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Microcanonical Entropy and Dynamical Measure of Temperature for Systems with Two First Integrals

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We consider a generic classical many particle system described by an autonomous Hamiltonian $H(x^1, \dots, x^{N+2})$ which, in addition, has a conserved quantity $V(x^1, \dots, x^{N+2}) = v$, so that the Poisson bracket $\{H, V\}$ vanishes. We derive in detail the microcanonical expressions for entropy and temperature. We show that both of these quantities depend on multidimensional integrals over sub-manifolds given by the intersection of the constant energy hyper-surfaces with those defined by $V(x^1, \dots, x^{N+2}) = v$. We show that temperature and higher order derivatives of entropy are microcanonical observable that, under the hypothesis of ergodicity, can be calculated as time averages of suitable functions. We derive the explicit expression of the function that gives the temperature.

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For an isolated many-body classical system, the ergodicity makes equivalent thermodynamics and dynamics. Thus, in these cases, one can measure thermodynamic quantities, like temperature and specific heat, as temporal averages of suitable functions along almost each trajectory of a given system, or, equivalently, as an integral over its phase space. The opportunity to pass from the dynamics to the microcanonical-thermodynamics and vice versa, gives the possibility to choose the smarter way to measure a given quantity. Very often the calculation of thermodynamic quantities in the microcanonical ensemble is an impracticable issue, thus one is forced to recur to the canonical ensemble, where these measures are more easily performed by resorting to numeric simulations, e.g. by Monte Carlo method. Of course, for a given system this step is performable only if there is equivalence between canonical and microcanonical ensembles in the thermodynamic limit. Furthermore, it is worth mentioning that in many cases, the convergence of thermodynamic quantities to their asymptotic values, is much faster if the averages are computed along the dynamics, rather than by an important sampling of the canonic phase-space. For these cases therefore, the dynamics is preferred respect to statistics. Furthermore, only for systems described by stable and tempered inter-particle interaction potentials is guaranteed the equivalence of the statistical ensembles in the thermodynamic limit. Nowadays, several of the most intriguing challenge for modern science, deals with systems of size intermediate between the macroscopic and the microscopic scales. Systems like polymers, DNA-helix, proteins, nanosystems, are large enough to allow a statistical treatment, but are absolutely far from the thermodynamic limit. Thus, for these systems, ensemble equivalence is hardly verified and one has no option but performing dynamical averages.

It is in this same spirit that Rugh, in [1], has presented a dynamical approach for measuring the temperature of

a Hamiltonian system in the microcanonical ensemble. He has shown that for an ergodic classical system, which has only one conserved quantity, i.e. the energy, the inverse temperature $1/T$, can be calculated as a temporal average of a suitable functional along the dynamics. The Rugh's seminal work has stimulated several papers [2–4] which have aroused widespread interest, especially among those who simulate the properties of liquids [5]. The calculation given by Rugh in Ref. [1] provides a microcanonical definition of temperature that allows its measure also in systems with nonstandard Hamiltonians. Nevertheless, this calculation works for systems with only one conserved quantity, i.e. the total energy. *In the present paper we extend the calculation of entropy and of microcanonical temperature to the case of Hamiltonian systems with two first integrals of motion.*

In the present paper we consider a classical system of $(N + 2)$ degrees of freedom (with $N > 0$), which is described by an autonomous Hamiltonian H , and which has a further independent conserved quantity V , such that $\{H, V\} = 0$. *We derive in detail the microcanonical expressions for entropy, i.e. the expression of the microcanonical invariant measure, and the temperature, moreover we give a formula to derive, recursively, all order of derivatives of the entropy.* We show that entropy and temperature depend on multidimensional integrals over sub-manifolds given by the intersection of the constant energy hyper-surfaces with those defined by $V(x^1, \dots, x^{N+2}) = v$. In particular, we show that temperature and higher order derivatives of entropy are microcanonical observable that, under the hypothesis of ergodicity, can be calculated as time averages of suitable functions. In Ref. [6] it has been studied the microcanonical ensemble of a classical system, whose Hamiltonian is parameter dependent and in presence of other first integrals and it has been showed a method, alternative to the present one, that allows one to obtain the first derivative

