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Article

Multiscale Mesoscopic Entropy of Driven Macroscopic Systems

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Abstract: How do macroscopic systems react to imposed external forces? Attempts to answer this question by a general principle have a long history. The general feeling is that the macroscopic systems in their reaction to imposed external forces follow some kind of optimization strategy in which their internal structure is changed so that they offer the least possible resistance. What is the potential involved in such optimization? It is often suggested that it is entropy or entropy production. But entropy is a potential arising in thermodynamics of externally unforced macroscopic systems. What exactly shall we understand by a mesoscopic entropy of externally driven systems and how shall we find it for a specific macroscopic system?

Keywords: nonequilibrium thermodynamics; mesoscopic entropy; entropy generation principle

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1. Introduction

Existence or absence of a sufficiently general principle guiding behavior of driven macroscopical systems has yet to be proven. Arguments for the existence have been introduced for instance in [1–8], arguments for the absence in [9]. All suggested general principles that we know of are formulated in the

setting of classical equilibrium thermodynamics and equilibrium statistical mechanics with the classical concept of equilibrium or local equilibrium entropy. Such setting limits interactions between the macroscopic systems and their surroundings and excludes investigations of driven systems requiring nano-scale microscopic physics. The arguments against a potential-based general principle have arisen in [9] in a detailed analysis of driven systems exhibiting emergence of highly organized patterns.

In both pro- and con-oriented investigations the following question arises: What if the analysis were carried on a (mesoscopic) level of description involving more details, or alternatively, what if the analysis were carried out simultaneously on several different levels of description? The mesoscopic level involving more details could be a level that includes extra state variables addressing microscopic details playing an important role for instance in biology or nanotechnology (such state variables are absent in [1–8]) or it also could be a level involving state variables with which details of mesoscopic structures emerging for instance in turbulent flows can be described (such state variables are absent in the formulations discussed in [9]). Since all the general principles suggested so far involve a potential that is closely related to entropy or its production, the more narrowly focused but closely related is then the question of what is the entropy of driven systems on a general mesoscopic (*i.e.*, beyond equilibrium and local equilibrium) levels of description. This is exactly the question that we investigate in this paper.

The equilibrium entropies (*i.e.*, those arising in the classical or local equilibrium thermodynamics or those on mesoscopic levels of description that are reduced from the Gibbs entropy arising on the microscopic level of equilibrium statistical mechanics) have a limited legitimacy outside equilibrium. Multiscale mesoscopic dynamics (MM dynamics) developed in [10,11] provides a setting for a new approach to defining nonequilibrium entropy (we shall call it mM entropy) on mesoscopic levels of description. In this paper we apply it to externally driven macroscopic systems. In Section 2 we recall MM dynamics and the mM entropy arising in it. In Section 3 we show that in the setting of equilibrium or local equilibrium thermodynamics the mM entropy coincides with the equilibrium or the local equilibrium entropy. Finally, in Section 4, we provide a specific example of the mM entropy.

2. Time Evolution of Externally Driven Macroscopic Systems

We begin by recalling that the physics taking place in macroscopic systems can be expressed on different levels of description. The levels have emerged in the effort to organize and understand experience collected in certain types (different for different levels) of experimental observations. The levels are initially independent and autonomous. For example water can be modeled on the completely microscopic level on which it is seen as being composed of atoms (we shall denote this levels by the symbol L_{MICRO}), or on more macroscopic levels as e.g. the level of kinetic theory (denoted L_{KT}), the level of classical fluid mechanics (denoted L_{leq}), and the level of classical thermodynamics (denoted L_{eq}).

We shall now regard macroscopic systems simultaneously on two levels. We assume that both levels have been found to provide a setting for describing the experimentally observed behavior. Let L_{meso} be the more macroscopic (*i.e.*, involving the least amount of details) and L_{MESO} the more microscopic level. The time evolution on L_{MESO} is seen to proceed in two stages. The first one brings the detailed description on the level L_{MESO} to a less detailed description on the level L_{meso}. This stage is then followed by the second stage in which the time evolution continues on the level L_{meso}. We shall refer to the first stage in the time evolution taking place on L_{MESO} as the *fast time evolution* and to the second as the

slow time evolution since the time interval needed to approach the level L_{meso} is small relative to the time intervals needed to observe changes due to the time evolution on the level L_{meso}. The existence of the split of the time evolution taking place on L_{MESO} into fast and slow is a consequence of the experimentally observed fact that our externally driven macroscopic system under consideration is found to be well described on both levels L_{meso} and L_{MESO}.

