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# A geometric, dynamical approach to thermodynamics

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**Abstract.** We present a geometric and dynamical approach to the micro-canonical ensemble of classical Hamiltonian systems. We generalize the arguments in Rugh (1997 *Phys. Rev. Lett.* **78** 772–4) 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 formulae by which the canonical ensemble itself can be reconstructed from micro-canonical measurements only. Using our geometrical tools we rederive formulae by Lebowitz *et al* and Pearson *et al*, relating, for example, 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.

## 1. Introduction

For an isolated classical Hamiltonian system the ergodic hypothesis implies 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 here, for short, the  $\mu$ -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, ch 3.7]). In the so-called thermodynamic limit of many weakly coupled systems in equilibrium one expects each individual system to behave according to the canonical or Gibbs ensemble. In this ensemble the free parameters [7] are the variables conjugated to (some of) the first integrals. Quite simple statistical principles argue in favour of such an approach but rigorous results are sparse [10]. 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].

Now, 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. However, even then it is *a priori* not clear how to describe the important role played by the variable conjugate to the energy, i.e. the inverse temperature. If 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 [11] we used elementary geometrical arguments to show that the  $\mu$ -temperature is in fact measurable in the  $\mu$ -ensemble itself. In particular, assuming ergodicity, thus relating dynamics to thermodynamics, we constructed explicitly an observable whose time/space average yields the  $\mu$ -temperature. In the present paper we shall carry these arguments over to a much wider range of  $\mu$ -observables.

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, for example, 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 (26) and (27). 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, for example in the number of degrees of freedom.

In the second example we consider the thermodynamics of particles in a box. Lebowitz *et al* [8] and also Pearson *et al* [9] established relations between, for example, the specific heat and fluctuations in the kinetic energy in the micro-canonical ensemble. We rederive these and other relations using our geometrical and 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. The case of relativistic particles concludes the example.

It is our hope that the reader will perceive the geometrical approach advocated here not only as elementary from the theoretical point of view but also as providing a tool which is easy and straightforward to apply in concrete cases. It is of interest to study what happens for systems out of equilibrium.

## 2. Energy derivatives

As phase space we take a  $2n$ -dimensional symplectic manifold  $(\mathcal{M}, \omega)$ , where  $\omega$  is a non-degenerate symplectic 2-form and the Liouville volume form  $m = \wedge^n \omega$  is nowhere vanishing. The standard example is (a subset of) Euclidean space  $\mathcal{M} = R^{2n}$  and  $m =$  Lebesgue measure (cf example B). A Hamiltonian function  $H : \mathcal{M} \rightarrow R$  generates [1, 2] a vector field  $I dH$  and a flow  $g_{I dH}^t$  which preserves the Liouville measure as well as the energy surface,  $\Sigma_E = \{\xi \in \mathcal{M} : H(\xi) = E\}$ . It follows ([1, ch 3.7]) that the flow also preserves the restricted Liouville measure, formally given by

$$\mu_E = m\delta(H - E) \quad (1)$$

at least when this is well defined. The  $\mu$ -measure of an observable  $\phi$  is then 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:

$$\langle \phi; E \rangle = \mu_E(\phi) / \mu_E(1). \quad (2)$$

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 dynamically measurable in the  $\mu$ -ensemble.

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

$$S(E) = \log \mu_E(1) \quad \frac{1}{T(E)} = \frac{\partial S(E)}{\partial E} = \frac{\partial \mu_E(1)/\partial E}{\mu_E(1)}. \quad (3)$$

The energy derivative and the  $\mu$ -averages are related through the following.

*Theorem 1.* Assume that  $\Sigma_E$  is a regular energy surface (cf later) of the Hamiltonian function  $H$  and that  $X$  is a vector field defined in a neighbourhood of  $\Sigma_E$  satisfying

$$dH(X) \equiv 1. \quad (4)$$

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

$$\frac{\partial}{\partial E} \mu_E(\phi) = \mu_E(\operatorname{div}(\phi X)) \quad (5)$$

$$\frac{\partial}{\partial E} \langle \phi; E \rangle = \langle \operatorname{div}(\phi X); E \rangle - \frac{\langle \phi; E \rangle}{T(E)}. \quad (6)$$

In coordinates,  $X \cdot \nabla = \sum_i X_i \partial/\partial x_i$ ,  $m = \rho dx_1 \wedge \dots \wedge dx_{2n}$ , one has the explicit formulae

$$\operatorname{div}(\phi X) = \frac{1}{\rho} \sum_i \frac{\partial}{\partial x_i} (\rho \phi X_i) \quad dH(X) = \sum_i X_i \frac{\partial H}{\partial x_i} \equiv 1. \quad (7)$$