of entropy respect to the conserved quantities. The aim of the present paper is to derive *explicitly* the functional by means of which the temperature can be calculated as a microcanonical average, in the case of a generic classical system, described by a many-body Hamiltonian with one further conserved quantity. Furthermore, our method allowed us to derive an iterative formula that gives the derivatives of $S(E)$ of all orders, for this class of systems. By this formula, one can measure more general quantities like, e.g. the specific heat.

Let $H(\mathbf{x}, x^{N+1}, x^{N+2})$ be a classical Hamiltonian describing an autonomous many-body system whose coordinates and canonical momenta (q_1, p_1, \dots) are represented as $(N+2)$ -component vectors $(\mathbf{x}, x^{N+1}, x^{N+2}) \in \mathbb{R}^{N+2}$, and let $V(\mathbf{x}, x^{N+1}, x^{N+2})$ be a further conserved quantity which is in involution with H . We shall assume that V is a smooth function of the coordinates. The system's motion takes place on the manifolds $\mathcal{M} = \Sigma_E \cap V_u$, where the $\Sigma_E = \{(\mathbf{x}, x^{N+1}, x^{N+2}) \in \mathbb{R}^{N+2} | H(\mathbf{x}, x^{N+1}, x^{N+2}) = E\}$ are energy level sets and $V_u = \{(\mathbf{x}, x^{N+1}, x^{N+2}) \in \mathbb{R}^{N+2} | V(\mathbf{x}, x^{N+1}, x^{N+2}) = u\}$ are subsets of \mathbb{R}^{N+2} where V is constant. Among the equivalent expressions allowed for the microcanonical entropy $S(E)$, the surface entropy [7]

$$S(E) = \ln \int d^N \mathbf{x} dx^{N+1} dx^{N+2} \delta(H(\mathbf{x}, x^{N+1}, x^{N+2}) - E) \times \delta(V(\mathbf{x}, x^{N+1}, x^{N+2}) - u) \quad (1)$$

has an interesting and useful geometric interpretation that we shall derive, following the calculation shown in the chapter on the theory of surfaces of Ref. [8]. Consistently with Ref. [8], we shall assume the level sets of H and V to be non-singular hyper-surfaces. Even if the energy level surfaces (or the level sets of V) in general constitute a singular foliation, thus for some values of E (or u) the energy surface (or V_u) is not a differential manifold, for generic values of E (or u) this is not an issue. For a generic point $x_0 \in \mathcal{M}$ of a non-singular level-set of H and V , $\nabla H(x_0) \neq 0$ and $\nabla V(x_0) \neq 0$. Furthermore, since H and V are in involution, almost everywhere $\nabla H(x_0)$ and $\nabla V(x_0)$ are independent vectors. Thus, in a neighborhood of x_0 we can suppose of reorder the coordinate indices in such a way that $\partial H / \partial x^{N+1} \partial V / \partial x^{N+2} - \partial V / \partial x^{N+1} \partial H / \partial x^{N+2} \neq 0$ for each x of the neighborhood. Now, each non-singular manifold \mathcal{M} , can be partitioned by a family \mathcal{F} of not overlapping subsets [15]. With the further condition that, in each subset we can reorder the coordinate indices, as said above, so that $\partial H / \partial x^{N+1} \partial V / \partial x^{N+2} - \partial V / \partial x^{N+1} \partial H / \partial x^{N+2} \neq 0$ everywhere in the subset. Now, by using the first N coordinates we give a parametric description of the same subset. Thus, in each of the subsets of \mathcal{F} we can choose $f^\alpha = id$ for $\alpha = 1, \dots, N$, and let us set $g(\mathbf{y}) := f^{N+1}(\mathbf{y})$ and $h(\mathbf{y}) := f^{N+2}(\mathbf{y})$, where $\mathbf{y} \in \mathbb{R}^N$. The metric induced by \mathbb{R}^{N+2} on \mathcal{M} results