The pairs of levels (L_{meso}, L_{MESO}) can be for example (L_{eq}, L_{MICRO}), (L_{leq}, L_{KT}). We shall discuss several examples below in Sections 3 and 4.

Now, we continue with our general observations about macroscopic time evolution. Having recognized the existence of two types of the time evolution (namely the fast and the slow), we can now say that our interest in the behavior of driven systems is in fact an interest in the slow time evolution. We shall argue however that the fast time evolution is still very pertinent since it provides potentials (namely the energy and the entropy) needed in the anticipated optimization strategy of responses of macroscopic systems to driving forces. We thus turn our attention first to the fast time evolution.

By analyzing many examples of relations inside pairs (L_{meso}, L_{MESO}), a common structure of the fast time evolution has emerged (see [10] and references cited therein). The elements of the structure that are pertinent to our interests in this paper are the following:

(i) The fast time evolution bringing L_{MESO} into L_{meso} is generated by two potentials, one is $E^{(MESO)}$ and the other $S^{(MESO\rightarrow meso)}$. The former is physically interpreted as the energy on the level L_{MESO}. The latter does not decrease during the fast time evolution and is physically interpreted as the entropy on the level L_{MESO}. As the time goes to infinity, $S^{(MESO\rightarrow meso)}$ reaches its maximum that we denote $S^{(meso\leftarrow MESO)}$. This is a new potential (a new entropy) on the level L_{meso}.

(ii) In the enlarge space that involves the state variables, their conjugates, and the generating potential (combining L_{MESO} $E^{(MESO)}$ and $S^{(MESO\rightarrow meso)}$), the fast time evolution appears to be a sequence (parametrized by time) of Legendre transformations.

(iii) The fast time evolution is distinguished among all time evolutions during which the level L_{MESO} is being reduced to a less microscopic (*i.e.*, involving less details) level L_{meso} by the following two properties: (a) $S^{(MESO\rightarrow meso)}$ does not decrease; and (b) the total entropy S created in the passage from L_{MESO} to L_{meso} (*i.e.*, $S = \int dt d(S^{(MESO\rightarrow meso)}/dt)$ reaches its extremum. If we realize that the state at which the system is found to be well described on the level L_{meso} is in fact a stationary state of the fast time evolution we can also formulate this result (for its proof, see [10]) as follows. Any open system develops toward a stationary state following a path on which the entropy generation reaches its extremum. The entropy is the potential generating the fast time evolution, the stationary state is a state that remains unchanged in time only with respect to the fast time evolution but, in general, changes in time (in a slower pace) in the slow time evolution.

Before proceeding with our investigation, we put the results that we have just recalled into the context of results of a similar nature that have been obtained previously. The fact that entropy depends on the level of description is well known (see for example [12–15]). In our setting, the entropy does not depend only on the level L_{MESO} on which the time evolution is originally formulated but also on the more macroscopic level L_{meso} to which L_{MESO} reduces during the time evolution. Every pair of well established levels (*i.e.*, levels well tested with experimental observations) is assocoated with one entropy $S^{(MESO\rightarrow meso)}$ on level L_{MESO} and one entropy $S^{(meso\leftarrow MESO)}$ on level L_{meso}. In most previous investigations

