PHYSICAL REVIEW E VOLUME 62, NUMBER 2 AUGUST 2000

Canonical deformations of surfaces of equilibrium states in thermodynamic phase space

Jacek Jurkowski*
Institute of Physics, Nicholas Copernicus University, Grudziądzka 5, 87-100 Toruń, Poland

(Received 9 December 1999)

Deformations of submanifolds of thermodynamic equilibrium states introduced by continuous contact maps on a phase-space manifold are considered in terms of the geometrical formulation of thermodynamics. The notion of a contact Hamiltonian is recalled in order to give some possible physical interpretations of such a function in terms of statistical quantities describing initial and deformed systems. Using contact flows we propose a very efficient method for constructing continuous families of thermodynamic systems. A few examples show the possible advantages of using contact Hamiltonians.

PACS number(s): 05.70.−a, 05.90.+m, 95.30.Tg

I. INTRODUCTION

For the last 25 years there has been growing interest in the application of methods of differential geometry in statistical physics and thermodynamics. The geometrical treatment is represented by two main lines of investigation: one according to the metric and the other according to the contact structure of thermodynamic phase space. The metric structure was phenomenologically introduced by Weinhold [1] whereas Ruppeiner [2] derived the form of the metric tensor from fluctuation theory working in an entropy representation of the fundamental relation. Using the metric tensor many authors have been able to calculate the scalar curvature for some statistical and thermodynamic models, and to investigate two hypotheses that immediately appeared concerning the connection between metric and physical quantities [3–6]. Ruppeiner put forward the idea that curvature is proportional to the inverse of the free energy of the system whereas Janyszek [5] proposed that the scalar curvature is divergent near critical points and, due to its connection with the second and third moments of fluctuation, can measure the stability of the system. Both hypotheses have been studied for a wide class of systems [3,4] including the van der Waals model [5,6], quantum gases [7], and model magnetic systems [8].

In 1973 Herman [9] suggested that the most suitable structure for classical thermodynamics is that of an odd-dimensional space endowed with the contact structure [10,11]. In [12] it was shown that both metric and contact structures have their origin in a statistical quantity called the microscopic entropy $\mathcal{S}=-\ln\rho$, where ρ is a representative distribution in mechanical phase space for a macrostate generated by fixed mean values of an ensemble of n observables, $\mathcal{F}^i$. The contact structure is related then to the mean value of a differential $\langle ds\rangle$ and the metric structure to the variance $\langle(ds-\langle ds\rangle)^2\rangle$, where $\langle\cdots\rangle$ denotes the statistical average. Both structures are independent but essential in the formulation of the laws of thermodynamics. Introducing a thermodynamic phase space naturally endowed with the contact structure, one obtains a reinterpretation of the set of equilibrium states in terms of an integral submanifold of a Pfaff equation for a contact form, a description for quasistatic thermodynamic processes in the language of contact transformations and vector fields [10], and the possibility of deformations of an equilibrium submanifold using contact tools [10,13]. Let us also mention that there exist many similarities in the structure of contact and symplectic (or Poisson) manifolds which allow one to describe dynamical systems and thermodynamics in the common language of differential geometry.

In this paper, we investigate only one of the many subjects mentioned above, concerning deformations of the set of equilibrium states (the equilibrium submanifold). In some sense the deformations are canonical, i.e., they naturally appear when the contact structure and contact transformations are assumed to act on thermodynamic phase space. In other words, we deal with deformations introduced by the contact flow. We show that, if there are two surfaces of equilibrium states for two different systems located in the same thermodynamic phase space, there exists a contact transformation that deforms one into the other. As an initial system (in the sense of evolution in thermodynamic phase space), we will choose statistical models of noninteracting particles or spins and we will deform them into systems with inner interactions (Sec. IV). But due to Theorem 1 below the initial and final systems can be chosen freely.

To prepare for the introduction of Theorem 1 in Sec. III, which turns out to be useful in the construction of deformations using contact flow, let us recall some basics of contact geometry. A more comprehensive discussion of contact geometry can be found in [14,15,12].