$$\eta_{\mu\nu} = \delta_{\mu\nu} + \partial_\mu g \partial_\nu g + \partial_\mu h \partial_\nu h, \quad (2)$$

where $\partial_\alpha \bullet = \partial \bullet / \partial x^\alpha$, whereas the its determinant can be derived by straightforward calculations and it results

$$\eta = 1 + \sum_{\alpha=1}^N \left[(\partial_\alpha g)^2 + (\partial_\alpha h)^2 \right] + \sum_{\substack{\mu, \nu=1 \\ \mu < \nu}}^N (\partial_\mu g \partial_\nu h - \partial_\mu h \partial_\nu g)^2. \quad (3)$$

The derivatives $\partial_\alpha g$, $\partial_\alpha h$, can be expressed as follows

$$\partial_\alpha g = [\partial_{N+2} V \partial_\alpha H - \partial_{N+2} H \partial_\alpha V] / D \quad (4)$$

$$\partial_\alpha h = [\partial_{N+1} H \partial_\alpha V - \partial_{N+1} V \partial_\alpha H] / D, \quad (5)$$

where $D = \partial_{N+1} H \partial_{N+2} V - \partial_{N+1} V \partial_{N+2} H$ [16]. From the expression above we derive the sub-manifold volume form

$$d\tau = d^N \mathbf{x} \sqrt{\eta} = d^N \mathbf{x} \frac{W}{D}, \quad (6)$$

where

$$W = \left[\sum_{\substack{\mu, \nu=1 \\ \mu < \nu}}^{N+2} \left(\frac{\partial H}{\partial x^\mu} \frac{\partial V}{\partial x^\nu} - \frac{\partial H}{\partial x^\nu} \frac{\partial V}{\partial x^\mu} \right)^2 \right]^{1/2}. \quad (7)$$

On the other hand, expression (1) can be cast in the following form. For each point \mathbf{x} we can introduce the following variables change

$$y^1 = h_{\mathbf{x}}^1(x^{N+1}, x^{N+2}), \quad y^2 = h_{\mathbf{x}}^2(x^{N+1}, x^{N+2}), \quad (8)$$

with the inverse transformations

$$x^{N+1} = G_{\mathbf{x}}^1(y^1, y^2), \quad x^{N+2} = G_{\mathbf{x}}^2(y^1, y^2), \quad (9)$$

where $h_{\mathbf{x}}^1(x^{N+1}, x^{N+2}) = H(\mathbf{x}, x^{N+1}, x^{N+2}) - E$, $h_{\mathbf{x}}^2(x^{N+1}, x^{N+2}) = V(\mathbf{x}, x^{N+1}, x^{N+2}) - u$, and $G_{\mathbf{x}}^1(y, z)$ and $G_{\mathbf{x}}^2(y, z)$ are the respective inverse transformations. From now on we will suppress the sub-index \mathbf{x} . After these definitions Eq. (1) can be expressed as follows

$$S(E) = \ln \int d^N \mathbf{x} dy^1 dy^2 \delta(y^1) \delta(y^2) |J(y^1, y^2)|,$$

where $|J(y^1, y^2)|$ is the determinant of the Jacobian matrix $\partial(x^{N+1}, x^{N+2}) / \partial(y^1, y^2)$. The inverse of the Jacobian matrix can be derived by Eqs. (8)-(9) and it results

$$\partial_1 G^1 = -\partial_2 h^2 / D = -\partial_{N+2} V / D, \quad (10)$$

$$\partial_1 G^2 = \partial_1 h^2 / D = \partial_{N+1} V / D, \quad (11)$$

$$\partial_2 G^1 = \partial_2 h^1 / D = \partial_{N+2} H / D, \quad (12)$$

$$\partial_2 G^2 = -\partial_1 h^1 / D = -\partial_{N+2} H / D. \quad (13)$$

Thus, the microcanonical entropy [17] results

$$S(E) = \ln \int_{\mathcal{M}} d^N \mathbf{x} \frac{1}{D} = \ln \int_{\mathcal{M}} \frac{d\tau}{W}. \quad (14)$$