the level L_{meso} was taken to be usually the level of classical equilibrium thermodynamics. But even in the investigations in which L_{meso} is a general mesoscopic level (for example those reported in [14,15]) the two entropies $S^{(MESO\rightarrow meso)}$ and $S^{(meso\leftarrow MESO)}$ have not been identified. We briefly explain why. The analysis of the time evolution on the level L_{MESO} is in [14,15] inspired by the Chapman-Enskog analysis of solutions to the Boltzmann equations and proceeds as follows. First, an entropy on the level L_{MESO} is suggested (it is for example the Boltzmann H-function in the context of the Boltzmann equation) and by its maximization subject to constraints corresponding to the level L_{meso} a manifold of states representing in L_{MESO} the state space used in L_{meso} is identified (in the context of the Chapman-Enskog method for solving the Boltzmann equation it is the manifold formed by local Maxwellian distribution functions). The time evolution taking place in L_{MESO} that is restricted to this manifold represents an initial approximation of the reduced time evolution taking place on the level L_{meso}. In order to improve this initial approximation the manifold is deformed (in the context of the Chapman-Enskog method for solving the Boltzmann equation such deformation is achieved by making the so called first Chapman-Enskog approximation). Many ingenious methods for making this type of deformations in a rather general setting are suggested in [14,15]. Having the deformed manifold, we are making a next step. We identify a deformation of the initial entropy (*i.e.*, deformation of the H-function in the case of the Boltzmann equation) that corresponds to the deformed manifold in the sense that the deformed manifold is the manifold obtained by its maximization (in the same way as the initial manifold is obtained by maximiaing the initial entropy). Such deformed entropy is then the entropy $S^{(MESO\rightarrow meso)}$. Beside this new feature of our analysis a whole new physics and mathematics enters our investigation through the contact-structure geometry formulation.

Now we return to the problem that is in the center of our interest in this paper and formulate a conjecture about responses of macroscopic systems to external forces.

Conjecture

Let L_{meso} *and* L_{MESO} *be two levels of description. We assume that* L_{MESO} *involves more details than* L_{meso} *and that both levels provide a description of behavior of a family of macroscopic system subjected to a family of external forces that is found in agreement with results of experimental observations. The experimental observations made on* L_{MESO} *are in general different from those made on* L_{meso}*. We conjecture that the potential* $S^{(meso\leftarrow MESO)}$ *(that is inherited on the level* L_{meso} *from* L_{MESO} *by investigating the time evolution in which* L_{MESO} *reduces to* L_{meso}*) plays an important role in describing the time evolution on the level* L_{meso}*.*

One of the anticipated roles of the potential $S^{(meso\leftarrow MESO)}$ (we also call it hereafter mM entropy) is its participation in an optimization strategy of macroscopic systems to adjust themselves to minimize their resistance to driving forces, the other in characterizing fluctuations. We shall comment about the former in Section 3 and about the latter in the rest of this section.

We place ourselves on the level L_{meso}. According to our assumption, predictions of the theory formulated on L_{meso} are found to agree with results of the family of experimental observations (denoted O_{meso}) that is associated with the level L_{meso}. Nevertheless, the fact that there are more microscopic levels L_{MESO} on which the systems under consideration can also be described can be seen in results of the observations O_{meso}. It suffices to increase precision of the observations O_{meso}. The results are suddenly seen to fluctuate. This is indeed one of the ways the more microscopic nature of the macroscopic systems under

consideration manifests itself on the level L_{meso}. We can now proceed and investigate details of the fluctuations. It is natural to anticipate that the mM entropy $S^{(meso \leftarrow MESO)}$, that, as we have seen, is itself a remnant of L_{MESO} on L_{meso}, is somehow related to the fluctuations. The argument relating entropy with fluctuations goes in fact back to Einstein. We shall recall the argument in the form presented in [10]. Let x_{meso} be the state variables used on the level L_{meso}. In order to take into account fluctuations, we promote x_{meso} into random variables and replace x_{meso} with the distribution function $f(x_{meso})$. The new mM entropy (now a function of $f(x_{meso})$) is a sum of the average entropy $\int dx_{meso} f(x_{meso}) S^{(meso \leftarrow MESO)}(x_{meso})$ and a new term $-k_B \int dx_{meso} f(x_{meso}) \ln f(x_{meso})$, k_B is the Boltzmann constant, representing the entropy corresponding to the fact that the state variables are random variables. Maximization (with respect to $f(x_{meso})$) of this entropy leads then to the Einstein distribution of fluctuations determined by the mM entropy $S^{(meso \leftarrow MESO)}$.