The contact structure is introduced on the odd-dimensional thermodynamic phase space $\mathcal{P}$ by a differential one-form Θ, called the contact form, satisfying the nondegeneracy condition

$$\Theta\wedge(d\Theta)^n\neq 0. \tag{1.1}$$

According to the Darboux theorem there exists a coordinate system $(x^0,x^1,\ldots,x^n,p_1,\ldots,p_n)$ (contact coordinates) in which the contact one-form Θ has the following form:

$$\Theta=dx^0+p_i dx^i. \tag{1.2}$$

On such a contact manifold one can introduce the contact transformation $\varphi:\mathcal{P}\rightarrow\mathcal{P}$ as a map preserving the contact one-form up to multiplication by a function

---

*Email address: jacekj@phys.uni.torun.pl

1063-651X/2000/62(2)/1790(9)/$15.00

$$\varphi^*\Theta=\lambda\Theta, \tag{1.3}$$

where the asterisk denotes pull-back [16] of the form and λ is a nowhere-vanishing function on $\mathcal{P}$. It is natural to investigate the case of one-parameter groups of contact transformations that are generated by vector fields. More precisely, let $\varphi_t:\mathcal{P}\to\mathcal{P}$ be such a map $(\varphi_t^*\Theta=\lambda_t\Theta)$; by the generator of this one-parameter group of contact transformations we mean a vector field X given by

$$X(p)=\left.\frac{d}{dt}\right|_{t=0}\varphi_t(p)\quad\text{for}\quad\varphi_0(p)=p, \tag{1.4}$$

i.e., the vector field tangent to the trajectory $\varphi_t(p)$ at any point $p\in\mathcal{P}$. It is easy to verify that if $\varphi_t^*\Theta=\lambda_t\Theta$ then

$$L_X\Theta=\frac{d}{dt}\lambda_t\Theta=\dot{\lambda}_t\Theta, \tag{1.5}$$

where L_X is the Lie derivative. We call the vector fields satisfying Eq. (1.5) contact vector fields.

We once again return to the fact that the odd-dimensional thermodynamic phase space endowed with the contact structure has many features similar to those of an even-dimensional mechanical phase space. Among them, the existence of vector fields that correspond to smooth, scalar functions is most useful for our purpose. Let us define the Reeb vector field ξ by

$$\begin{aligned} i_\xi d\Theta&=0,\\ i_\xi\Theta&=1. \end{aligned} \tag{1.6}$$

Then it is easy to check that a vector field X_f given by

$$\begin{aligned} i_{X_f}d\Theta&=-df+\xi(f)\Theta,\\ i_{X_f}\Theta&=f, \end{aligned} \tag{1.7}$$

where i_{X_f} is the contraction of a differential form with the vector field X_f, fulfills the relation

$$L_{X_f}\Theta=\xi(f)\Theta. \tag{1.8}$$

Due to Eq. (1.5) this means that this field generates the contact transformation. As in mechanics, f is called the contact Hamiltonian, although it has nothing to do with the notion of energy. f plays only the role of a generating function for the contact vector field X_f.

Because contact deformations are due to contact flows we emphasize the role of contact Hamiltonians, which will generate further objects (Sec. III). For example, from Eqs. (1.7) and (1.2) we deduce that the contact field X_f generated by the contact Hamiltonian f has the following form in contact coordinates:

$$X_f=\left(f-p_i\frac{\partial f}{\partial p_i}\right)\frac{\partial}{\partial x^0}+\left(p_i\frac{\partial f}{\partial x^0}-\frac{\partial f}{\partial x^i}\right)\frac{\partial}{\partial p_i}+\frac{\partial f}{\partial p_i}\,\frac{\partial}{\partial x^i}. \tag{1.9}$$

Note that if x^0 were absent then the relation (1.9) would reduce to the well-known formula for the Hamiltonian vector field in mechanics.

The scope of this paper is also to give a physical interpretation to contact Hamiltonians that provide deformations as well as to show possible applications and advantages that occur while dealing with such contact transformations. With this aim, in Sec. III we formulate Theorem 1, which is a powerful tool for the discussion of the thermodynamic meaning of the contact Hamiltonian. It turns out that in some cases such a contact Hamiltonian remains in close connection with statistical quantities describing both systems. This enables us to give an explicit formula for the contact Hamiltonian when the initial and final systems are given and to produce some thermodynamic systems. When the systems are described in terms of the canonical ensemble, it is possible to give the relation between the contact Hamiltonian and statistical Hamiltonians of both the initial and the final systems. In this case, the contact Hamiltonian ''measures'' how much the statistical Hamiltonians differ as a consequence of, for example, the difference between potentials of particle interactions in both systems.