It is worth emphasizing that the invariant measure is independent from the partition of \mathcal{M} , since W is invariant under exchange of the indices of the coordinates.

In order to derive the temperature in the microcanonical ensemble, according to the definition $T(E) = (\partial S(E)/\partial E)^{-1}$, we shall use the following generalization [18] of the Federer-Laurence derivation formula [9–13]. The flux Φ_ξ with a non-vanishing component in the direction orthogonal to the constant energy hyper-surfaces, but tangent to the level hyper-surfaces of V , can be defined by the vector $\xi = n^H - (n^H \cdot n^V)n^V$, where $n^H = \nabla H / \|\nabla H\|$ and $n^V = \nabla V / \|\nabla V\|$. Let us define $n^\xi = \xi / \|\xi\|$, so the generalized derivation formula results

$$\frac{\partial^k}{\partial E^k} \int_{\mathcal{M}} d\tau \psi = \int_{\mathcal{M}} d\tau A^k(\psi), \quad (15)$$

where [19]

$$A(\bullet) = \frac{1}{\nabla H \cdot n^\xi} [\nabla(n^\xi \bullet) - \bullet n^V \cdot (n^V \cdot \nabla)(n^\xi)]. \quad (16)$$

The proof of the extension of the Federer-Laurence theorem to varieties of codimension two, is rather complicated and lengthy. Furthermore it is outside of the main motivation of the present paper, thus it will be given in a further paper [14]. After Eqs. (17) and (18), we obtain that the inverse temperature is given by

$$\frac{1}{T(E, V)} = \langle \Phi(x) \rangle_{\mu c}, \quad (17)$$

where

$$\Phi(x) = \frac{W}{\nabla H \cdot n^\xi} \left[\nabla \left(\frac{n^\xi}{W} \right) - \frac{(n^V \cdot \nabla)(n^\xi)}{W} \cdot n^V \right], \quad (18)$$

and $\langle \rangle_{\mu c}$ stands for the microcanonical average.

When (\mathbb{R}^{N+2}, H) is ergodic with respect to the Liouville measure $d\tau/W$ restricted to a nonsingular manifold \mathcal{M} for almost every initial condition $x(0) \in \mathcal{M}$ one has

$$\frac{1}{T(E, V)} = \lim_{s \rightarrow \infty} \frac{1}{s} \int_0^s ds' [\Phi(x(s'))]. \quad (19)$$

Simple geometric applications.

i) As a simple application we shall derive the invariant metric η in the case of a simple form for H as that one of a four-dimensional hypersphere $H = x^2 + y^2 + z^2 + w^2$ of unit radius, and with a condition given by the hyperplane $V = z + w = 0$. By direct calculations we derive $\partial_x H = 2x$, $\partial_y H = 2y$, $\partial_z H = 2z$, $\partial_w H = 2w$, thus it results $D = \partial_z H \partial_w V - \partial_z V \partial_w H = 2(z - w)$. With the notations introduced above, Eqs. (4) and (5) become $\partial_x g = x/(z - w)$, $\partial_y g = y/(z - w)$, $\partial_x h = -x/(z - w)$, and $\partial_y h = -y/(z - w)$, thus the invariant metric results

$$\eta = 1 + 2 \left[\left(\frac{x}{z - w} \right)^2 + \left(\frac{y}{z - w} \right)^2 \right], \quad (20)$$

and is defined for $D \neq 0$ ($z \neq w$) that is on the subsets

$$\{(x, y, \pm \sqrt{\frac{1 - x^2 - y^2}{2}}, \mp \sqrt{\frac{1 - x^2 - y^2}{2}}) | x^2 + y^2 < 1\}.$$

