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A thermodynamical formalism describing mechanical interactions

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Abstract – The dynamical behavior of an overdamped mechanical model devoid of any usual thermal effects is analyzed by a formalism that is similar to usual thermodynamics, and completely independent of any ad hoc assumption of a probability distribution of states in phase space of the mechanical model. It leads to the definition of a new entropy function, which does not coincide with the usual thermodynamical entropy. The new step making the difference to previous studies of this system is the identification of two non-equivalent mechanical interaction mechanisms, which are defined and identified as work and pseudo-heat. Together with the introduced effective temperature $\theta$, they make it possible to characterize the equivalent to isothermal, adiabatic, isobaric, and isochoric processes. Three statements, formally analogous to the zeroth, first, and second law of thermodynamics, are issued. The statement of the second law results from the asymmetry in the way energy can be exchanged along the two processes. A Carnot cycle is defined, for which the efficiency is expressed in terms of $\theta$ in the operating pseudo-heat reservoirs. The analogous Clausius theorem for the system operating an arbitrary reversible cycle is proved, leading to the new entropy function. Consequences of the extension of thermodynamic formalism to mechanical models with different processes of transferring energy are discussed.

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The entropy function was introduced into thermodynamics as a result of Clausius theorem, which is itself a mathematical consequence of the statement of the second law according to Kelvin or to Clausius [1]. Rather than being an ad hoc concept, the thermodynamic entropy follows from phenomenological statements that certain events have never been observed in nature. Some time later, the statistical entropy based on the microscopic distribution probability was introduced into physics in the pioneering works by Boltzmann and Gibbs [2]. The entropy measures both the ability of the system to deliver mechanical work as well as its microscopic disorder. Additional efforts to define entropy along a mathematically rigorous way lead to axiomatic formulations, among which that due first to Shannon and afterwards to Khinchin is most acknowledged in the literature [3,4]. In the latter case, four postulates requiring basic entropy properties like the dependence on the probability distribution only, maximum at equiprobability, addition of a new zero-probability state, and conditional additivity, lead to a specific functional dependence that is generally referred to as the celebrated Boltzmann-Gibbs (BG) entropy. If the fourth postulate is modified or excluded from the axiomatic formulation, other functional forms can be used to define statistical entropies [5–7].

For physical systems, the BG entropy is generally accepted as the actual statistical definition, mainly for the fact that, for a very large number of systems, the derived results agree with those obtained by the thermodynamical formalism and by highly precise experimental records. However, experimental deviations from the predicted theoretical results based on the BG distribution are reported. Such failures are explained by the incompleteness of the data, or the presence of out-of-equilibrium states, or the inadequacy of the BG formalism (see, e.g., ref. [8] for a list of examples). The search for a better physical explanation
of such data sets is the main reason for the proposition of statistical entropies other than the BG one.

In this work, we investigate whether other entropies can be introduced into physics. However, instead of introducing a new functional relation between entropy and probability distribution, we follow the same steps of the standard thermodynamical formalism. In opposition to the procedure adopted in previous works [9–12], we show that it is possible to introduce a new entropy for a class of systems that are subject to mechanical interactions only.

The model we consider has a large number of constituents and obeys proper boundary conditions, with the additional remark that, if two or more samples of the same system share a common boundary, they are allowed to interact with each other along a series of distinct processes. All such processes may cause a displacement of the boundaries. However, for the sake of simplifying the analysis, we restrict our discussion to the cases in which no exchange of thermal heat or particles between the systems is allowed. Based on the observed global properties, we enounce a series of statements that are valid to all similarly interacting systems. These statements play the same role as the zeroth, first, and second laws of standard thermodynamics, allowing us to prove the analogue of the Clausius theorem for this class of interacting systems. As a corollary, we obtain the exact expression of a new entropy function, which differs from the one of usual thermodynamics. We emphasize that such expression is derived without any approximation, which differs from the one of usual thermodynamics.

The above equations lead to the mean energy per particle \( u \), we obtain

\[
\rho_{st}(x) = R \left( x^2 - x^2 \right), \quad |x| < x_c,
\]

\[
\rho_{st}(x) = 0, \quad |x| > x_c.
\]  

\[
R \text{ and } 0 < x_c \leq L_y/2 \text{ are macroscopic parameters depending on the particles mass and on the forces acting in the system, which are controlled by } f_0, \lambda, \text{ and } \alpha.
\]

The numerical integration of system (1) with initial conditions satisfying \( |x_i(t = 0)| \leq L_y/2, 0 < y_i(t = 0) < L_y \) always leads to a steady equilibrium state described by an average density of particles,

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Fig. 1: Schematic illustration of an isolated system (a), of two systems interacting with the isochoric condition $d\alpha = 0$ (b), and an isothermal process where $\theta \sim L_y^{-1}$ is constant (c).