3. Local Equilibrium

We now illustrate the general considerations presented above on the example in which L_{meso} is taken to be the level of the classical equilibrium (denoted L_{eq}). First, we recall that on this level the macroscopic systems are at thermodynamic equilibrium. This means that their states are characterized by two real numbers (e.g., (e,v), where e is the specific internal energy and v specific volume—for the sake of simplicity we restrict ourselves to one component systems) and that they are surrounded by thermodynamic walls. A state of thermodynamic equilibrium is a state reached in a preparation process in which the macroscopic system under consideration is left sufficiently long time surrounded by unchanging thermodynamic walls. The thermodynamic walls are defined as modes of interaction with surrounding that make possible to measure the conjugate state variables. We recall that the conjugate of e is the temperature T and the conjugate of v is the pressure P. The measurement process is based on the existence of a potential $s = s(e,v)$, called an entropy, that is required to reach maximum if the systems involved in the measurement interact through the thermodynamic walls. The interaction through e-passing thermodynamic wall (also called heat-passing) leads to equilibration of temperatures on both sides of the wall and the v-passing thermodynamic wall (a mechanical piston) leads to equilibration of pressures on both sides of the wall. The entropy $s = s(e,v)$ is the potential $S^{(eq \leftarrow MESO)}$ inherited from an analysis of the fast time evolution that is, in this example, the time evolution taking place in the process needed to prepare the macroscopic systems to thermodynamic equilibrium states. The level L_{MESO} can be any level involving internal time evolution.

It can be for instance the completely microscopic level L_{MICRO} (*i.e.*, the level on which the macroscopic systems are seen as composed of atoms). In this case the setting for the analysis of $L_{MICRO} \rightarrow L_{eq}$ becomes the setting of Gibbs' equilibrium statistical mechanics. We recall that in Gibbs' analysis the time evolution on the level L_{MICRO} is drastically reduced, with the help of the ergodicity-type hypothesis, to only global conservation laws of classical mechanics.

Another example of the level L_{MESO} that involves more details than the level L_{eq} is the level of local equilibrium L_{leq}. It differs from L_{eq} by allowing the thermodynamic equilibrium states to be different from one place to another (*i.e.*, to be local). The state variables are the same as on L_{eq} except that they are local (*i.e.*, instead of real number they are fields) and a field having the physical interpretation of the flow velocity is adopted as a new state variable. The entropy is assumed to be the same as on the level L_{eq} except that it is local.

The time evolution on the level L_{eq}, *i.e.*, the slow time evolution, is no time evolution except the time evolution reflecting imposed time changes in thermodynamic walls. The slow time evolution on the level L_{leq} is the time evolution studied in the classical fluid mechanics.

The classical example of a driven system on the level L_{eq} is Carnot's engine. Its input is the heat flow induced by imposed temperature gradient and its output is a mechanical work. In this example the physical interpretation of the entropy as a measure of organization inside the macroscopic systems is revealed. In order to transform the macroscopically disorganized internal energy into macroscopically organized mechanical energy one needs to begin with an organization of the internal energy. This is done in Carnot's engine by sustaining heat flux. But in order to sustain the heat flux, it is obviously impossible to transform all the disorganized internal energy into the organized mechanical energy. A part of the energy flux is used in the organization process (see more in [8])

Importance of the entropy (or the entropy generation) in many other examples of macroscopic systems on the levels L_{eq} and L_{leq} that are open to the environment through thermodynamic walls has been revealed in [1–8]. The investigations and applications reported in these papers (see also references cited therein) provide support for the existence of a universal principle guiding the behavior of driven macroscopic systems and for the conjecture formulated in Section 2.

4. Beyond the Local Equilibrium

Many practical applications require however formulations on levels L_{meso} that are more detailed (more microscopic) than the levels L_{eq} and L_{leq}. We illustrate this need on the example of Rayleigh-Bénard system (a horizontal layer of a fluid subjected to the gravitation force and temperature gradient). This macroscopic system is open to its surrounding through thermodynamic walls (as the systems discussed in the previous section are) and in addition it is subjected to a force field (the gravitational force field). Experimental observations show the following behavior. If the imposed temperature gradient is small, the fluid, that is initially at rest, remains at rest and only heat flows through the layer. This behavior is found to be well described by the classical fluid mechanics (*i.e.*, on the level L_{leq}). We now gradually increase the temperature gradient ΔT. When it reaches a certain value ($(\Delta T)_{crit}$, called a critical value), the fluid inside the layer begins to flow in macroscopically organized manner. Emergence of this new macroscopic pattern is seen in experimental observations and it is also seen in the mathematical formulation as a bifurcation in solutions to the governing equations of fluid mechanics. From the physical point of view, the emergence of an internal macroscopic motion inside the fluid (that becomes the turbulent motion for large temperature gradients) transforms the originally simple fluid into a complex fluid with an internal structure. The level L_{leq} of classical fluid mechanics that is well suited for describing the behavior of simple fluids (*i.e.*, the behavior seen if the imposed temperature gradient is smaller than $(\Delta T)_{crit}$) is not anymore sufficient to describe the time evolution of such complex fluid. This also means that the classical local entropy, playing the important role described in Section 1 in many applications discussed in [1–8], is not playing such role in complex fluids. We however anticipate that the potential, $S^{(cf \leftarrow MESO)}$ where L_{cf} is the level suitable for describing the complex fluid under investigation and L_{MESO} is a more microscopic level of description, will assume the role that the local entropy plays for simple fluids. We hope to identified an appropriate level L_{MESO} on which we formulate dynamics of the Rayleigh-Bénard system and extract from it the fast

