir (1909-2000), Ilya Prigogine (1917-2003) and Sybren Ruurds De Groot (1916-1994). Indeed, the analysis of the irreversible processes is essential in the study of nonlinear sciences, which need a nonlinear dynamical approach. Thermodynamics is just a theory of collective behaviour of complex systems from engines to biological structures, from transport phenomena to black holes, etc., and all these phenomena obey to the second law. To develop this law to small system a mechanical formulation is required [60].

For a non equilibrium stationary state of a nanosystem in interaction with its environment the entropy production rate can be defined as:

$$\dot{\Sigma} = \frac{\dot{Q}}{T_0} \qquad (4)$$

where $\dot{Q}$ is the heat power exchanged between the system and its environment, at the thermostatic temperature T_0. This quantity has been proved to be microscopically obtainable by using the mechanical properties of the non equilibrium, but, stationary, system [61].

It must be highlighted that the entropy of the system cannot be defined because non equilibrium temperature has never been defined, while it is possible to define the entropy variation due to interaction between system and thermostats because it is possible to define the thermostat temperature. This consideration is fundamental because it is the basis of the recent approach to molecular machines and Lodschmidt paradox [39]: the irreversibility of nanosystems can be evaluated in the interaction between the nanosystem and its environment, considered as a thermostat.

The consequences of this result can be improved in the following considerations. In relation to the equation (4), we can consider the first law in its power expression [4,5]:

$$\dot{Q} - \left(\dot{W} - \dot{W}_\lambda \right) = \dot{U} \qquad (5)$$

where $\dot{Q}$ heat power exchanged between the system and the thermostat, $\dot{W}$ is the mechanical power produced, $\dot{W}_\lambda$ is the mechanical power lost by irreversibility and $\dot{U}$ is the internal energy. In relation to fluctuations, no work is produced the relation (5) becomes:

$$\dot{Q} = \dot{U} - \dot{W}_\lambda \qquad (6)$$

and the relation (4) becomes:

$$\dot{\Sigma} = \frac{\dot{U} - \dot{W}_\lambda}{T_0} \qquad (7)$$

Now, considering the effect of the fluctuation as the interaction between an irreversible open system and its environment, the usual entropy balance can be written as [62]:

$$\frac{\partial S}{\partial t} + \int_V v\nabla \cdot \left[\frac{\mathbf{Q}}{T_0} + \rho s\left(\dot{\mathbf{x}} - \dot{\mathbf{x}}_{eq}\right)\right] dV = \dot{\Sigma} \tag{8}$$

where S is the entropy variation related to the interaction between an irreversible system and its environment, which has a velocity $\dot{\mathbf{x}}$ and a density ρ, considering the mean velocity the one of the equilibrium $\dot{\mathbf{x}}_{eq}$, s is the entropy density and $\mathbf{Q}$ is the heat flow. Comparing the relations (7) and (8) and considering, it follows:

$$\frac{\partial S}{\partial t} + \int_V v\nabla \cdot \left[\frac{\mathbf{Q}}{T_0} + \rho s\left(\dot{\mathbf{x}} - \dot{\mathbf{x}}_{eq}\right)\right] dV = \frac{\dot{U}}{T_0} - \frac{\dot{W}_\lambda}{T_0} \tag{9}$$

Considering that:

1. For an ideal system $\dot{Q} = \dot{U}$;

2. The irreversibility is related to the interaction of the system and the environment, that is represented by the flow $\mathbf{Q}$ and velocity fluctuation $\delta\dot{\mathbf{x}} = \left(\dot{\mathbf{x}} - \dot{\mathbf{x}}_{eq}\right)$;

it is possible to argue that:

$$\frac{\partial S}{\partial t} = \frac{\dot{U}}{T_0}$$
$$\int_V v\nabla \cdot \left[\frac{\mathbf{Q}}{T_0} + \rho s\left(\dot{\mathbf{x}} - \dot{\mathbf{x}}_{eq}\right)\right] dV = -\frac{\dot{W}_\lambda}{T_0} \tag{10}$$

But, as a consequence of the Gouy-Stodola theorem, it is possible to define the entropy generation as [4,5]:

$$S_g = \frac{\dot{W}_\lambda}{T_0} \tag{11}$$

so, it follows that:

$$S_g = \frac{\partial S}{\partial t} - \dot{\Sigma} \tag{12}$$

In conclusion, the results obtained can be summarized as:

1. It isn't possible to define the entropy of a nanosystem because it isn't possible to define the non equilibrium temperature;

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2. On the contrary, it is possible to define the nanosystem entropy variation rate as the consequence of the internal energy fluctuations rate;

3. The entropy production rate is the result of the heat power exchanged between the system and its environment;

4. The entropy generation rate is the global result of the previous effects, a macroscopic quantity related to the interaction between system and its environment;