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

$$\frac{\partial}{\partial E} \langle \phi; E \rangle = \frac{\partial \mu_E(\phi)/\partial E}{\mu_E(1)} - \frac{\mu_E(\phi)}{\mu_E(1)} \frac{\partial \mu_E(1)/\partial E}{\mu_E(1)}. \quad (8)$$

According to Khinchin [6], when a metric is given, the  $\mu$ -canonical measure is proportional to  $d\Sigma/\|\nabla H\|$  where  $d\Sigma$  is the differential area element on the energy surface. Thus, for an observable  $\phi$  we have

$$\int_{H \leq E} m \phi = \int_{-\infty}^E du \int_{H=u} \frac{d\Sigma}{\|\nabla H\|} \phi. \quad (9)$$

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  $dH(X) \equiv 1$  and  $i_X m$  denotes the interior product of  $X$  with the volume form  $m$ . When the energy surface is regular, which is to say that  $dH$  does not vanish on the energy surface, one can always find such a vector field in a neighbourhood of this 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. To see this, write the area element as a vectorial quantity  $d\Sigma$  (in the direction of  $\nabla H$ ) and the metric as a scalar product. Then, by a slight abuse of notation,

$$i_X m = X \cdot d\Sigma = \frac{dH(X) \nabla H \cdot d\Sigma}{\|\nabla H\|^2} = \frac{d\Sigma}{\|\nabla H\|}. \quad (11)$$

The identity  $i_X(dH \wedge i_X m) \equiv dH(X) i_X m = i_X m$  and the fact that  $m$  is of maximal degree implies  $dH \wedge i_X m = m$ . Thus,  $\mu = i_X m$  satisfies the relation

$$m = dH \wedge \mu \quad (12)$$

and the volume integral splits into an energy integral and an integral over each energy surface. The (exterior) derivative of  $\mu\phi$  ( $\phi$  being an observable) is given by

$$\overline{d(\mu\phi)} = d(i_X m\phi) = d(i_{\phi_X} m) = m \operatorname{div}(\phi X) \quad (13)$$

where the divergence of  $X\phi$  was given by equation (7). Stokes theorem and the relation (12) then yield

$$\int_{H=E} \mu\phi = \int_{H \leq E} d(\mu\phi) = \int_{-\infty}^E du \int_{H=u} \mu \operatorname{div}(X\phi). \quad (14)$$

Hence, taking a further energy derivative,

$$\frac{\partial}{\partial E} \mu_E(\phi) = \mu_E(\operatorname{div}(\phi X)) \quad (15)$$

as we wanted to show.

### 3. 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  $\operatorname{div}(\phi X)$ . 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 (6) and  $\langle \phi; E \rangle \equiv 1$  that

$$\frac{1}{T(E)} = \langle \operatorname{div} X; E \rangle. \quad (16)$$

Neither this formula nor those in theorem 1 make any reference to metric properties of  $\mathcal{M}$ . 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  $1/T(E) = \langle \nabla \cdot (\nabla H / \|\nabla H\|^2); E \rangle$  as was found in [11].

- Iteration. Given the analytic expression for a vector field  $X$  and of  $\phi$  as in theorem 1 the above formulae may be iterated indefinitely. Thus, formula (6) implies that any energy derivative of a  $\mu$ -average can be measured within the  $\mu$ -ensemble. In particular, any derivative of the temperature, for example specific heat, is also measurable in the  $\mu$ -ensemble.

- Fluctuations. Using the identity  $\operatorname{div}(\phi X) = (X \cdot \nabla)\phi + \phi \operatorname{div} X$  we may rewrite equation (6) as follows,

$$\frac{\partial}{\partial E} \langle \phi; E \rangle = \langle (X \cdot \nabla)\phi; E \rangle + \langle \delta\phi \delta(\operatorname{div} X); E \rangle \quad (17)$$

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  $\operatorname{div} X$ , cf example B.

- Other ensembles. Our presentation is closely tied to the ergodic hypothesis, emphasizing the dynamical aspects of the  $\mu$ -canonical approach. Other definitions of the  $\mu$ -ensemble are possible, for example by considering the enclosed bulk volume instead of the area of the energy surface. Such a choice seems less natural from the dynamical point of view.