time evolution leading to $S^{(cf \leftarrow MESO)}$ in a future paper.

4.1. Illustration: Cattaneo Heat Conduction

In this paper we illustrate the mM entropy in a simpler setting involving only heat conduction. We introduce three levels of description:

(1) L_{eq}

This is the level of classical equilibrium thermodynamics. We limit ourselves only to one state variable, namely to the energy e (in this discussion we consider e to be energy per unit volume). No time evolution takes place on this level.

(2) L_{leq}

This is the level of local equilibrium. The state variable is the field of energy $e(\mathrm{r})$ that is related to the energy e serving as state variable on the level L_{eq} by: $e = \frac{1}{V}\int d\mathrm{r}\, e(\mathrm{r})$, V is the volume of the region in R^3 in which the macroscopic system under consideration is confined. The energy field evolves in time.

(3) L_{Catt}

This is the mesoscopic level introduced by Cattaneo [16]. The state variables on this level are ($e(\mathrm{r})$, $\mathrm{w}(\mathrm{r})$), where $e(\mathrm{r})$ is the same field as the one serving as state variable on the level L_{leq} and the new field $\mathrm{w}(\mathrm{r})$ is a vector field that is, as we shall see below, a conjugate variable to the heat flux. The energy e serving as state variable on the level L_{eq} is expressed, in terms of $e(\mathrm{r})$, as: $e = \frac{1}{V}\int d\mathrm{r}\, e(\mathrm{r})$. Both state variables ($e(\mathrm{r})$, $\mathrm{w}(\mathrm{r})$) evolve in time.

4.1.1. $L_{leq} \rightarrow L_{eq}$

We investigate first the time evolution in which the level L_{leq} reduces to the level L_{eq}. This time evolution is observed in closed systems that are not prevented by external influences from reaching the total thermodynamic equilibrium. This fast time evolution (recall that no time evolution takes place on the level L_{eq} so that any time evolution on the level L_{leq} has to be a fast time evolution) is governed by the Fourier equation:

$$\frac{\partial e(\mathrm{r})}{\partial t} = -\frac{\partial}{\partial r_i}\left(\lambda \frac{\partial S_{e(\mathrm{r})}^{(leq \rightarrow eq)}}{\partial r_i}\right) \tag{1}$$

where $\mathrm{r} = (r_1, r_2, r_3)$ is the position vector, t is the time, $\lambda > 0$ is the material parameter (coefficient of heat conductivity), $S^{(leg \rightarrow eg)}$ is the entropy generating the fast time evolution, we use the shorthand notation $S_{e(\mathrm{r})}^{(leq \rightarrow eq)} = \frac{\partial S^{(leq \rightarrow eq)}}{\partial e(\mathrm{r})}$, and also we use the summation convention.