5. The entropy generation rate expression is formally equal to the Lagrangian rate expression;

6. All the previous non equilibrium relations are related to the unit time, so time results a fundamental quantity in the non equilibrium thermodynamic analysis, while in equilibrium thermodynamics it isn't usually considered;

7. The non equilibrium temperature T_{neq} could be related to the entropy generation; indeed, temperature is a quantity related to the internal energy of the system considered, i.e.:

$$T \propto U \tag{13}$$

so, considering the equation (10) and (12) and introducing the mean time τ of two successive fluctuations, the relation (13) becomes:

$$T_{neq} \propto \frac{\delta U}{\tau} = T_0 \frac{S_g + \delta\Sigma}{\tau} \tag{14}$$

where δ means fluctuation as defined in the relation (2).

Now, an example will be developed. In 1926, Johnson measured electronic noise with $1/f$ frequency dependence, being f the frequency, up today without any physical explanation. Let us consider the electrons inside the matter as an ideal gas. In this way, the variation of the internal energy can be obtained as the work lost for viscosity, as follows:

$$\delta U = W_\lambda = -\mathbf{F} \cdot \mathbf{l} = \eta \, \nabla v \cdot \mathbf{l} \tag{15}$$

where $\mathbf{F}$ is the friction force due to viscosity, v is the mean velocity of the electrons and $\mathbf{l}$ is the free mean path of the electrons. Following the classical kinetic theory it follows:

$$\eta = \frac{\langle E_k \rangle}{6} \tau \tag{16}$$

$$\mathbf{l} = \mathbf{v}\tau$$

where E_k is the total kinetic energy of the gas and τ is the time required by an electron to walk the free mean path l at the mean velocity v. So, the relation (15) becomes:

$$\delta U = \frac{\langle E_k \rangle}{6} \tau \, \nabla v \cdot \mathbf{v}\tau \tag{17}$$

and the non equilibrium temperature results

$$T_{neq} \propto \frac{\delta U}{\tau} = \frac{1}{6} \langle E_k \rangle \tau \, \nabla v \cdot \mathbf{v} = \frac{\langle E_k \rangle |\nabla E_k|}{6M} \tau \tag{18}$$

where M is the total mass of the electrons. This results confirms that the non-equilibrium temperature is proportional to the characteristic time of the system. Moreover, the electronic noise is due to the thermal motion of the electrons inside the matter, so the measure of the frequency of the noise represents an indirect measure of the non-equilibrium temperature, because the noise is generated by the collisions of the electrons at the frequency $f = 1/\tau$. But, it represents also a physical explanation of the $1/f$ effect, up today without any explanation.

Conclusions

During the 19th Century, thermodynamics began its development as a physical science as the results of the studies of Sadi Carnot (1796-1832), Julius Robert von Mayer (1814-1878), Hermann Helmholtz (1821-1894), William Thomson (1824-1907) and Rudolf Clausius (1822-1888). In 1929, it was Walter Schottky (1886-1976) first to spread the approach to thermodynamics for industrial applications. Recently, just the thermodynamic formalism and the related links between macroscopic and microscopic approach to entropy have become clear to play an important role in nonlinear sciences and complex systems with particular regards to power engineering, environmental sciences, quantum theory, low temperature physics, large scale and small scale physics, biophysics, biochemistry and biomedicine, information sciences, etc.. Strictly related to

this topic it is the analysis of the self-organization systems introduced on the basis of the interaction between the system and its surrounding.

Moreover, the interest in designing of nanosystems is growing. Mechanical engineering uses a great number of optimization approaches to design macroscopic machines. If these methods could be introduced in the designing of nanosystems it would be a great improvement in nanotechnologies. But, to do so, it is necessary to extend classical thermodynamic analysis to nanosystems [34,39,40].

Here some considerations on this link between engineering thermodynamics and nanosystems has been introduced. Last, some considerations on the fundamental problems in non-equilibrium systems have been discussed and a new approach has been introduced. The results open new questions:

1. How can we evaluate the non equilibrium temperature of the relation (14)?
2. How can we evaluate the time in the same relation?
3. What does it mean that the non equilibrium temperature is related to time?
4. Can this temperature be measured?

Last, some considerations must be considered. Fluctuations are not random but simply reactions to small forces that maintain the system at the free energy minimum, so, fluctuations drive evolution toward the free energy minimum in the same way as large forces: the proper starting point is an evolutionary equation, namely the principle of least action in its original form due to Maupertuis 41-51]. Consequently, temperature is simply average energy of the system at any instant of evolution. But, in non-equilibrium systems, the average energy can be measured, however, not exactly as it is constantly in change for an evolving system. Indeed, also the mere act of measurement will change temperature. This effect is non-negligible for a nanosystem.

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