Microcanonical phase transitions in small systems

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I. INTRODUCTION

The work of D.H.E. Gross [1] has recently pointed out the attention on the fact that a microcanonical description of systems which may display phase transitions is in general more adequate than the traditional canonical one. This is because the canonical description may “smear out” important information contained in the microcanonical description which is richer [1]. For example negative specific heats, which have recently been observed experimentally in mesoscopic systems [2, 3, 4], can be accounted for in the microcanonical ensemble but not in the canonical one [2]. Indeed it is well known that canonical ensemble and microcanonical ensemble are not in general equivalent, even when the thermodynamic limit is considered [1, 4, 7, 8].

The statistical mechanical analysis of physical systems based on canonical ensemble is quite well established and universally agreed upon. Roughly speaking one has to compute the partition function $Z(\beta)$ and derive the thermodynamics of the system from the free energy $F = -\beta^{-1}\ln Z(\beta)$. Things are not quite so broadly agreed upon in the case of the microcanonical ensemble. In fact since the pioneering works of Boltzmann and Gibbs two possibilities were given for the microcanonical analysis of physical systems, which correspond to two different definitions of entropy (see for example the textbook of Gibbs [8] or the more recent textbook of Huang [10]). Following [11] and [12] we shall refer to these two entropies as “surface entropy” and “volume entropy”. The surface entropy is defined as:

$$S_\Omega(E) = \ln \Omega(E)$$

(1)

where

$$\Omega(E) = \int dz \delta(E - H(z))$$

(2)

with $\delta(x)$ denoting Dirac delta function. Sometimes this is also referred to as Boltzmann entropy or Boltzmann-Planck entropy. The volume entropy is defined as:

$$S_\Phi(E) = \ln \Phi(E)$$

(3)

where

$$\Phi(E) = \int dze^{\theta(E - H(z))}$$

(4)

with $\theta(x) = \int_{-\infty}^x dy \delta(y)$ denoting Heaviside step function. The quantities $\Omega$ and $\Phi$ are related through the differential equation [13]:

$$\Phi'(E) = \Omega(E)$$

(5)

where the prime symbol denotes derivation with respect to $E$. These entropies are named surface entropy and volume entropy because they are calculated as the logarithm of the area of the hyper-surface of constant energy in phase space and the volume of phase space that it encloses respectively.

With reference to the literature about microcanonical phase transitions the surface entropy is certainly the most popular. For example Barré et. al. [2] method based on large deviation techniques uses the surface entropy. The surface entropy is used also in Rugh’s microcanonical formalism adopted in Ref. [14]. The strongest advocate of surface entropy is perhaps Gross [15]. Nonetheless pioneers of microcanonical phase transitions, such as Thirring [16] and Lynden-Bell [5], used the volume entropy.

The two entropies coincide in the thermodynamic limit but when the number of degrees of freedom of the system under study is small relevant differences may appear, therefore it is necessary to choose properly. Some authors [12, 17] have already pointed out that the surface entropy is not adequate when dealing with small systems because it does not account properly for finite-size effects. On the other hand there is a number of theoretical reasons to prefer the volume entropy when the number of degrees of freedom becomes small. Here we shall review these reasons and we will illustrate the employment of the volume entropy in the study of phase transition with a small Lennard-Jones chain which displays a region of negative heat capacity.
II. WHY VOLUME ENTROPY

In this section we will summarize some old and recent results concerning the volume entropy. These results indicate that, no matter the number of degrees of freedom of the system under study, the volume entropy always provides a good mechanical analogue of thermodynamic entropy. For example Helmholtz [18] proved that the logarithm of the area enclosed in phase space by the trajectory of a 1-dimensional system (i.e., the 1D volume entropy $S_V$) provides a mechanical analogue of physical entropy in the sense that if one considers the quantities $P = (\frac{\partial E}{\partial T})_V$, and $T = (2K)$, where $K$ is the kinetic energy, $V$ is an external parameter on which the Hamiltonian depends and $\langle \cdot \rangle_t$ denotes time average, then,

$$\frac{dE + PdV}{T} = \text{exact differential} = dS_{\Phi} \quad (6)$$

This result, known as Helmholtz Theorem [6, 11], says that the volume entropy is a good mechanical analogue of thermodynamic entropy in the sense that it reproduces exactly the fundamental law of thermodynamics (i.e. the heat theorem [6]). The Helmholtz Theorem has been recently generalized to multi-dimensional ergodic (i.e. metrically indecomposable) systems (see Ref. [11] or Ref. [19] for a different but equivalent approach). The resulting Generalized Helmholtz Theorem essentially states that the volume entropy reproduces the heat theorem no matter the number of degrees of freedom $N$. The same cannot be said about surface entropy which has been proved to reproduce it only up to corrections of the order $O(1/N)$ [6]. As a matter of fact Gibbs presents the volume entropy in his celebrated Principles of Statistical Mechanics [6] as the entropy that naturally satisfies the fundamental principle of thermodynamics (that is the heat theorem) [20].