For reasons that will become clear later on, we refer to $\theta$ as the effective temperature, while $\sigma = 3(\delta u/\delta \alpha)\theta$ plays the role of a variable that is the thermodynamically conjugate to $\alpha$ [12]. If usual heat exchange and temperature variation were allowed, eq. (6) should also include a term $\sim C d\theta$, where $C$ indicates the proper specific heat of the system.

After inverting the expression for $\sigma$ and expressing $\theta$ as a function of $\alpha$ and $\sigma$, we obtain a very simple expression for $u$ as a function of $\alpha$ and $\sigma$

$$u = u(\sigma, \alpha) = \sigma \alpha.$$  

(7)

In this case, the differential $du$ can be written as

$$du = \alpha d\sigma + \sigma d\alpha.$$  

(8)

So far we have considered an isolated system that, in the usual thermodynamic framework, is enclosed by rigid, impermeable and adiabatic walls. However, nothing prevents from allowing two different systems, described by the same set of equations of motion (1), to interact with each other. Equations (6) and (8) allow us to characterize different interaction processes between two systems, as schematically represented in fig. 1. Panel (a) illustrates an isolated system. The vertical height corresponds to $L_y$, while the horizontal width depends on the confining potential $\phi(x)$ gauged by $\alpha$. In fig. 1(b) we represent a process along which the systems 1 and 2 may change their potential $L_{1,2}$, but the sum $L_{1,2}$ is kept constant. The values of $\alpha$ for both systems remain invariant, so that it corresponds to an isochoric process. If it is described with the help of eq. (6), we have $d\alpha = 0$ but $d\sigma \neq 0$, since $\Delta L_y 
eq 0 \rightarrow \Delta \alpha \neq 0 \rightarrow \Delta \theta \neq 0$.

Figure 1(c) illustrates a different kind of process, where the width of each system $L_{y,j}$ remains constant, but the horizontal extension, proportional to $\alpha^{-1/3}$, can change. It corresponds to an isothermal process ($\theta = \text{const}$), in which the sum of the squares of the two confinement regions $\sim \alpha_1^{-2/3} + \alpha_2^{-2/3}$ remains constant. Therefore, $du$ receives a contribution from $d\alpha$ only, since $n = N/L_y$ is kept invariant and $d\theta = 0$.

The changes in the values of $L_{y,j}$ (fig. 1(b)) are due only to differences in momentum delivered to the wall. The location of the intermediary wall is updated after a small number of integration steps. For the horizontal interactions in fig. 1(c), the values of $\alpha_j$ (as well as the location of the center of the potential wells) are also periodically updated by least square fits of the density of particles. In this case, we allow also for inter-particle interaction between particles of different types, but each particle type feels its specific confining potential.

To push forward the correspondence with the thermodynamic framework, let us now identify the pseudo-heat $\delta Q$ and work $\delta W$ transferred to/from the system in an infinitesimal quasi-static process, and state the first law. So, based on eq. (8) we define

$$\delta Q = \alpha d\sigma,$$  

(9)

and

$$\delta W = \sigma d\alpha.$$  

For the sake of brevity, from now on we will refer to $Q$ (consequently $dQ$) as heat, but its meaning is given by eq. (9). Indeed, as commented before, the usual heat exchange $C d\theta$ is not permitted in this work and we use the same letter $Q$ to indicate a form of energy exchange that plays a similar role as the heat exchange in usual thermal processes. Definition (9) immediately leads to adiabatic and isochoric processes where, respectively, $\delta Q = d\sigma = 0$ and $\delta W = d\alpha = 0$. Then, it is straightforward to evaluate the energy change for each process as $\Delta Q_{\text{adiab.}} = \Delta W_{\text{adiab.}} = \sigma(\alpha_2 - \alpha_1)$ and $\Delta u_{\text{adiab.}} = \Delta W_{\text{isoth.}} = \sigma(\alpha_2 - \alpha_1)$.

The isothermal process can be described either by setting $d\theta = 0$ in (6) or by using (8) with the subsidiary condition $\theta = \text{const}$. As before, it is a simple task to show that $\Delta Q_{\text{isoth.}} = -2(\sigma_2 \alpha_3 - \sigma_1 \alpha_1)$ and $\Delta W_{\text{isoth.}} = 3(\sigma_2 \alpha_2 - \sigma_1 \alpha_1)$, so that $\Delta u_{\text{isoth.}} = \sigma_2 \alpha_2 - \sigma_1 \alpha_1$.