II. SUBMANIFOLDS OF EQUILIBRIUM STATES

The equilibrium states of a thermodynamic system, described in an appropriately chosen phase space $\mathcal{P}$, are located on some subspaces of $\mathcal{P}$. The subspaces, which are called Legendre submanifolds, have dimension equal to n [16,14]. In [14] a theorem is proved that gives the local description of such submanifolds. We recall that for any disjoint partition $I\cup J$ of the set of indices $\{1,\ldots,n\}$ and for a function $\Phi(x^J,p_I)$ of n variables x^j, $j\in J$, p_i, $i\in I$, the $n+1$ equations

$$p_J=-\frac{\partial\Phi}{\partial x^J},\quad x^I=\frac{\partial\Phi}{\partial p_I},\quad x^0=\Phi-p_I\frac{\partial\Phi}{\partial p_I} \tag{2.1}$$

define a Legendre submanifold $\mathcal{L}$ of $\mathcal{P}$. Conversely, every Legendre submanifold of $\mathcal{P}$ is defined in the neighborhood of every point by such equations for at least one of the 2^n possible choices of the subset I. We call Φ the function generating the Legendre submanifold $\mathcal{L}$.

Suppose that we are given a submanifold of equilibrium states $\mathcal{L}$ and a function f generating contact vector field X_f whose integral curve through a point $p\in\mathcal{L}$ is $\varphi_t(p)$. There are two possibilities: either the curve $\varphi_t(p)$ stays on $\mathcal{L}$ for all t, i.e., the vector field X_f is tangent to the submanifold of equilibrium states $\mathcal{L}$, or the curve leaves the subspace $\mathcal{L}$. In the first case, the trajectory goes through equilibrium states of the system and it can sometimes be interpreted as a quasistatic process which changes the equilibrium states [17,10]. It can be proved that X_f is tangent to $\mathcal{L}$ if and only if f vanishes on $\mathcal{L}$, i.e., $\mathcal{L}\subset f^{-1}(0)$ [10]. In the second case, X_f introduces a dynamic flow that deforms the submanifold of equilibrium states continuously and takes it into another such submanifold. This case is of great interest for our paper.

One can also state the inverse problem [18], which in this context means that we look for a function f when two submanifolds of equilibrium states, the initial $\mathcal{L}_0$ and the final $\mathcal{L}_1$, are given, so that the flow generated by X_f transforms

$\mathcal{L}_0$ into $\mathcal{L}_1$. The inverse problem in thermodynamics in a simpler case was investigated in [17]. Now we want to give an explicit expression for the contact Hamiltonian f in terms of $\Phi_{(0)}$ and $\Phi_{(1)}$—the functions that generate the submanifolds $\mathcal{L}_0$ and $\mathcal{L}_1$, respectively.

III. THE CONTACT HAMILTONIAN

In this section, we formulate a theorem that connects the contact Hamiltonian deforming the initial submanifold $\mathcal{L}_0$ into the final $\mathcal{L}_1$ with functions $\Phi_{(0)}$ and $\Phi_{(1)}$ generating $\mathcal{L}_0$ and $\mathcal{L}_1$, respectively. We use the notation of Theorem 1 below, i.e., x^J and p_I are the independent variables. We recall that I and J are disjoint subsets of $I\cup J=\{1,\dots,n\}$ and x^J, p_I denote the sets $\{x^j,\ j\in J\}$ and $\{p_i,\ i\in I\}$, respectively. The remaining variables x^I, p_J, and x^0 are functions of the independent ones. The whole set of $2n+1$ variables (x^0,x^J,x^I,p_I,p_J) builds up the thermodynamic phase space $\mathcal{P}$.

Following [19], we formulate our main theorem.

Theorem 1. Let $\mathcal{L}_0$ and $\mathcal{L}_1$ be two Legendre submanifolds given by the generating functions $\Phi_{(0)}(x^J,p_I)$ and $\Phi_{(1)}\times(x^J,p_I)$, respectively. Then

$$f(x^J,p_I)=\Phi_{(1)}(x^J,p_I)-\Phi_{(0)}(x^J,p_I) \tag{3.1}$$

is the contact Hamiltonian generating the vector field, the integral curves of which transform the submanifold $\mathcal{L}_0$ for $t=0$ into $\mathcal{L}_1$ for $t=1$. $t\in[0,1]$ is the parameter of the integral curve.