Hertz [21] pointed out that the volume entropy is an adiabatic invariant already in 1910, and based his approach to statistical mechanics on it. Among the textbooks that adopt the same approach, those of Münster [22], Becker [23], and the more recent book of Berdichevsky [24] are worth mentioning. Adiabatic invariance is another good property of volume entropy because it reproduces quite well Clausius’ requirement that “For every quasi static process in a thermally isolated system which begins and ends in an equilibrium state, the entropy of the final state is equal to that of the initial state” [25]. Of course the surface entropy is not an adiabatic invariant, although it becomes approximately such as the number of degrees of freedom increases [11].

Very recently it has been also proved that non-adiabatic transformations occurring in isolated systems which are initially in a state of thermal equilibrium always result in an increase of the expectation value of the volume entropy [26, 27]. This result too does hold no matter the number of degrees of freedom $N$ and cannot be proved in general for surface entropy. Thus the volume entropy explains quite satisfactorily also Clausius’ law of entropy increase “For every non quasi static process in a thermally isolated system which begins and ends in an equilibrium state, the entropy of the final state is greater than that of the initial state” [26].

Recently more and more authors are becoming aware of the theoretical value of volume entropy. For example, on the basis of a Laplace transform technique for the microcanonical ensemble, Pearson et. al. [28] reached the conclusion that the volume entropy “is the most correct definition for the entropy, even though it is unimportant for any explicit numerical calculation”, meaning that in the thermodynamic limit the difference with surface entropy becomes negligible. On the other hand for small system, such intrinsic correctness of the volume entropy becomes very important. Adib [22] argues that the finite size corrections to surface entropy found in Ref. [29] would be unneeded if the volume entropy were used instead.

It is worth mentioning that the volume entropy has another property that is particularly important for small systems which have negative heat capacity, namely it is a naturally nonextensive entropy. According to Lynden-Bell [3], in fact, systems with negative heat capacity are necessarily nonextensive. The property of nonextensivity of volume entropy follows directly from the composition rule of enclosed volumes, $\Phi = 1, 2$, of two systems with total energy $E = E_1 + E_2$ [13]:

$$\Phi(E) = \int dE_1 \Phi_1(E_1) \Phi_2(E - E_1) \quad (7)$$

which is not a simple multiplication but a form of convolution which accounts for all possible partitions of energies between the two systems. It has to be stressed that, despite of what is often stated in literature, the surface entropy is nonextensive too, as the composition rule for surface integrals $\Omega_i$ is the convolution, not the multiplication [12]:

$$\Omega(E) = \int dE_1 \Omega_1(E_1) \Omega_2(E - E_1) \quad (8)$$

In sum, the volume entropy accounts for certain basic principles of thermodynamics, like the heat theorem and Clausius formulation of the second law equally well for large and small systems, whereas the surface entropy accounts for them only in the case of large system. For this reason it is the most appropriate mechanical analogue of thermodynamic entropy when dealing with small systems.

III. LENNARD-JONES CHAIN

According to the Helmholtz Theorem [11] the mechanical analogue of thermodynamic entropy of a one dimensional system is

$$S_{\Phi}(E, V) = \log 2 \int_{x_-(E,V)}^{x_+(E,V)} dx \sqrt{2m(E - \varphi(x, V))} \quad (9)$$
where $x_\pm (E, V)$ denote the turning points of the trajectory. If the potential is such that there is only one trajectory per energy level (ergodicity), then $S_\Phi$ satisfies Eq. (6) \[6, 11\]. Nonetheless, if the system has more than one trajectory per energy level for a certain range of energies and the system is on one of them, still we can use the above formula and say that the heat theorem is satisfied as long as the energies considered lie within that energy range. In this case $P$ and $T$ would be calculated as time averages over the actual trajectory and $S_\Phi$ would be given by the area enclosed by that trajectory only. Let us illustrate this with a practical example. Let us consider a 1D chain composed of three particles which interact via a Lennard-Jones potential. Let us fix the position of two of them and let us place the third one in between, so that the first two particles act as walls of a 1D box. Let us now study the behavior of the particle inside the box. Let the interaction potential be:

