A geometric, dynamical approach to thermodynamics

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We present a geometric and dynamical approach to the micro-canonical ensemble of classical Hamiltonian systems. We generalize the arguments in [10] and show that the energy-derivative of a micro-canonical average is itself micro-canonically observable. In particular, temperature, specific heat and higher order derivatives of the entropy can be observed dynamically. We give perturbative, asymptotic formulas by which the canonical ensemble itself can be reconstructed from micro-canonical measurements only. In a purely micro-canonical approach we rederive formulas by Lebowitz et al. [8], relating e.g. specific heat to fluctuations in the kinetic energy. We show that under natural assumptions on the fluctuations in the kinetic energy the micro-canonical temperature is asymptotically equivalent to the standard canonical definition using the kinetic energy.

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I. INTRODUCTION

For an isolated classical Hamiltonian system the ergodic hypothesis asserts that the time average of an observable along almost any trajectory may be replaced by a space average over a suitable subset of the phase space, typically the energy surface. Such an average is denoted the micro-canonical ensemble average or for short, $\mu$-average. The thermodynamic variables in this ensemble are the first integrals as well as extensive quantities like volume and particle numbers (cf e.g. Abraham and Marsden [1, Chapter 3.7]). In the so-called thermodynamic limit of many systems coupled weakly one expects in equilibrium each individual system to behave according to the canonical or Gibbs ensemble. In this ensemble the free parameters are the variables conjugated to (some of) the first integrals. Quite simple statistical principles argue in favor of such an approach but rigorous results are sparse [9]. Whereas the theory of the canonical ensemble has been elaborated to almost perfection, making it a corner stone in modern physics, our present understanding of the $\mu$-ensemble and the equivalence of the two ensembles is remarkably incomplete. On the other hand modern computer technology makes it ever more important to understand and give precise interpretations for dynamical measurements in the $\mu$-ensemble [5].

From a geometrical point of view the $\mu$-ensemble is an average of smooth quantities over a (generically smooth) sub-manifold of phase space, fixed by the first integrals. For the sake of clarity we restrict ourselves to the case where the energy is the only extensive parameter. But even in this simple picture it is not a priori clear how to describe the important role played by the variable conjugate to the energy, i.e. the inverse temperature. When the Hamiltonian contains one or more separate terms of the form momentum squared the canonical average of such a term yields precisely the (canonical) temperature. The time-average of such a term is therefore often used as a measure of the physical temperature of the system (cf. [1, Example 3.7.27] or [8]). This approach, however, presumes both the ergodic hypothesis and the equivalence of ensembles. In [1] we used simple geometrical arguments to show how the $\mu$-temperature is in fact measurable in the $\mu$-ensemble itself. In particular, assuming ergodicity only, we constructed explicitly an observable whose average yields the $\mu$-temperature. In the present article we shall show that these arguments in fact carries over to a much wider range of $\mu$-observables.

Below we establish (Theorem 1) two fundamental identities that will allow us to measure any energy-derivative of a $\mu$-average within the $\mu$-ensemble itself. Thus not only the temperature but also the specific heat and any higher order derivatives of the $\mu$-canonical entropy can be observed dynamically.

We give two main examples to illustrate these principles. In the first we use a perturbative expansion to show that by measuring all energy derivatives in the micro-canonical ensemble we can in principle reconstruct the canonical ensemble, cf. equations (23) and (24). This approach is, however, based upon a Gaussian expansion which itself relies on analyticity. On general grounds one would expect such results to be at best asymptotic, e.g. in the number of degrees of freedom.

In the second example we consider the thermodynamics of particles in a box. Lebowitz et al. [8] established relations between e.g. the specific heat and fluctuations in the kinetic energy in the micro-canonical ensemble. We rederive these relations in a purely micro-canonical approach. We also show that when both the kinetic energy and the square of fluctuations in the kinetic energy are of order $N$ our micro-canonical derivation of temperature is asymptotically equivalent to the standard canonical definition of temperature which uses the average kinetic energy. It is of interest to study deviations in the two approaches for systems out of equilibrium.
II. ENERGY DERIVATIVES