The proof goes as follows. From Eq. (1.9), remembering that f depends only on (x^J,p_I), we get the following evolution equations for the whole set of variables:

$$\dot{x}^0=f-p_I\frac{\partial f}{\partial p_I},$$

$$\dot{p}_J=-\frac{\partial f}{\partial x^J},\quad \dot{p}_I=0, \tag{3.2}$$

$$\dot{x}^I=\frac{\partial f}{\partial p_I},\quad \dot{x}^J=0.$$

We see immediately that p_I and x^J do not evolve and remain constant. On the other hand, due to Eq. (2.1), we can write out parametric equations for the submanifolds in the case when the generating functions $\Phi_{(0)}$ and $\Phi_{(1)}$ depend on (x^J,p_I):

$$p_J^{(k)}=-\frac{\partial\Phi_{(k)}}{\partial x^J},\quad x^I_{(k)}=\frac{\partial\Phi_{(k)}}{\partial p_I},$$
$$x^0_{(k)}=\Phi_{(k)}-p_I\frac{\partial\Phi_{(k)}}{\partial p_I},\quad k=0,1, \tag{3.3}$$

where the subscript k refers to the system $\mathcal{L}_0$ or $\mathcal{L}_1$. Let us turn back to Eq. (3.2). The calculation of $\dot{x}^0$ by use of Eqs. (3.3) and (3.1) gives

$$\begin{aligned}\dot{x}^0&=f-p_I\frac{\partial f}{\partial p_I}=\Phi_{(1)}-\Phi_{(0)}-p_I\left(\frac{\partial\Phi_{(1)}}{\partial p_I}-\frac{\partial\Phi_{(0)}}{\partial p_I}\right)\\&=\Phi_{(1)}-\Phi_{(0)}+x^0_{(1)}-\Phi_{(1)}+\Phi_{(0)}-x^0_{(0)}=x^0_{(1)}-x^0_{(0)}.\end{aligned} \tag{3.4}$$

Both $x^0_{(1)}$ and $x^0_{(0)}$ depend only on (x^J,p_I), which stay constant during the evolution, and that is why we can integrate Eq. (3.4). The resulting evolution for x^0, taking into account the initial condition $x^0(0)=x^0_{(0)}$, is

$$x^0(t)=(x^0_{(1)}-x^0_{(0)})t+x^0_{(0)}. \tag{3.5}$$

In an analogous way we get

$$p_J(t)=(p_J^{(1)}-p_J^{(0)})t+p_J^{(0)}, \tag{3.6}$$

$$x^I(t)=(x^I_{(1)}-x^I_{(0)})t+x^I_{(0)}. \tag{3.7}$$

The above equations complete the proof because it is obvious that $x^0(1)=x^0_{(1)}$, $p_J(1)=p_J^{(1)}$, $x^I(1)=x^I_{(1)}$, and the evolution generated by X_f with f of the form (3.1) transforms the submanifold of equilibrium states of the initial system into that of the final system.

Once the Hamiltonian (3.1) is obtained, we can use it to construct a continuous family of thermodynamic systems given by generating functions

$$\Phi_{(t)}(x^J,p_I)=x^0(t)+p_Ix^I(t), \tag{3.8}$$

where $x^0(t)$ and $x^I(t)$ are given by Eqs. (3.5) and (3.7), respectively. We would expect that the systems would possess ''intermediate'' properties in comparison to the initial and final systems, but this will be the subject of further investigation. As an illustration of the considerations above, at the end of Example 1 in Sec. IV we construct a continuous family of van der Waals–like systems different from that obtained in [10].

IV. CONNECTIONS WITH STATISTICAL THERMODYNAMICS

In this section, we give a physical interpretation of the contact Hamiltonian that transforms one submanifold of equilibrium states into another, showing that it can be associated with statistical quantities describing the initial and final systems. Let us imagine that there is a continuum of systems at our disposal which we can pass through during the transformation from the initial (first) system to the final (deformed) one.