#### 4. Example A. The canonical ensemble

As an illustration of theorem 1 we will show that the canonical ensemble can be measured through  $\mu$ -averages. The canonical ensemble is most conveniently defined here as the Laplace transform of the  $\mu$ -ensemble [3, 4]. More precisely, the weighted partition function is given by

$$Z(\beta, \phi) = \int m e^{-\beta H} \phi = \int dE e^{-\beta E} \mu_E(\phi). \tag{18}$$

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

$$\mu_{E+s}(\phi) = e^{s\partial/\partial E} \mu_E(\phi) = \mu_E(e^{sD_X} \phi). \tag{19}$$

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

$$Z(\beta, \phi) = \int ds e^{-\beta(E+s)} \mu_E(e^{sD_X} \phi) \tag{20}$$

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, for example 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:

$$S(E) = S(E_0) + \sum_{k>0} \frac{(E - E_0)^k}{k!} s_k. \tag{21}$$

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<sup>†</sup>. We write the partition function as

$$Z(\beta) = \int dE e^{-\beta E + S(E)} = e^{-F(\beta)}. \tag{22}$$

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 (21).  $\Gamma(\beta)$  satisfies (cf also Bailyn [3, section 11.6]):

$$\beta = \frac{\partial S}{\partial E}(\Gamma(\beta)) \quad 1 = \frac{\partial^2 S}{\partial E^2}(\Gamma(\beta)) \frac{\partial \Gamma}{\partial \beta}. \tag{23}$$

Inserting  $E = \Gamma(\beta) + z$  in the exponent in (22) we get

$$-\beta \Gamma(\beta) + S(\Gamma(\beta)) + \frac{\partial^2 S}{\partial E^2}(\Gamma(\beta)) z^2 \frac{1}{2} + V(z) \tag{24}$$

<sup>†</sup> 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.

where  $V(z) = v_3 z^3/3! + v_4 z^4/4! + \dots$  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,

$$\int dz e^{(-z^2/2a)+V(z)} = \int dz e^{(-z^2/2a)+z\partial_x} e^{V(x)}|_{x=0} = C e^{(a/2)\partial_x^2} e^{V(x)}|_{x=0} \quad (25)$$

to obtain the (exact) asymptotic formula

$$F(\beta) = F_{cl}(\beta) - \log[e^{\frac{1}{2}(-\partial\Gamma/\partial\beta)(\partial_x)^2} e^{V(x)}|_{x=0}] \quad (26)$$

where

$$F_{cl}(\beta) = \text{constant} + \beta\Gamma(\beta) - S(\Gamma(\beta)) - \frac{1}{2} \log\left(-\frac{\partial\Gamma}{\partial\beta}\right). \quad (27)$$

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 quantum field theory). Taking a  $\beta$  derivative we get for the average energy in the canonical ensemble

$$\langle H; \beta \rangle = F'_{cl}(\beta) = \Gamma(\beta) - \frac{1}{2} \frac{\Gamma''(\beta)}{\Gamma'(\beta)}. \quad (28)$$

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

$$c(\beta) = -\beta^2 \frac{\partial\langle H; \beta \rangle}{\partial\beta} = -\beta^2 \Gamma' \left[ 1 - \frac{\Gamma'''}{2(\Gamma')^2} + \frac{(\Gamma'')^2}{2(\Gamma')^3} \right]. \quad (29)$$

As a trivial but analytically accessible example (cf [11]) 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

$$\langle H; \beta \rangle = \frac{n - 1}{\beta} - \frac{1 - 2(n - 1)/\beta^3}{2(n - 1)/\beta^2} = \frac{n}{\beta} \quad c(\beta) = n \quad (30)$$

which happens to recover the exact canonical results.

### 5. 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 make use of a very particular choice of vector field (for theorem 1) which highlights the important role the kinetic energy plays. We shall compare exact micro-canonical computations with formulae obtained from 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. These results were previously obtained by Pearson *et al* [9] and in an approximative form by Lebowitz *et al* [8]. Lebowitz *et al* used an ingenious and quite general technique of inverting ensemble averages through an (approximative) inversion of a Laplace transform. Their method relies, however, on unstated analytic properties of the ensembles involved. Pearson *et al* showed that when the kinetic energy is a quadratic form in the momenta one may carry out Laplace transforms to obtain exact formulae. Their method can be adapted to some other forms for the kinetic energy but does not offer a general approach, cf the relativistic example below. The geometrical approach we have presented makes no reference to the particular structure neither of the Hamiltonian nor the phase space. It is only in the choice of the vector field  $X$  that such a structure is reflected. In practical situations other choices of the vector field may well turn out to be superior in terms of minimizing numerical fluctuations.