The phase space is an $n = 2N$-dimensional symplectic manifold $(\mathcal{M}, \omega)$ where $\omega$ is a non-degenerate symplectic two-form and the Liouville volume form $m = \wedge^N \omega$ is nowhere vanishing. The standard example is (a subset of) Euclidean space $\mathcal{M} = \mathbb{R}^{2N}$ and $m =$ Lebesgue measure (cf. Example B below). A Hamiltonian function $H: \mathcal{M} \rightarrow \mathbb{R}$ generates \cite{1} then a vector field $IdH$ and a flow $g^t_{IdH}$ which preserves the Liouville measure as well as the energy surface, $\Sigma_E = \{ \xi \in \mathcal{M} : H(\xi) = E \}$. It follows (\cite{1}, chapter 3.7) that the flow also preserves the restricted Liouville measure, formally given by:

$$\mu_E = m \delta (H - E).$$

(1)

The $\mu$-measure of an observable $\phi$ is given by $\mu_E(\phi) = \int m \delta(H - E) \phi$ and is a function of the energy. The $\mu$-ensemble is the corresponding probability distribution, yielding the $\mu$-average of $\phi$ over the energy surface:

$$\langle \phi; E \rangle = \mu_E(\phi)/\mu_E(1).$$

(2)

If the Hamiltonian flow is ergodic with respect to the restricted Liouville measure then by Birkhoff’s theorem this $\mu$-average equals the time average of $\phi$ for almost any initial point on the energy surface $\Sigma_E$. We say that $\langle \phi; E \rangle$ is measurable in the $\mu$-ensemble.

Of particular importance is the $\mu$-entropy and the associated (inverse) temperature:

$$S(E) = \log \mu_E(1) , \quad \frac{1}{T(E)} = \frac{\partial S(E)}{\partial E} = \frac{\partial}{\partial E} \mu_E(1)/\mu_E(1).$$

(3)

The energy derivative and the $\mu$-averages can now be related through the following:

Theorem:

Assume that $\Sigma_E$ is a regular energy surface of the Hamiltonian function $H$ and that $X$ is a vector field defined in a neighborhood of $\Sigma_E$ satisfying:

$$dH(X) \equiv 1.$$  

(4)

Then the $\mu$-measure and the $\mu$-average of a observable $\phi$ verify the identities:

$$\frac{\partial}{\partial E} \mu_E(\phi) = \mu_E(\text{div} (\phi X)),$$

$$\frac{\partial}{\partial E} \langle \phi; E \rangle = \langle \text{div} (\phi X); E \rangle - \langle \phi; E \rangle T(E).$$

(5)  (6)

In coordinates, $X \cdot \nabla = X_i \frac{\partial}{\partial x_i}$, $m = \rho \, dx_1 \wedge \ldots \wedge dx_n$, one has the explicit formulae:

$$\text{div} (\phi X) = \frac{1}{\rho} \sum_i \frac{\partial}{\partial x_i} (\rho \phi X_i) , \quad dH(X) = \sum_i X_i \frac{\partial H}{\partial x_i} \equiv 1.$$  

(7)

It is sufficient to verify the identity (5) since the other follows from (3) and

$$\frac{\partial}{\partial E} \langle \phi; E \rangle = \frac{\partial}{\partial E} \mu_E(\phi)/\mu_E(1) - \mu_E(\phi) \frac{\partial}{\partial E} \mu_E(1)/\mu_E(1).$$

(8)

According to Khinchin \cite{6}, the $\mu$-canonical measure is proportional to $d\Sigma/\|\nabla H\|$ where $d\Sigma$ is the area element on the energy surface. Thus for an observable $\phi$ we have

$$\int_{H \leq E} m \phi = \int_{-\infty}^E du \int_{H = u} \frac{d\Sigma}{\|\nabla H\|} \phi.$$  

