THE IMPLICATIONS OF THE BREAKDOWN OF THERMODYNAMIC STABILITY IN ENERGY GENERATION AND CONVERSION NANODEVICES

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EXTENDED ABSTRACT

The concept of stability is essential when describing the behaviour and properties of matter [1]. At the microscopic level, the stability of atoms becomes manifest through the existence of chemical elements. Macroscopic thermodynamic systems show stability through the existence of distinct phases which can coexist under the same physical conditions.

Unlike macroscopic systems, the existence of boundaries in small systems confers them peculiar characteristics. Finite size induces non-homogeneities of the interaction energy which may give rise to free-energy barriers separating two different configuration or aggregation (metastable) states. Passing from one of these configurations to the other is a matter of thermodynamic transformation theory, a well-understood problem in classical thermodynamics [2, 3].

When a macroscopic system is subjected to destabilizing conditions, it separates into two or more phases that may coexist in equilibrium [2, 3]. This partitioning involves the formation of new free-energy barriers associated to interfaces and finally, from the thermodynamic point of view, to the emergence of new systems with their own free energy which determines their physical properties: compressibilities, specific heats, etc. [3]

However, when the system is finite and small enough, the formation of an interface could become energetically unfavourable. This energetic restriction has been observed, for instance, in the formation of magnetic domains in ferromagnetic materials [4] or in atomic nanoclusters with magical numbers, and may be responsible for peculiar effects on the behaviour and properties of the system [5, 6].

A deeper analysis related to this last question must account for the implications of the finite size of the system on its thermodynamic behaviour. This analysis has shown that inflexions and barriers in the thermodynamic free energy are related to irreversible processes. This is revealed through the calculus of the entropy produced in a transformation implying the transition over a free energy barrier. This process is possible due to the existence of a thermodynamic affinity whose origin resides in the external constrains. Since these irreversible processes may be cyclical, they can be used to generate or convert energy at the nanoscale if the external constraints force the state of the system to reside in an region of the order parameter in correspondence with the unstable region of the free energy. Under these circumstances, we show that an oscillation between the two metastable states separated by the free energy barrier may be triggered. This cyclical motion persists while these external constraints maintain the system out of equilibrium. The results obtained are of great interest since they underlay the physics of energy generation and conversion nanodevices [7]. Potential applications have been recently reported for energy nanogenerators [8], systems based on the pyroelectric effect [9] and also for some storage systems [10]. Coupling of several small systems may lead to interesting effects that are in the thermodynamic origin of the electric hysteresis [11, 12]. Oscillating behaviours are also useful in energy-converting nanodevices whose operation depends on the pressure conditions imposed by the heat bath [13].

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