From Equation (1) we obtain immediately the following two results:

($L_{leq} \to L_{eq}$: Result 1)

$$\frac{dS^{(leq\to eq)}}{dt} = \int d\mathrm{r} S^{(leq\to eq)}_{e(\mathrm{r})} \frac{\partial e(\mathrm{r})}{\partial t} = \int d\mathrm{r} \left(\frac{\partial S^{(leq\to eq)}_{e(\mathrm{r})}}{\partial r_i} \lambda \frac{\partial S^{(leq\to eq)}_{e(\mathrm{r})}}{\partial r_i} \right) \geq 0 \tag{2}$$

provided $\lambda > 0$. If $-S^{(leg\to eg)}$ is a convex function of $e(\mathrm{r})$ then Equation (2) implies that this function plays the role of the Lyapunov function which then means that solutions to Equation (1) approach, as $t \to \infty$, states that are solutions to

$$\frac{\partial S^{(leq\to eq)}_{e(\mathrm{r})}}{\partial \mathrm{r}} = 0 \tag{3}$$

Such states are the thermodynamic equilibrium states at which the level L_{eq} applies.

($L_{leq} \to L_{eq}$: Result 2)

The function $S^{(eq\leftarrow leq)} = S^{(leq\to eq)}|_{(solutions\ to\ (3))}$ is the equilibrium entropy $s = s(e)$ on the level L_{eq} (*i.e.*, in other words, $s = s(e)$ is the fundamental thermodynamic relation in the classical equilibrium thermodynamics).

4.1.2. $L_{Catt} \to L_{eq}$

The time evolution on the level L_{Catt} during which the level L_{Catt} reduces to the level L_{eq} is again observed only in closed systems that are not prevented from reaching the complete thermodynamic equilibrium. This fast time evolution is governed by the Cattaneo equations:

$$\frac{\partial e(\mathrm{r})}{\partial t} = \frac{\partial}{\partial r_i}\left(S^{(Catt\to eq)}_{w_i(\mathrm{r})} \right) \tag{4}$$

$$\frac{\partial w_i(\mathrm{r})}{\partial t} = \frac{\partial}{\partial r_i}\left(S^{(Catt\to eq)}_{e(\mathrm{r})} \right) + \Lambda S^{(Catt\to eq)}_{w_i(\mathrm{r})} \tag{5}$$

where $\Lambda > 0$ is a material parameter. From Equation (4) we see clearly the physical interpretation of the vector field w(r): $-S^{(Catt\to eq)}_{w_i(\mathrm{r})} = heat\ flux$.

Equations (4) and (5) represent a simplified version of the Cattaneo dynamics. The version that possesses all the elements of the structure shared with many other well established fast time evolutions (see [10]) has been introduced in [17]. The difference between the Cattaneo Equations (4) and (5) and the Cattaneo equations appearing in [17] is in the nondissipative part of the time evolution (*i.e.*, the time evolution governed by the right hand side of Equation (4) and the first term on the right hand side of Equation (5)). In both versions this time evolution is Hamiltonian and preserves the entropy $S^{(Catt\to eg)}$ and the energy $E^{(Catt)} = \int d\mathrm{r} e(\mathrm{r})$. The difference is in the Hamiltonian structure. In [17] the energy is preserved since it serves as the generating potential and the entropy is preserved due to the degeneracy of the Hamiltonian structure. In Equations (4) and (5) the reasons for conservations of energy and entropy are reversed. The results about the Cattaneo time evolution presented bellow hold for both versions. Proofs are however simpler and more straightforward for the version in Equations (4) and (5). This is the reason

why we use it in this paper.

The result that corresponds to Result 1 in the investigation of $L_{leq} \rightarrow L_{eq}$ is now:

($L_{Catt} \rightarrow L_{eq}$: Result 1)

$$\begin{aligned} \frac{dS^{(Catt\rightarrow eq)}}{dt} &= \int d\mathrm{r}\left(S^{(Catt\rightarrow eq)}_{e(\mathrm{r})} \frac{\partial e(\mathrm{r})}{\partial t} + S^{(Catt\rightarrow eq)}_{w_i(\mathrm{r})} \frac{\partial w_i(\mathrm{r})}{\partial t} \right) \\ &= \int d\mathrm{r} \frac{\partial}{\partial r_i}\left(S^{(Catt\rightarrow eq)}_{e(\mathrm{r})} S^{(Catt\rightarrow eq)}_{w_i(\mathrm{r})} \right) + \int d\mathrm{r} S^{(Catt\rightarrow eq)}_{w_i(\mathrm{r})} \Lambda S^{(Catt\rightarrow eq)}_{w_i(\mathrm{r})} \end{aligned} \tag{6}$$