The sum of the integrals of $\sqrt{\eta}$ upon these subsets brings to the result 4π which is the right hyper-surface volume. This solution can be checked noting that in the original problem the condition $V = z + w = 0$ can be lifted by a suitable change of variables. Let us introduce the variables $s = (z - w)/\sqrt{2}$ and $t = (z + w)/\sqrt{2}$. H and V can be expressed in the new variables as $H = x^2 + y^2 + s^2 + t^2 = 1$ and $V = t = 0$. Thus the metric η is that one of the three-dimensional unitary sphere $x^2 + y^2 + s^2 = 1$ that is (see [8]) $\eta = 1 + (x/s)^2 + (y/s)^2$. This indeed is the expression (20). The sum of the integrals of $\sqrt{\eta}$ upon the two hemispheres, $s > 0$ and $s < 0$, gives the right value 4π .

ii) Let us now consider a simple case where all the geometric quantities can be explicitly calculated in order to check the Eqs. (15) and (16). We shall consider $H = x_1^2 + x_2^2 + x_3^2 = E$, a sphere of radius \sqrt{E} in three dimensions and $V = x_3/\sqrt{x_1^2 + x_2^2} = u$, that is a cone with an angle $\arctan(u)$ at the vertex. In this case \mathcal{M} is a circle of radius $a = \sqrt{E/(1 + u^2)}$.

If we choose $\psi = 1$, we get easily

$$\frac{\partial}{\partial E} \int_{\mathcal{M}} d\tau = \frac{\partial}{\partial E} 2\pi a = \frac{\pi a}{E}.$$

The terms that appear in Eq. (16) result $\nabla H \cdot n^\xi = 2\sqrt{E}$, $\nabla n^\xi = 2/\sqrt{E}$ and $n^V \cdot (n^V \cdot \nabla)(n^\xi) = 1/\sqrt{E}$. Thus $A(1) = 1/(2E)$ and consequently $\int_{\mathcal{M}} d\tau A(1) = \pi a/E$.

By choosing $\psi = 1/W$ we get $W = 2E/a^2$, and

$$\frac{\partial}{\partial E} \int_{\mathcal{M}} \frac{d\tau}{W} = \frac{\partial}{\partial E} \frac{a^2}{2E} 2\pi a = \frac{\pi}{2(1 + u^2)^{3/2} \sqrt{E}}. \quad (21)$$

Again, Eq. (16) contains $\nabla H \cdot n^\xi = 2\sqrt{E}$, $\nabla(n^\xi/W) = a^2/E^{3/2}$ and $n^V \cdot (n^V \cdot \nabla)(n^\xi)/W = a^2/(2E^{3/2})$. Thus $A(1/W) = a^2/(4E^2)$ and consequently $\int_{\mathcal{M}} d\tau A(1/W) = \pi a^3/(2E^2)$ which indeed coincides with result (21).

Dynamical system.

Let us now consider a lattice system described by the Hamiltonian

$$H = \frac{\nu}{8} \sum_m (p_m^2 + q_m^2)^2 - \sum_m (p_m p_{m+1} + q_m q_{m+1}) \quad (22)$$

and the usual Poisson brackets $\{q_m, p_n\} = \delta_{m,n}$ for $n, m = 1, \dots, M$, with periodic boundary conditions. The dynamics generated by this Hamiltonian conserves the quantity $N = \sum_m (q_m^2 + p_m^2)/2$, thus the Eqs. (17) and (18) are in order to calculate the microcanonical temperature. The ground-state is achieved by solving the