The Hamiltonian is taken to be of the form

$$H(p, q) = \sum_{i=1}^N \mathbf{p}_i^2/2 + U_{\text{int}}(q) + U_{\text{ext}}(q) \quad (31)$$

with the standard symplectic structure on  $R^{6N}$ . Here  $K(p) = \sum_i \mathbf{p}_i^2/2$  is the kinetic energy,  $U_{\text{ext}} = \sum_{j=1}^N U_j(\mathbf{q}_j)$  is a box confining potential and  $U_{\text{int}}$  is an interaction potential, for example a sum of two-body interactions.

For the vector field  $X$  we choose  $X_1 = \mathbf{p}/2K(p)$  with  $\mathbf{p} = (\mathbf{p}_1, \dots, \mathbf{p}_N, 0, \dots, 0)$ . The reader might worry about the singularity at  $\mathbf{p} = \mathbf{0}$  but as we shall see later this singularity is integrable when the number of particles is sufficiently large (at least two particles are needed in the applications). Since

$$\text{div}(X_1) = \sum_i \frac{\partial}{\partial \mathbf{p}_i} \cdot \left( \frac{\mathbf{p}_i}{2K(p)} \right) = (3N - 2)/(2K(p)) \quad (32)$$

the inverse temperature is given by

$$\frac{1}{T(E)} = \frac{3N - 2}{2} \langle 1/K(p); E \rangle. \quad (33)$$

In order for this 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 neighbourhood of  $p = 0$ . This is the case when  $3N > 2$ , i.e. when the system contains at least one particle.

The inverse specific heat,

$$\frac{1}{c} = \frac{\partial}{\partial E} T(E) = -T(E)^2 \frac{\partial}{\partial E} \frac{1}{T(E)}$$

can be calculated using (6) from which

$$\left( \frac{1}{T(E)} + \frac{\partial}{\partial E} \right) \frac{1}{T(E)} = \left\langle \text{div} \left( \frac{3N - 2}{K} X_1 \right); E \right\rangle = \frac{(3N - 2)(3N - 4)}{4} \langle 1/K^2; E \rangle \quad (34)$$

and thus

$$\frac{1}{c(E)} = 1 - \frac{(3N - 4) \langle 1/K^2; E \rangle}{(3N - 2) \langle 1/K; E \rangle^2}. \quad (35)$$

This time we need  $1/K^2(p)$  to be integrable and this happens when  $3N > 4$ , i.e. at least two particles should be present.

The standard definition of the (canonical) temperature is

$$T_c(E) = \frac{2}{3N} \langle K(p); E \rangle. \quad (36)$$

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

$$T_c(E)/T(E) = \frac{3N - 2}{3N} \langle K; E \rangle \langle 1/K; E \rangle. \quad (37)$$

We may also calculate the inverse specific heat this time using the canonical temperature. From (6) and the obvious identity  $\text{div}(K X_1) \equiv 3N/2$  we obtain

$$\frac{1}{c_c(E)} = \frac{\partial}{\partial E} T_c(E) = 1 - \frac{T_c(E)}{T(E)}. \quad (38)$$

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

$$K = \langle K(p); E \rangle + \delta K. \quad (39)$$

Our assumption in the following will be that  $\langle K \rangle = \langle K(p); E \rangle$  and  $(\delta K)^2$  are both of order  $N$ . Such an assumption seems physically justified when interactions have short range and  $N$  is large (for non-interacting particles the statement is rather trivial by the law of large numbers but a rigorous argument in the general case is lacking). In particular, for  $N$  large enough we assume that the singularities are integrable and that we have an expansion of the form

$$\frac{1}{K} = \frac{1}{\langle K \rangle} - \frac{\delta K}{\langle K \rangle^2} + \frac{(\delta K)^2}{\langle K \rangle^3} + o(N^{-2}). \quad (40)$$

Taking the average on both sides yields

$$\left\langle \frac{1}{K} \right\rangle = \frac{1}{\langle K \rangle} + \frac{\langle (\delta K)^2 \rangle}{\langle K \rangle^3} + o(N^{-2}) \quad (41)$$

and similarly by squaring before taking the average:

$$\left\langle \frac{1}{K^2} \right\rangle = \frac{1}{\langle K \rangle^2} + 3 \frac{\langle (\delta K)^2 \rangle}{\langle K \rangle^4} + o(N^{-3}). \quad (42)$$

Using (41) and (42) and retaining only terms to order  $N^{-1}$ , both (35) and (38) reduce to

$$\frac{1}{c(E)} = \frac{2}{3N} - \frac{\langle (\delta K)^2; E \rangle}{\langle K; E \rangle} + o(N^{-1}). \quad (43)$$

We note that the assumption on  $\delta K$  gives a sufficient condition for the equivalence not only of  $T(E)$  and  $T_c(E)$  (the ratio (37) differs from one by a term of order  $N^{-1}$ ) but also for the derived expressions for the inverse specific heat to be valid to order  $N^{-1}$ . Even close to a phase transition where  $1/c(E)$  tends to zero we would expect that our assumptions (41) and (42) are not violated.