The first term on the right hand side of the second line in Equation (6) equals zero provided appropriate boundary conditions are chosen and the second term is positive provided $\Lambda > 0$. If moreover $-S^{(Catt\rightarrow eg)}$ is a convex function of e(r) and w(r) then this function plays the role of the Lyapunov function for the approach, as $t \rightarrow \infty$, of solution to Equation (4) to states that are solutions to:

$$S^{(Catt\rightarrow eq)}_{\mathrm{w}(\mathrm{r})} = 0 \tag{7}$$

In order to continue with the investigation of the passage $L_{Catt} \rightarrow L_{eq}$, it is useful to recall a very familiar analysis of the passage $L_{KT} \rightarrow L_{eq}$, where L_{KT} is the level of kinetic theory on which time evolution is governed by the Boltzmann kinetic equation. In this context, equation that plays the role of Equation (6) (with $S^{(Catt\rightarrow eg)}$ replaced by the Boltzmann H-function) is the well known Boltzmann's H-theorem and solutions to equations playing the role of Equation (7) are known as local Maxwell distribution functions. It is important to realize that Equation (6) (or the Boltzmann H-theorem in the context of kinetic theory) do not characterize all important aspects of the approach to equilibrium. What in particular is missing in Equation (6) is the role of the nondissipative part of the time evolution (*i.e.*, the right hand side of Equation (4) and the first term in Equation (5), or, in the context of the Boltzmann equation it is the free flow term—recall that the term corresponding in the Boltzmann equation to the second term on the right hand side of Equation (5) is the Boltzmann collision term) in the total time evolution. In Equation (6) the nondissipative part of the time evolution gives no contribution (see the first term on the right hand side of the second line in Equation (6)). In the complete time evolution governed by Equations (4) and (5) the nondissipative part plays an important role. It is responsible for the approach to thermodynamic equilibrium states rather than just to the states that solve Equation (7).

A more detailed picture of the time evolution involved in the reduction of the level L_{Catt} to the level L_{eq} is revealed in splitting this reduction into two stages. In the first stage the fast time evolution brings L_{Catt} to L_{leq}, and in the second stage the time evolution discussed in the preceding section brings L_{leq} to L_{eq}. In this two stage approch to equilibrium, the time evolution in the first stage is fast and in the second stage slow. We recall that in the context of the Boltzmann equation, the first stage is the passage from kinetic theory to fluid mechanics and the second stage is the time evolution of the classical fluid mechanics.

4.1.3. $L_{Catt} \rightarrow L_{leq} \rightarrow L_{eq}$

The fast time evolution $L_{Catt} \rightarrow L_{leq}$ can be observed also in open systems that reach only the local equilibrium but are prevented by external forces from reaching the total equilibrium described on the level L_{eq}. With this time evolution we are illustrating $L_{MESO} \rightarrow L_{meso}$ discussed in Section 2. In this time evolution we let to evolve only the field w(r). Its evolution is governed by:

$$\frac{\partial w_i(\mathrm{r})}{\partial t} = \Gamma S_{w_i(\mathrm{r})}^{(Catt\to leq)} \tag{8}$$

where $\Gamma > 0$ is a material parameter. The entropy $S^{(Catt\to leg)}$ introduced in Equation (8) has to be specified. We proceed now to do it.

In order that the time evolution governed by Equation (8) followed by the time evolution governed by Equation (1) represents the time evolution governed by Equations (4) and (5), the following has to be true:

(I) The states approached as $t \to \infty$ in the time evolution governed by Equation (8) are the same as the one approached in the time evolution governed by Equation (5)

(II) Equation (4) evaluated on these states is the same as Equation (1).

Mathematically formulated, these two conditions become two equations:

(I)

$$\begin{gathered} solutions\, to \left[S_{w_i(\mathrm{r})}^{(Catt\to leq)} = 0 \right] are\, the\, same\, as \\ solutions\, to \left[\frac{\partial}{\partial r_i}\left(S_{e(\mathrm{r})}^{(Catt\to eq)} \right) + \Lambda S_{w_i(\mathrm{r})}^{(Catt\to eq)} = 0 \right] \end{gathered} \tag{9}$$

and:

(II)

$$\left[S_{w_i(\mathrm{r})}^{(Catt\to eq)} \right]_{S_{w_i(\mathrm{r})}^{(Catt\to leq)}=0} = -\lambda \frac{\partial S_{e(\mathrm{r})}^{(leq\to eq)}}{\partial r_i} \tag{10}$$

relating $S^{(Catt\to leg)}$ appearing in Equation (8) to quantities appearing in Equations (1), (4) and (5).