(9)
In the language of differential geometry the $\mu$-canonical measure can be expressed as a differential $(2n-1)$-form:

$$\mu = i_X m, \quad (10)$$

where $X$ is any vector field for which $dH(X) \equiv 1$. Provided $H$ has no critical points on the energy surface one can always find such a vector field in a neighborhood of that energy surface. Although $\mu$ is not unique, its restriction to an energy surface is unique and equivalent to the weighted area element in Khinchin’s formula. The (exterior) derivative of $\mu \phi$ ($\phi$ being an observable) is given by:

$$d(\mu \phi) = d(i_X m \phi) = d(i_{\phi} X m) = m \text{div}(\phi X), \quad (11)$$

where the divergence of $X \phi$ was given by equation $(9)$ above. Stokes Theorem and the relation $m = dH \wedge \mu$ yields then

$$\int_{H=E} \mu \phi = \int_{H \leq E} d(\mu \phi) = \int_{-\infty}^{E} du \int_{H=u} \mu \text{div}(X \phi). \quad (12)$$

Hence, taking a further energy derivative:

$$\frac{\partial}{\partial E} \mu_E(\phi) = \mu_E(\text{div}(\phi X)), \quad (13)$$

as we wanted to show.

### III. GENERAL REMARKS

- **Non-uniqueness:** Note that the vector field $X$ is far from unique. One may add any vector field tangent to the energy surfaces. This corresponds to a reparametrization of the surfaces and does not change the average of $\text{div} \ (\phi X)$. It does, however, affect fluctuations in this observable and hence a wise choice of $X$ could lead to better convergence in numerical experiments.

- **Setting $\phi \equiv 1$** it follows from $(9)$ and $\langle \phi; E \rangle \equiv 1$ that:

$$\frac{1}{T(E)} = \langle \text{div} \ X; E \rangle. \quad (14)$$

Neither this formula nor those in the Theorem make any reference to metric properties of $M$. A metric on $M$ allows one to compute gradients of functions and this gives one natural choice of the vector field $X$, namely $X = \nabla H / \|\nabla H\|^2$. In the case of Euclidean space and Lebesgue measure this leads to the formula $1/T(E) = \langle \nabla \cdot \frac{\nabla H}{\|\nabla H\|^2}; E \rangle$ as was found in $(10)$.

- **Iteration:** Given the analytic expression for a vector field $X$ and of $\phi$ as in the Theorem the above formulas may be iterated indefinitely. Thus formula $(9)$ implies that any energy derivative of a $\mu$-average can be measured within the $\mu$-ensemble. In particular, any derivative of the temperature, e.g. specific heat, is also measurable in the $\mu$-ensemble.

- **Fluctuations:** Using the identity $\text{div}(\phi X) = (X \cdot \nabla)\phi + \phi \text{div} X$ we may rewrite the equation $(9)$ as follows:

$$\frac{\partial}{\partial E} \langle \phi; E \rangle = \langle (X \cdot \nabla)\phi; E \rangle + \langle \delta \phi \delta(\text{div}X); E \rangle. \quad (15)$$

where $\delta \phi = \phi - \langle \phi; E \rangle$ etc. Thus the energy derivative has a contribution coming from the derivative of $\phi$ in the direction of $X$ as well as from the product of fluctuations in the observables $\phi$ and $\text{div} X$, cf. example B below.
IV. EXAMPLE A: THE CANONICAL ENSEMBLE

As an illustration of the Theorem we will show that the canonical ensemble can be measured through $\mu$-averages. The canonical ensemble is most conveniently here defined as the Laplace transform of the $\mu$-ensemble \(^3\). More precisely, the weighted partition function is given by:

$$Z(\beta, \phi) = \int m \ e^{-\beta H} \phi = \int dE \ e^{-\beta E} \mu_E(\phi). \quad (16)$$

Assuming that $\mu_E(\phi)$ has an analytic extension in $E$ and $s$ is small enough we may expand the partition function by iterating (7). It is convenient to write $D_X(\phi) \equiv \text{div} (\phi X)$ in terms of which

$$\mu_{E+s}(\phi) = e^{s \frac{\partial}{\partial E}} \mu_E(\phi) = \mu_E(e^s D_X \phi). \quad (17)$$