equation $\delta(H - \chi N) = 0$ in which the Lagrangian multiplier χ has been introduced to take in account the conservation of N . By direct calculations, we got the solution $q_{0m} = \sqrt{2N/M} := q_0$, $p_{0m} = 0$ and $\chi = \nu N/M - 2$ [20]. Small fluctuations around this ground-state correspond to $T \gtrsim 0$, in the following we show that this prevision is verified by Eq. (17) and (18), whereas the formula for $1/T$ given in [1], that holds in the case of systems with only one first integral (energy), does not work. The reason of this comparison is to show that the equation derived in [1], which is valid in the case of system with only one first integral, cannot be used in the case of systems with more than one first integrals. In Ref. [6] has been derived an equation similar to Eqs. (17) and (18). The inverse temperature $1/T$ can be derived by Eqs. (12) and (17) of Ref. [6] after having found two vectors, X_0 and X_1 , such that $dH(X_0) = 1$, $dH(X_1) = 0$, $dV(X_0) = 0$ and $dV(X_1) = 1$. One can use $X_0 = c_{VV}\nabla H/d - c_{VH}\nabla V/d$ and $X_1 = -c_{VH}\nabla H/d + c_{HH}\nabla V/d$, where $c_{HH} = \|\nabla H\|^2$, $c_{VV} = \|\nabla V\|^2$, $c_{VH} = \nabla V \nabla H$, and $d = c_{HH}c_{VV} - c_{VH}^2$. Thus it results $1/T = \langle \nabla \cdot X_0 \rangle_{\mu c}$. The latter expression seems inequivalent to Eqs. (17) (18). Indeed, it does not contain $1/W$ which is related to the invariant measure. It is worth emphasizing that an analogous term $1/\|H\|$, which is related to the microcanonical measure of a sys-

tem with one first integral, indeed appears in the formula for $1/T$ derived in [1]. In any case a comparison between these two equations, would require a numerical simulation, but this is out of the aim of the present paper. By expanding H in terms of the displacements Q_n and P_n from the minimum points $q_n = q_0$ and $p_n = 0$, and by calculating the terms appearing in (17) and (18) in the limit $Q_n, P_n \rightarrow 0$, after some boring algebra we got the correct low-energy temperature, being $1/T = \langle \Phi \rangle_{\mu c} \rightarrow \infty$.

It is worth emphasizing that by using the formula derived in Ref. [1] $1/T = \langle \nabla (\nabla H / \|\nabla H\|^2) \rangle_{\mu c}$, which is correct for systems with only one first integral, one obtains the erroneous result: $T = [(\frac{\nu}{2}q_0^2 - 2)q_0]^2 / (2\nu q_0^2)$.

In conclusion, we have presented a dynamical approach for measuring the temperature of a Hamiltonian system with two first integrals in the microcanonical ensemble. The formula we have derived allows one to measure the inverse temperature as a time-average, instead of as an average over the phase-space, also in the case of systems with two first integrals. *Furthermore, by Eq. (15) higher orders of derivatives of $S(E)$ can be obtained. Therefore the method here presented allows one to measure g.e. the specific-heat.*

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 - [17] The analogous expression valid for systems with only one first integral, derived in [7], is the following $S(E) = \ln \int_{\Sigma_E} d\sigma / \|\nabla H\|$.
 - [18] The Federer-Laurence derivation formula [9, 10] is $\partial^k (\int_{\Sigma_E} \psi d\Sigma) / \partial E^k = \int_{\Sigma_E} A^k(\psi) d\Sigma$, where $A(\bullet) = 1 / \|\nabla H\| \nabla (\nabla H / \|\nabla H\| \bullet)$.
 - [19] Here, and in the following
- $$n^\nu \cdot (n^\nu \cdot \nabla)(n^\epsilon) = \sum_{j,k} n_j^\nu n_k^\nu \partial_k(n_j^\epsilon).$$
- [20] Another and equivalent solution is given by $q_{0m} = 0$, $p_{0m} = \sqrt{2N/M}$ and $\chi = \nu N/M - 2$.