The adiabatic process ($dQ = 0$) illustrated in fig. 2 involves changes in $\theta$ (hence in $L_y$) and $\alpha$. These changes are such that the system inflates (deflates) in both the $x$- and the $y$-direction when $du > 0$ ($du < 0$).
It is possible to extend the above thermodynamic framework to state the property of transitivity of effective temperature equilibrium (zeroth law) and extend the concept of a thermal machine. In the first case, the statement that if systems $A$ and $B$ are in thermal equilibrium (i.e. equal density of particles along the $y$-direction), and if $B$ and $C$ are also in thermal equilibrium, the same holds for systems $A$ and $C$. These conditions indicate that no heat flows between any pair of systems, which is a consequence of the mechanical equilibrium [1] between all of them, represented by the diagram on the r.h.s. of fig. 1, panel (b).

This thermal machine is an actual construction to allow the system described by eq. (1) to operate in cycles, by coupling it in a suitable sequence to heat and work reservoirs. Here, the concept of reservoir has the usual thermodynamic meaning [1,2]: it can deliver or accept heat (work) from a given system without changing its thermal (mechanical) properties. Thus, the reservoir effective temperature $\theta$ and mechanical features ($\alpha = \alpha_R$) remain the same if it interacts with a finite-size system.

The Carnot theorem assures that the Carnot cycle has the highest possible efficiency $\eta = \eta_C$ for an engine operating between two heat reservoirs at given temperatures $T_1$ and $T_2$ ($T_2 < T_1$). Moreover, it implies that $\eta_C$ does not depend on the engine itself, but only on the values of $T_1$ and $T_2$. If we compute the efficiency for a Carnot cycle operated by our system (see ref. [12]) in terms of heat and work defined by eq. (9), we arrive at

$$\eta_C = 1 - \frac{|Q_{34}|}{|Q_{12}|} = 1 - \frac{\theta_2}{\theta_h}. \quad (10)$$

Indeed, it is only necessary to observe that

$$Q_{12} = 2(\sigma_A\alpha_1 - \sigma_B\alpha_2) = 2\sigma_A\alpha_1(1 - \sqrt{\sigma_A\sigma_B}),$$

$$Q_{34} = 2(\sigma_B\alpha_3 - \sigma_A\alpha_4) = 2\sigma_B\alpha_3(1 - \sqrt{\sigma_B\sigma_A}). \quad (11)$$

This result shows that the definitions introduced in eq. (9) are consistent with the use of a thermodynamical framework to describe system (1). Figure 2 shows the conformation of the system in the four points where the isotherm and adiabatic paths intercept each other in a Carnot cycle, as emphasized in an infinitesimal cycle in fig. 3. Note that the heat reservoir operating at constant $\theta$ is also able of delivering work, as required by the isothermal process described in (6) with $d\theta = 0$.

Given the previous definitions and the results obtained for an exhaustive series of numerical simulations, we take the following statement to be true: it is impossible to have a process in which the only effect is to extract the heat (at a low effective temperature or particle density $n$) and deliver it at a larger effective temperature (larger $n$). Within our framework, it plays the same role as the Clausius statement of the second law of thermodynamics.

Therefore, it is possible to proceed to the final part of this work, which consists in stating and proving the analogue of the Clausius theorem (ACT). In usual thermodynamics, Clausius theorem states that [1]

$$I = \oint_C \frac{\delta Q}{T} = 0,$$  \quad (12)

where $C$ indicates a closed path describing any reversible process the system can follow. For a gas, such path is usually represented in the $PV$ plane. At each point of this plane, the temperature is obtained by using the (known) equations of state. The ACT states that eq. (12) is also valid for the system investigated here, provided $P$, $V$, and $T$ are replaced, respectively, by $\sigma$, $\alpha$, and $\theta$.