Here the last exponential should be interpreted through its power series. Therefore, formally:

$$Z(\beta, \phi) = \int ds e^{-\beta (E+s)} \mu_E(e^s D_X \phi), \quad (18)$$

where in this last expression $E$ has a fixed value. Dividing (normalizing) by the factor $\mu_E(1) = e^{S(E)}$ we see that all the terms in the expansion of the exponential can be measured in the $\mu$-ensemble. Thus, up to a constant factor the canonical partition function can in principle be evaluated in the $\mu$-ensemble. Of course, this approach does raise the question about convergence. In general one can only hope for the expansion to be asymptotic, e.g. in the number of degrees of freedom in the system. To make our statements more explicit consider the standard partition function ($\phi \equiv 1$) and the following expansion of the $\mu$-entropy:

$$S(E) = S(E_0) + \sum_{k>0} \frac{(E - E_0)^k}{k!} s_k. \quad (19)$$

As a consequence of Theorem 1 all the numbers $s_k$ (but not $S(E_0)$) are measurable in the $\mu$-canonical ensemble. We shall assume in the following that $s_2$ is strictly negative\(^1\). The partition function we write as:

$$Z(\beta) = \int dE e^{-\beta E + S(E)} = e^{-F(\beta)}. \quad (20)$$

Now, let $\beta$ be close to $s_1 = \partial S/\partial E(E_0)$ and let $\Gamma(\beta)$ be the extremal point (the conjugated variable in the Legendre transform) of the exponent $-\beta E + S(E)$. Again it is possible to calculate $\Gamma(\beta)$ perturbatively from the known quantities $s_k$ and equation (19). $\Gamma(\beta)$ satisfies (cf. also Bailyn \(^3\), Section 11.6) :

$$\beta = \frac{\partial S}{\partial E}(\Gamma(\beta)), \quad 1 = \frac{\partial^2 S}{\partial E^2}(\Gamma(\beta)) \frac{\partial \Gamma}{\partial \beta}. \quad (21)$$

Inserting $E = \Gamma(\beta) + z$ we get for the exponent:

$$-\beta \Gamma(\beta) + S(\Gamma(\beta)) + \frac{\partial^2 S}{\partial E^2}(\Gamma(\beta)) z^2 \frac{1}{2} + V(z) \quad (22)$$

where $V(z) = v_3 z^3/3! + v_4 z^4/4! + ...$ can also be calculated in terms of the coefficients $s_k$. As the second derivative was assumed negative, we may carry out the Gaussian integral by standard techniques to obtain the (exact) asymptotic formula:

$$F(\beta) = F_{cl}(\beta) - \log[e^{\frac{1}{2}(\frac{\partial}{\partial x})(\partial_x)} e^{V_0(x)}]_{x \equiv 0}. \quad (23)$$

with

\(^1\)This corresponds to the assumption of thermodynamic stability, i.e. that the specific heat should be positive in the $\mu$-ensemble. At least in the thermodynamic limit there are mathematical arguments justifying such an assumption.
\[ F_{cl}(\beta) = \text{const} + \beta \Gamma(\beta) - S(\Gamma(\beta)) - \frac{1}{2} \log(-\frac{\partial \Gamma}{\partial \beta}). \]  

(24)

For the sake of clarity we shall in the following neglect the \( V \)-term and use the last expression (corresponding to the classical action in QFT). Taking a \( \beta \) derivative we get for the average energy in the canonical ensemble :

\[ \langle H; \beta \rangle = F_{cl}'(\beta) = \Gamma(\beta) - \frac{1}{2} \frac{\Gamma''(\beta)}{\Gamma'(\beta)}, \]  

(25)

Differentiating once more we obtain the approximative formula for the specific heat :

\[ c(\beta) = -\beta^2 \frac{\partial (H; \beta)}{\partial \beta} = -\beta^2 \Gamma'(1 - \frac{\Gamma''}{2(\Gamma')^2} + \frac{(\Gamma'')^2}{2(\Gamma')^3}). \]  

(26)

As a trivial but analytically accessible example (cf. [10]) we consider \( N \) harmonic oscillators for which the \( \mu \)-entropy equals \( S(E) = (N - 1) \log E \) and the extremum of \( -\beta E + S(E) \) is attained for \( \Gamma(\beta) = (N - 1)/\beta \). We get :

\[ \langle H; \beta \rangle = \frac{N - 1}{\beta} - \frac{1}{2} \frac{-2(N - 1)/\beta^3}{(N - 1)/\beta^2} = \frac{N}{\beta}, \quad c(\beta) = N, \]  

(27)

which happens to recover the exact canonical results.