$$u(x) = \frac{1}{x^{12}} - \frac{1}{x^6}$$ \tag{10}$$

and let us place the “walls” at $x = \pm V/2$. Then the particle in the box is subject to the following potential:

$$\varphi(x, V) = u(x + V/2) + u(x - V/2)$$ \tag{11}$$

For values of $V$ larger than a certain critical value $V_c \approx 2.5$, this system has a critical energy $E_c(V) = \phi(0, V)$ such that for energy below $E_c(V)$ ergodicity is broken and there are two trajectories per energy level. Above $E_c$ the dynamics is ergodic and there is only one trajectory per energy level. Figure 1 shows a contour plot of various energy levels in phase space for a particle of mass $m = 1$ in the Lennard-Jones box of size $V = 4 > V_c$. For energy $E = E_c$ we have a separatrix. Below $E_c$ the curve of constant energy splits into two disconnected curves, whereas for values of $E$ larger than $E_c$ we have only one curve. Below the critical energy the volume integral $\Phi$ is given by the area enclosed by one of the two possible trajectories. As the energy crosses the critical value the integral $\Phi$ jumps discontinuously. In formulae we have:

$$\Phi(E) = \left[ \frac{1}{2} \theta(E_c - E) + \theta(E - E_c) \right] \times \int [2m(E - \varphi(x, V))]^{1/2} \, dx \tag{12}$$

The symbol $[y]^{1/2}$ denotes a function that is equal to $\sqrt{y}$ for $y \geq 0$ and is null otherwise. The volume entropy, which is calculated by taking the logarithm of the expression above, then displays a jump at the critical energy as well. Figure 2 shows a plot of $S$ as a function of $E$, for the values $m = 1$ and $V = 4 > V_c$. The critical energy is $E_c = -0.0308$. Figure 3 shows the temperature plotted against the energy calculated, according to Eq. (6), as $\Omega$:

$$T = \langle 2K \rangle_t = \frac{\Phi(E)}{\Omega(E)} = \left( \frac{\partial S_\Phi}{\partial E} \right)^{-1} \tag{13}$$

There is a region of negative slope in the graph which correspond to a negative heat capacity.
Further, at the separatrix, the period of motion, which leads to a discontinuity in the entropy\[37\]. When a separatrix is crossed there is a sudden open-up of a larger portion of phase space for the trajectory to enclose which leads to a discontinuity in the entropy\[37\]. Further, at the separatrix, the period of motion, which for a well known theorem of classical mechanics is given by $\Phi' = \Omega$ becomes infinite. Therefore the temperature, i.e., $T = \Phi/\Omega$ goes to zero. Since the temperature $T \approx 2 < K >_t = < p^2/m >_t$ is definite positive, below the critical energy there necessarily is a region of negative slope, that is negative heat capacity. The appearance of a negative heat capacity is associated with a convex intruder in the entropy (see Fig. 4) which signals the approach to the separatrix from below. It is important to notice that using the surface entropy would lead to a drastically different result. In this case the temperature would be calculated as $T_\Omega = \Omega/\Omega'$, which might not tend to zero at the critical energy! Note also that $T_\Omega$ is not proportional to the average kinetic energy and can be negative. Therefore, in agreement with Ref. 17 we believe that surface entropy is not suited for low dimensional systems with broken ergodicity.

The volume entropy could be used to address microcanonical phase transitions in small dimensional systems with either long or short range interactions, like the $\phi^4$ model, chains of particles interacting via Lennard-Jones potential or the Hamiltonian Mean Field model. All these models are expected to undergo a breaking of ergodicity, thus there are separatrix trajectories and possible phase transitions that the volume entropy can detect.

The advantage of using the volume entropy is that it provides a good mechanical analogue of thermodynamic entropy even for small system, thus accounting properly for the finite-size effects. As the development of technology is allowing experimentalists to probe the thermodynamic behavior of smaller and smaller systems, this is becoming an increasingly important task. The main limitation of the present approach is that it is restricted to classical statistical mechanics, thus it does not account for quantum-mechanical phenomena.

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[34] In this work we adopt the convention that Boltzmann constant $k_B$ is equal to 1.
[35] This equation is essentially the microcanonical equipartition theorem which is an exact result in classical Hamiltonian mechanics.
[36] A similar behavior has been observed in a chain of particles interacting via a $\phi^4$ potential studied with volume entropy and has been predicted for the pendulum.
[37] The idea that microcanonical phase transitions are associated to sudden open-up of phase space has been expressed also in Ref.