Next, consider the  $\mu$ -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. A convenient expression for the pressure,  $P$ , is then obtained through the Virial theorem (see, e.g., Becker [4, p 98] or Abraham and Marsden [1, example 3.7.32]).

The  $j$ th particle  $j = 1, \dots, N$  having coordinates  $q_j$  is confined by the external potential  $U_j(q_j)$ . The force,  $d\mathbf{F} = P d\mathbf{A}$ , exerted on the surface element  $d\mathbf{A}$  is given by the (time) average of the external forces in a small neighbourhood  $\delta V$  of that surface element, i.e.  $P d\mathbf{A} = \langle \sum_j \nabla U_j : q_j \in \delta V \rangle$ .

This vectorial formula is transformed into a scalar quantity 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

$$P \int \mathbf{q} \cdot d\mathbf{A} = \left\langle \sum_j \mathbf{q}_j \cdot \nabla U_j \right\rangle \quad (44)$$

and, finally, using Stokes theorem we see that the left-hand side equals  $3PV$ . Now, by the Virial theorem the time average of  $(p\partial_p - q\partial_q)H$  vanishes (since it is a total time derivative). A rearrangement of the terms then yields

$$PV/N = \frac{1}{3N} \langle 2K(p) - \Phi; E \rangle \quad (45)$$

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

We, therefore, obtain the following derivative:

$$\frac{\partial}{\partial T} (PV/N) = c(E) \frac{\partial}{\partial E} (PV/N) = 1 - \frac{c(E)}{3N} \frac{\partial}{\partial E} \langle \Phi; E \rangle. \quad (46)$$

Equation (17) implies the exact formula

$$\frac{\partial}{\partial T}(PV/N - T) = c(E) \frac{3N - 2}{6N} \langle \delta\Phi \delta(1/K); E \rangle \tag{47}$$

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

$$\frac{\partial}{\partial T}(PV/N - T) = \frac{2c(E)}{(3NT(E))^2} \langle \delta\Phi \delta K; E \rangle + o(1). \tag{48}$$

As a final application, consider the relativistic case when the kinetic energy from above is replaced by (in units where the speed of light is one)

$$K(p) = \sum_{i=1}^N \sqrt{m_i^2 + \mathbf{p}_i^2}. \tag{49}$$

Again we write  $p = (p_1, \dots, p_i, 0, \dots, 0)$  for which

$$dH(p) = dK(p) = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{\sqrt{m_i^2 + \mathbf{p}_i^2}} \tag{50}$$

and we use the (singular) vector field,  $X = p/dK(p)$ . Then

$$\operatorname{div} X = \frac{3N - 2}{dK(p)} - \sum \frac{(\mathbf{p}_i^2)^2}{\sqrt{m_i^2 + \mathbf{p}_i^2}^3} / \left( \frac{\mathbf{p}_i^2}{\sqrt{m_i^2 + \mathbf{p}_i^2}} \right)^2 \tag{51}$$

is an observable whose average yields the  $\mu$ -temperature for the relativistic gas. The first term here has the same form as in the non-relativistic case, whereas the last gives a relativistic correction. In the zero-mass limit we obtain

$$K(p) = \sum_i |\mathbf{p}_i| = dK(p) \tag{52}$$

and the observable for the temperature (the non-relativistic constant  $3N - 2$  turns into  $3N - 3$ ):

$$\operatorname{div} X = \frac{3N - 3}{K(p)}. \tag{53}$$

The approximative formulae, (43) and (48), were previously derived by Lebowitz *et al* [8]. Pearson *et al* [9] derived these formulae as well as their exact counterparts (33), (35) and (47). In our approach we have emphasized the underlying geometrical structure of the problem and constructed a very general scheme which also applies in a straightforward manner to cases where the kinetic energy has a more complicated form as illustrated by the relativistic example, equations (51) and (53).

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