One particular solution of these two equations is:

$$\Lambda = \frac{1}{\lambda} \tag{11}$$

$$S^{(Catt\to eq)} = S^{(leq\to eq)} + \frac{1}{2}\int d\mathrm{r}\, \alpha w_i(\mathrm{r}) w_i(\mathrm{r}) \tag{12}$$

$$S^{(Catt\to leq)} = S^{(leq\to eq)} + \frac{1}{2}\int d\mathrm{r}\, \alpha w_i(\mathrm{r}) w_i(\mathrm{r}) + \int d\mathrm{r}\, \lambda w_i \frac{\partial S_{e(\mathrm{r})}^{(leq\to eq)}}{\partial r_i} \tag{13}$$

where α is a material parameter. It is easy to verify that Equations (9) and (10) indeed hold if Equations (11)–(13) hold.

4.1.4. $S^{(leg\leftarrow Catt)}$

If we evaluate $S^{(Catt\to leg)}$ given in Equation (13) on states that are solutions of $S_{w_i(\mathrm{r})}^{(Catt\to leq)} = 0$ (*i.e.*, on states that are reached in the fast time evolution governed by Equation (8) as $t \to \infty$) then we obtain:

$$S^{(leq\leftarrow Catt)} = S^{(leq\to eq)} - \int d\mathrm{r} \frac{\lambda^2}{2\alpha} \frac{\partial S_{e(\mathrm{r})}^{(leq\to eq)}}{\partial r_i} \frac{\partial S_{e(\mathrm{r})}^{(leq\to eq)}}{\partial r_i} \tag{14}$$

This is the entropy on the level L_{leq} obtained in the comparison of the level L_{leq} with a more microscopic level L_{Catt}. Another entropy on the same level L_{leq} is the entropy $S^{(leg\rightarrow eg)}$ (introduced in Equation (2)) that has been obtained in the comparison of the level L_{leq} with a less microscopic level L_{eq}. Both these entropies illustrate emergence of entropy in the comparison of levels of description. If we make a comparison of a given level (in this illustration it is the level L_{leq}) with two different levels we obtain two different entropies. Indeed, the entropies $S^{(leg\rightarrow eg)}$ and $S^{(leg\leftarrow Catt)}$, both belonging to the level L_{leq}, are different. The entropy $S^{(leg\leftarrow Catt)}$ involves a nonlocal term (a term involving spatial gradients) and also a coefficient appearing in the slow dynamics on the level L_{leq} in its dissipative part.

5. Concluding Remarks

Any past or future formulation of thermodynamics of open systems has to address the concept of entropy outside its natural realm of equilibrium thermodynamics and equilibrium statistical mechanics. While in many applications of considerable practical interest (see e.g., [1–8]) the equilibrium entropy (including the local equilibrium entropy and the entropies arising in equilibrium statistical mechanics) is found to be sufficient, important applications in nano-technology and bio-technology have to face this problem. In this paper, following [10,11], we suggest and briefly explore a systematic path leading from the classical equilibrium entropy to entropies of driven systems on mesoscopic levels of description. Starting point is a dynamical viewpoint of the classical equilibrium entropy. We see the origin of the entropy in the process required to prepare systems to states in which classical equilibrium thermodynamics is applicable. The time evolution taking place in the preparation process is generated by a potential that then, if evaluated at the states reached in the preparation process, becomes the entropy. This dynamical point of view of entropy is then shown to extend naturally to different levels of description and to mesoscopic descriptions of driven macroscopic systems. Entropy arises in the comparison of two well established (*i.e.*, well tested with experimental observations) levels of description one of which involves more details than the other. There is therefore as many entropies as there is pairs of such levels. Beside bringing a clear definition of the general concept of entropy, this viewpoint also puts into focus the importance of multiscale mesoscopic investigations of complex systems encountered in nano- and bio-technologies. The general discussion is illustrated in this paper on the example of heat conduction.

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Conflicts of Interest

The authors declare no conflict of interest.

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