The proof of the ACT follows the same strategy used for the Clausius theorem, so that we just call the attention to the most relevant steps. In first place, let us cover any arbitrary cyclic process $C$ in the $(\sigma, \alpha)$-plane by a set of infinitesimally close adiabatic curves $A_i$. Each $A_i$ intercepts $C$ at points $(\sigma_{i,1}, \alpha_{i,1})$ and $(\sigma_{i,2}, \alpha_{i,2})$, where $\theta_{i,1} = \theta_{i,1}(\sigma_{i,1}, \alpha_{i,1}) > \theta_{i,2}(\sigma_{i,2}, \alpha_{i,2}) = \theta_{i,2}$. Next let us decompose the process $C$ into a sequence of cycles $C_i$ formed by four curves bounded by the points $a_i = (\sigma_{i,1}, \alpha_{i,1})$, $b_i = (\sigma_{i+1,1}, \alpha_{i+1,1})$, $c_i = (\sigma_{i+1,2}, \alpha_{i+1,2})$, and $d_i = (\sigma_{i,2}, \alpha_{i,2})$. The two curves between $a_i$ and $b_i$, and between $c_i$ and $d_i$ follow the cycle $C$, while the points $b_i$ and $c_i$, and $d_i$ and $a_i$, are connected adiabatic curves linking each pair of them. The net work resulting from the inclusion of the paths along the points $a_i$ and $d_i$ is zero, since each path is covered twice but in opposite directions. Finally, let us replace each infinitesimal path $a_i$ by an equivalent path formed by a sequence of three curves: an adiabatic, an isotherm, and another adiabatic.

The two adiabatic curves are the same going through the points $a_i$ and $b_i$, while $\bar{T}_{i,1}$, the effective temperature of the isotherm is chosen in such a way that the work done along $C$ is equal to the work along the equivalent path. In general, $\bar{T}_{i,1} \neq \bar{T}_{i,1} \neq \bar{T}_{i+1,1}$. The same procedure is performed for the segments $c_i$-$d_i$.

Thus, $C$ can be replaced by a set of Carnot cycles $\bar{C}_i$, each one operating at a effective temperatures $\bar{T}_{i,1}$ and $\bar{T}_{i,2}$. The two adiabatic curves warrants that heat is introduced into (or extracted from) the system only when it is in
contact with these reservoirs. To complete the proof, we select a constant reservoir at an arbitrary large effective temperature \( \theta_0 \), so that each \( \mathcal{C}_i \) can be described by two Carnot cycles between reservoirs at temperatures \( \theta_0 \) and \( \theta_{1,1} \) and \( \theta_0 \) and \( \theta_{1,2} \). The relation between \( \Delta Q'_i \), the heat extracted from (or delivered to) the \( \theta_0 \) reservoir, and \( \delta Q_i \) is

\[
\Delta Q' \geq \theta_0 \delta Q_i \frac{\theta_i}{\theta_0}.
\] (13)

Performing a sum over the whole set of infinitesimal curves leads to

\[
Q' = \sum_i \Delta Q'_i \geq \theta_0 \sum_i \delta Q_i \frac{\theta_i}{\theta_0} \rightarrow \theta_0 \int_C \frac{\delta Q}{\theta} = \theta_0 \int_C \frac{\delta Q}{\theta} = \theta_0 L.
\] (14)

Finally, we obtain Clausius results by resorting to Kelvin’s statement of the second law. For a Carnot cycle, \( \sum_{i=1}^{\infty} \delta Q_i = 0 \), which is valid both when the system works as a thermal engine or as a refrigerator. If the arbitrary process is reversible, it is possible to state from eq. (14) that \( \theta_0 L \leq 0 \), and at the same time, that \( \theta_0 L \geq 0 \). So, these two inequalities can only be satisfied when \( \theta_0 L = 0 \).

Since the cycle \( \mathcal{C} \) is arbitrary, an entropy \( s \) can be defined as

\[
s_2 - s_1 = \int_{\mathcal{C}} \frac{\delta Q}{\theta},
\] (15)

which leads to the analytical expression

\[
s = \left[ c - \frac{b^2}{5V^{2/3}} \left( \frac{\alpha}{\theta} \right)^{1/3} \right],
\] (16)

where \( c \) depends on a properly chosen fiducial state.

Equation (16) completes the description of purely mechanical interactions of system (1) within a framework with the same structure of usual thermodynamics. A first remark on the achieved result is that, as expected, there is no dependence on the temperature \( T \) in eq. (16). It depends only on the mechanical parameters \( \theta \sim L^{-1} \) and \( \alpha \) controlling two distinct energy exchange processes that are not symmetric. It actually measures the degree of asymmetry of processes that are performed at \( \alpha = \text{const} \) or \( \theta = \text{const} \). Nevertheless, eq. (16) constitutes a particular case of a general entropy function, depending also on \( T \), valid when the usual heat exchange is included in eqs. (6) and (9). Consistently, if we set \( \alpha = 0 \) in these equations, which corresponds to eliminating one of the energy exchange processes, the function \( s \) becomes a constant.