V. EXAMPLE B: INTERACTING PARTICLES

Our second application is concerned with the thermodynamics of \( N \) particles in a box of volume \( V \) in \( R^3 \). We shall compare the micro-canonical computations, e.g. of temperature, given here with formulæ obtained from the canonical ensemble theory. It turns out that a natural assumption on the fluctuations in the kinetic energy is sufficient to obtain equivalence of the two approaches.

The Hamiltonian is taken to be of the form

\[ H(p, q) = \sum_{i=1}^{3N} \frac{p_i^2}{2} + U_{\text{int}}(q) + U_{\text{ext}}(q), \]  

(28)

with the standard symplectic structure on \( R^{6N} \). Here \( K(p) = \sum_{i=1}^{3N} \frac{p_i^2}{2} \) is the kinetic energy, \( U_{\text{ext}} = \sum_{j=1}^{N} U_j(\vec{q}_j) \) is a box confining potential and \( U_{\text{int}} \) is an interaction potential, e.g. a sum of two-body interactions. Note that for notational convenience the momentum vector is here considered as a \( 3N \) dimensional vector whereas the configuration coordinates are considered as \( N \) three-dimensional vectors.

For the vector field \( X \) we choose : \( X_1 = \vec{p}/2K(p). \) The reader might worry about the fact that this vector field is singular at \( \vec{p} = \vec{0} \) but as we shall see below the singularity is integrable when the number of particles is sufficiently large (at least 2 particles are needed in the applications below). A direct computation shows that :

\[ \text{div} \ (X_1) = (3N - 2)/(2K(p)). \]  

(29)

The temperature is then given by :

\[ \frac{1}{T(E)} = \frac{3N - 2}{2} \langle 1/K(p); E \rangle. \]  

(30)

In order for the average to be well-defined it is necessary that \( 1/K(p) \) is integrable at \( p = 0 \), i.e. that \( \int 1/p^2 d^{3N} p < \infty \) where the integral is over a neighborhood of \( p = 0 \). This is the case when \( 3N > 2 \), i.e. when the system contains at least one particle.

The inverse specific heat, \( 1/c = \frac{\partial}{\partial E} T(E) = -T(E)^2 \frac{\partial}{\partial E} \frac{1}{T(E)} \), can be calculated using (29) from which

\[ \left( \frac{1}{T(E)} + \frac{\partial}{\partial E} \right) \frac{1}{T(E)} = \langle \text{div}(\frac{3N - 2}{K}X_1); E \rangle = \frac{(3N - 2)(3N - 4)}{4} \langle 1/K^2; E \rangle. \]  

(31)
and thus

\[ \frac{1}{c(E)} = 1 - \frac{(3N - 4)(1/K; E)}{(3N - 2)(1/K; E)²}. \tag{32} \]

This time we need that \(1/K²(p)\) is integrable and this happens when \(3N > 4\), i.e. at least two particles are present. The standard definition of the (canonical) temperature is

\[ T_c(E) = \frac{2}{3N} \langle K(p); E \rangle. \tag{33} \]

Had the average been in the canonical ensemble this would indeed have been the canonical temperature. We have the following formula for the ratio:

\[ \frac{T_c(E)}{T(E)} = \frac{3N - 2}{3N} \langle K; E \rangle \langle 1/K; E \rangle. \tag{34} \]

We may also calculate the inverse specific heat this time using the canonical temperature. From (6) and the obvious identity \(\text{div}(KX) = 3N/2\) we obtain:

\[ \frac{1}{c(E)} = \frac{\partial}{\partial E} T_c(E) = 1 - \frac{T_c(E)}{T(E)}. \tag{35} \]

In order to compare the above formulas we shall consider the fluctuations in the kinetic energy, defined by

\[ K = \langle K(p); E \rangle + \delta K. \tag{36} \]

