Adiabatic invariance with first integrals of motion

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(Received 11 May 2002; published 1 October 2002)

The construction of a microthermodynamic formalism for isolated systems based on the concept of adiabatic invariance is an old but seldom appreciated effort in the literature, dating back at least to P. Hertz [Ann. Phys. (Leipzig) **33**, 225 (1910)]. An apparently independent extension of such formalism for systems bearing additional first integrals of motion was recently proposed by Hans H. Rugh [Phys. Rev. E **64**, 055101 (2001)], establishing the concept of adiabatic invariance even in such singular cases. After some remarks in connection with the formalism pioneered by Hertz, it will be suggested that such an extension can incidentally explain the success of a dynamical method for computing the entropy of classical interacting fluids, at least in some potential applications where the presence of additional first integrals cannot be ignored.

DOI: 10.1103/PhysRevE.66.047101 PACS number(s): 05.20.Gg, 05.45.−a, 05.70.−a, 02.40.Vh

Consider an isolated collection of particles with f degrees of freedom evolving in time according to the usual laws of classical particle mechanics (e.g., a gas of $N=f/3$ particles inside a closed cylinder). The dynamics of this system can be uniquely described by a trajectory in the $2f$-dimensional phase space of the canonically conjugate variables $\mathbf{q}=(q_1,\ldots,q_f)$ and $\mathbf{p}=(p_1,\ldots,p_f)$. Let $H(\mathbf{q},\mathbf{p};\lambda)$ be the Hamiltonian of the system depending (for simplicity) on a single external parameter λ (e.g., the volume set by the position of the piston in the cylinder). Assume further that no other first integrals exist (see below, however). Then, for constant λ, the trajectory of the system will be confined to and will (almost) fill out the whole surface of constant energy $H(\mathbf{q},\mathbf{p};\lambda)=E_\lambda$, provided ergodicity is assumed. Consider now a process in which $\lambda=\lambda(t)$ varies very slowly in comparison to a typically small ''observation time'' τ, which in turn is a sufficiently large quantity with regard to microscopic processes, such that the time averages of phase space functions taken over it approximate the corresponding microcanonical averages at constant λ (this is an idealized instance of an otherwise precisely observed process, e.g., a reversible compression/expansion of the gas in the cylinder above). Such processes are usually referred to as *adiabatic* (though an additional *quasistatic* qualifier would be certainly very welcome), and it was shown by Hertz [1,2] that the (τ-averaged) phase space volume $\Omega(E,\lambda)$ enclosed by the surfaces of constant energy $H(\mathbf{q},\mathbf{p};\lambda)=E_\lambda$ is a conserved quantity during processes of this kind (justifying then, the label *adiabatic invariant*), much like the macroscopic entropy of Clausius under the same conditions. Thermodynamics could thus be constructed from mechanical arguments, leading directly to a microscopic form of entropy $S_\Omega=\ln\Omega$, which should be contrasted to the usual form inspired by Boltzmann's ideas involving the phase space area $\omega=\partial\Omega/\partial E$, $S_\omega=\ln\omega$, the difference between these two being particularly relevant for finite systems [3–5]. These results of Hertz were greatly appreciated by Einstein (see Ref. [6], in particular) and are often taken as the starting point of statistical mechanics in the German literature [7,8]. However, these simple and elegant observations seem to have escaped the attention of modern [9–11] and even classic [12] treatments (some rare exceptions are Refs. [13,14]). The underlying derivation is simple and accessible and thus will not be reproduced here (this so-called *ergodic adiabatic invariance* problem, however, is far from being exhausted by Hertz's original papers, being constantly addressed at different levels in the literature, see, e.g., [15–18]). It suffices to mention here that, in connecting Rugh's derivation with Hertz's results, an infinitesimal change of the parameter λ under the presence of *parameter-independent* first integrals $F_i(\mathbf{q},\mathbf{p})=I_i$ maintains straightforwardly the adiabatic conservation of the phase space volume $\Omega(E,I,\lambda)$, with $I\equiv\{I_i\}$, and thence of the entropy S_Ω, this observation following immediately from the fact that $(\partial\Omega/\partial I_i)dI_i=0$ under a change $d\lambda$ [compare, for example, Eq. (I. 236) of Ref. [7] or Eq. (34.4) in Ref. [8]]. Another important result presented in Ref. [19] was the possibility of computing the ''bulk'' temperature by means of a microcanonical (and therefore temporal) average at constant E,I, and λ, namely, $T_\Omega=\langle\mathbf{Y}\cdot\nabla H(\mathbf{Y})|E,I,\lambda\rangle$, with $\mathbf{Y}$ parallel to the surfaces $F_i(\mathbf{q},\mathbf{p})=I_i$ and satisfying $\nabla\cdot\mathbf{Y}=1$. I note in passing that a similar form of this generalized equipartition theorem was obtained by Münster [7] for the case of arbitrary cyclic coordinates present in the Hamiltonian (which when cast in terms of appropriate variables, e.g., center of mass for the conservation of linear and angular momentum or action angle for more general integrals, translates essentially into the above requirement of parallelism).

Finally, I would like to bring attention to the fact that the extension provided by Rugh of Hertz's original ideas can incidentally explain the success of the so-called adiabatic switching method [20] for computing entropies of classical interacting fluids (which is one of the very few works to make explicit use of Hertz's results), at least for the applications discussed below. This method takes full advantage of the adiabatic invariance of S_Ω by initially considering a ''reference'' system with Hamiltonian H_0 whose entropy is known explicitly (e.g., an ideal gas) and slowly turning on the interactions such that the final Hamiltonian equals the

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desired one, H_1. If this process is sufficiently slow, it can be considered as adiabatic (in the sense defined above), the phase space volume $\Omega(E,\lambda)$ (and thus the entropy S_Ω) being a conserved quantity throughout the whole switching process [24]. Therefore, a thermodynamic quantity which is not a phase space function and hence not immediately obtained by means of the usual microcanonical-temporal average [21] can be, in principle, easily computed. However, this method is usually applied in the ''molecular-dynamics ensemble'' in which the total linear momentum **P** is exactly conserved due to the use of periodic boundary conditions (see, e.g., Ref. [21], Sec. 2.10 and references therein). Such additional first integrals of motion should be carefully considered when using the Hertz invariant, since the manifold accessible to the system clearly does not coincide with the whole constant-energy surface. This fact seems to have passed unnoticed by the authors of Ref. [20], although the above observations by Rugh really give a strong theoretical support to their method. Indeed, it is easy to see that all three components of **P** are parameter independent in this case: the switching on of the internal interactions (which depend on the relative position of the particles only) clearly does not break the translational invariance of the Lagrangian. This same idea can be equally well applied to a more correct formulation of this ensemble that was only recently realized [22,23], in which three additional first integrals (the components of the center of mass **R**) are considered. It is worth emphasizing that this simple result was only possible because of the parameter independence of the integrals of motion. The opposite and more general case, however, is still an open issue, as pointed out by Rugh.

It is my pleasure to thank V. L. Berdichevsky, C. Jarzynski, and W. P. Reinhardt for the extremely fruitful correspondence. Financial support and computational resources were provided by Dartmouth College and its Field Theory/Cosmology group, respectively.

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[24] Although the use of an ideal system is incompatible with ergodicity and thus, in principle, should prevent the method from working, surprisingly neither ergodic time-scales nor ergodicity itself seems to be essential, suggesting that the latter is not a necessary but rather a sufficient condition for its success [20].