Next we stress the fact that, although the same functional form expressed by eq. (16) has appeared in some other works on system (1) [9–12], all previous derivations were related by specific property of distribution functions obeying suitable non-linear Fokker-Planck (FP) equations. These studies indicate that, from the microscopic point of view, this entropy measures the uncertainty of finding a specific vortex in an equilibrium position.

In particular, a general expression for the entropy depending on \( T \) and \( \theta \) has been derived in [9]. Arriving at this expression without resorting to any probabilistic assumption is the most important result of this work, and represents an important step towards generalizing the thermodynamical formalism based on the existence of non-equivalent, asymmetric ways of exchanging mechanical energy. For usual thermodynamics, the identification of two different processes for energy exchange (heat and work) together with the phenomenological observation that they do not play a symmetric role in nature are the key elements that culminate with the definition of the entropy function. This work shows that it is possible to follow the same path to derive a similar framework for systems subject to mechanical interactions only, i.e., without usual heat transfer. At the same time it shows that the achieved derivation is associated to a probabilistic approach, in which the same expression for the entropy is obtained in terms of the probability distribution function. Since the general guidelines of the adopted approach can be used to treat other similar situations, our results may impact many other models and situations in natural systems: probabilistic derivation of entropy can be related to the existence of asymmetric energy exchanging processes, going beyond the usual heat and work processes to include different mechanical energy exchange. It is clear that, for the formalism to be valid, the phenomenological observations summarized in statements corresponding to the zeroth, first and second laws must be valid for any realization of the system.

The presented formalism does not substitute the usual thermodynamical description of the system. For instance, if system (1) describes the interaction of vortices in type-II superconductors [9–14,17], the thermal behavior related to usual heat and work exchanges, including phase transition to the superconducting state, is described by usual thermodynamics. Equation (1) describes the interaction among meso- or macroscopic excitations in the system.

The schematic illustrations of distinct processes in fig. 1 are associated to procedures that are easily implemented in the numerical integration of the system (1). In fig. 1(b), the changes carried on the values of \( L_{\theta,i} \) are due only to differences in momentum delivered to the wall. The location of the intermediary wall is updated after a small number of integration steps. For the horizontal interactions (fig. 1(c)), the values of \( \delta \alpha_i \) (as well as the location of the center of the potential wells) are also periodically updated by least square fits of the density of particles. In this case, we allow also for inter-particle interaction between particles of different types, but each particle type feels its specific confining potential. The experimental realization of these processes, for instance in the case of type-II superconductors, is an interesting challenge. Nowadays, it is possible to control many properties of these vortices including motion and density, which are related to \( \theta \) [18–21]. We conjecture that devices able to track the position of each vortex in the system can be coupled to wall and field controls able to reset the corresponding values.
of $\alpha$, and $L_{y,i}$ to drive both systems to new equilibrium conditions.

Once the formalism is not based on any pre-assumed form of the probability distribution of microscopic states, the relation between the thermodynamic entropy to any statistic entropy is left open for a general case. As already remarked, eq. (16) is exactly the same one obtained in ref. [11] within a framework involving a non-linear FP equation which is consistent with a non-BG microscopic probability distribution in phase space [6,22–27]. So, the parameters $b$ and $V$ that are present in the equations of state can be expressed in terms of the microscopic parameters of the model as $\mu, f_0$, and $\lambda$. More precisely, the entropy and internal energy were calculated as [9,11,12],

\[
    s = k \left[ 1 - \frac{3^{2/3}}{5} \left( \frac{\alpha \lambda^2}{kB} \right)^{1/3} \right], \tag{17}
\]

\[
    u = \frac{3^{2/3}}{10} \left( \frac{\alpha \lambda^2}{kB} \right)^{1/3} c^{2/3}, \tag{18}
\]

from which one obtains the phenomenological parameters $b = (3\pi f_0 \lambda^3)^{1/3}, V = \pi f_0 \lambda^2/k$, and $c = k$.

Hence, we have shown that the results summarized in eq. (16), which have been derived without resorting to any previous knowledge, are in best accordance with the results of refs. [11] and [12]. We stress that in these works, a consistent thermodynamic framework was constructed by neglecting thermal noise, provided one defines appropriately an effective temperature, as well as its associated entropic form. As shown previously, the statistical definition of this entropy falls into the class of Tsallis entropy, typical of non-extensive statistical mechanics, and it is interpreted herein from the microscopic point of view, as a measure of the uncertainty of finding a specific vortex in an equilibrium position.

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