Our assumption in the following will be that \(\langle K \rangle = \langle K(p); E \rangle\) and \((\delta K)²\) are both of order \(N\). In particular, that for large enough \(N\) the singularities are integrable and we have the expansion:

\[ \frac{1}{K} = \frac{1}{\langle K \rangle} - \frac{\delta K}{\langle K \rangle²} + \frac{(\delta K)²}{\langle K \rangle³} + o(N^{-2}). \tag{37} \]

Taking the average on both sides yields:

\[ \langle \frac{1}{K} \rangle = \frac{1}{\langle K \rangle} + \frac{((\delta K)²)}{\langle K \rangle³} + o(N^{-2}) \tag{38} \]

and similarly by squaring before taking the average:

\[ \langle \frac{1}{K²} \rangle = \frac{1}{\langle K² \rangle} + \frac{3((\delta K)²)}{\langle K \rangle⁴} + o(N^{-3}) \tag{39} \]

Using (38)-(39) and retaining only terms to order \(N⁻¹\) both (32) and (33) reduces to

\[ \frac{1}{c(E)} = \frac{2}{3N} \cdot \frac{⟨(δK)²; E⟩}{⟨K; E⟩} + o(N^{-1}). \tag{40} \]

We have here given a micro-canonical derivation of an expression which relates the specific heat to fluctuations in the kinetic energy. This was previously found by Lebowitz et al. using an ingenious technique of inverting ensemble averages. Their method, however, relies on (unstated) analytic properties of the ensembles involved whereas the method presented here makes the assumptions explicit in terms of the fluctuations in the kinetic energy. We also note that our assumption on \(δK\) gives a sufficient condition for the equivalence not only of \(T(E)\) and \(T_c(E)\) (the ratio (34) differs from 1 by a term of order \(N^{-1}\) but also for the derived expressions for the inverse specific heat (to order \(N^{-1}\)). Even close to a phase transition where \(1/c(E)\) tends to zero we would expect that our assumptions (38)-(39) are not violated.

As a final application consider the \(μ\)-canonical pressure exerted by the \(N\) particles on the walls of the container. We may define it as the average force per surface area of the container. The pressure, \(P\), can then be calculated through the Virial Theorem (see e.g. Becker [4, p. 98] or Abraham and Marsden [1, Example 3.7.32]). The \(j\)th particle \(j = 1, \ldots, N\) having coordinates \(q_j\) is confined by the external potential \(U_j(q_j)\). The force, \(dF = P dA\), exerted on the
surface element $d\vec{A}$ is given by the (time-) average of the external forces in a small neighborhood $\delta V$ of that surface element, i.e. $P d\vec{A} = \langle \sum_j \vec{\nabla}U_j : q_j \in \delta V \rangle$.

This formula is vectorial but a scalar quantity is obtained by taking the scalar product with the coordinate of the volume element in question. Summing over the whole surface removes the restriction on the $q_j$’th coordinate, thus yielding

$$P \int \vec{q} \cdot d\vec{A} = \langle \sum_j \vec{q}_j \cdot \vec{\nabla}U_j \rangle$$

and finally, using Stokes Theorem we see that the left hand side equals $3PV$. By the Virial Theorem the time average of $(p\partial_p - q\partial_q)H$ vanishes (since it is a total time derivative). Hence

$$PV/N = \frac{1}{3N}(2K(p) - \Phi; E),$$

with $\Phi = \sum_{j=1}^N \vec{q}_j \cdot \partial U_{\text{int}}(q)/\partial \vec{q}_j$.

We therefore obtain the following derivative:

$$\frac{\partial}{\partial T} (PV/N) = c(E) \frac{\partial}{\partial E} (PV/N) = 1 - \frac{c(E)}{3N} \frac{\partial}{\partial E} (\Phi; E).$$

Equation (15) implies the exact formula:

$$\frac{\partial}{\partial T} (PV/N - T) = c(E) \frac{3N - 2}{6N} (\delta\Phi \delta(1/K); E),$$

which under the assumption above on the kinetic energy fluctuations reduces to

$$\frac{\partial}{\partial T} (PV/N - T) = \frac{2c(E)}{(3NT(E))^2} (\delta\Phi \delta K; E) + o(1).$$

This again is a micro-canonical rederivation of a formula previously obtained by Lebowitz et al \cite{8} under the aforementioned analyticity assumption of ensemble inversion.

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