A. Nonideal gas models

Let us first work in a five-dimensional phase space $\mathcal{P}$ locally described by thermodynamic variables $(x^0,x^1,x^2,p_1,p_2)=(U,V,S,p,-T)$, where U, V, S, p, and T stand for energy, volume, entropy, pressure, and temperature, respectively. In such coordinates one can calculate from Eq. (1.9) that the function $f(U,V,S,p,T)$ generates a vector field of the form

$$X_f=\left(f-p\frac{\partial f}{\partial p}-T\frac{\partial f}{\partial T}\right)\frac{\partial}{\partial U}+\frac{\partial f}{\partial p}\frac{\partial}{\partial V}-\frac{\partial f}{\partial T}\frac{\partial}{\partial S}+\left(p\frac{\partial f}{\partial U}-\frac{\partial f}{\partial V}\right)\frac{\partial}{\partial p}+\left(T\frac{\partial f}{\partial U}+\frac{\partial f}{\partial S}\right)\frac{\partial}{\partial T}. \tag{4.1}$$

In order to give some physical meaning to both functions f and Φ let us first choose the function generating the submanifold of equilibrium states as

$$\Phi(T,V;N)=-kT\ln Z(T,V;N), \tag{4.2}$$

where k is the Boltzmann constant and $Z(T,V;N)$ is the partition function of the N-particle system. (At this point we consider N as a parameter, not a variable.) (T, V) are chosen to be independent variables, because in such a case we can imagine that the partition function originates from the canonical ensemble for a system described by the dynamical Hamiltonian $\mathcal{H}(\mathbf{q},\mathbf{p})$, where $(\mathbf{q},\mathbf{p})$ denote all the $2N$ dynamical phase-space variables,

$$Z(T,V,N)=\frac{1}{h^{3N}N!}\int_{\Omega_V}\exp\left(-\frac{\mathcal{H}(\mathbf{q},\mathbf{p})}{kT}\right)d\mathbf{q}\,d\mathbf{p}, \tag{4.3}$$

where the integration runs over the dynamical phase space Ω_V. $\Phi(T,V;N)$ is then the Helmholtz thermodynamic potential.

Using Theorem 1, we can give a statistical interpretation to the contact Hamiltonian. Indeed, let $Z_0(T,V;N)$ and $Z_1(T,V;N)$ be two partition functions of the initial and final systems, respectively; then from Eq. (3.1) we get

$$f(T,V;N)=\Phi_{(1)}(T,V;N)-\Phi_{(0)}(T,V;N)=-kT\ln\frac{Z_1(T,V;N)}{Z_0(T,V;N)}. \tag{4.4}$$

The contact Hamiltonian turns out to be in a simple relation with the ratio of partition functions of the final and initial systems. When we want to change the initial or the final system we must simply reparametrize curves generated by X_f. Let us stress that we want the partition function or thermodynamics potentials to play a crucial role in the theory and their origin is less important. Let us give a few examples.

Example 1: Deformation of an ideal gas into the van der Waals model

In this example, we calculate the function f that generates the deformation of an ideal gas into the van der Waals gas and show how the contact field transforms thermodynamic variables and relations. We use the appropriate partition functions [20]

$$Z_0(T,V;N)=\frac{V^N}{N!}\left(\frac{2m\pi kT}{h^2}\right)^{3N/2}, \tag{4.5}$$

$$Z_1(T,V;N)=\frac{(V-Nb)^N}{N!}\left(\frac{2m\pi kT}{h^2}\right)^{3N/2}\exp\left(\frac{aN^2}{VkT}\right), \tag{4.6}$$

where m is the mass of the particle, a, b are the van der Waals parameters, and h is the Planck constant. Then using Eq. (4.4) we get

$$f(T,V;N)=-NkT\ln\frac{V-Nb}{V}-\frac{aN^2}{V}. \tag{4.7}$$

The contact Hamiltonian (4.7) produces the vector field

$$\begin{aligned}\dot U&=-\frac{aN^2}{V},\\ \dot V&=0,\\ \dot S&=Nk\ln\frac{V-Nb}{V},\\ \dot p&=\frac{N^2kTb}{V(V-Nb)}-\frac{N^2a}{V^2},\\ \dot T&=0.\end{aligned} \tag{4.8}$$

The solution of the above set of equations leads, according to Theorem 1, to the following thermodynamic relations for the van der Waals gas:

$$\begin{aligned}U_1&=U(1)=U_0-\frac{aN^2}{V_1}=\frac{3}{2}NkT_1-\frac{aN^2}{V_1},\\ V_1&=V(1)=V_0,\\ S_1&=S(1)=S_0+Nk\ln\frac{V_1-Nb}{V_1}\\ &=\tfrac{3}{2}Nk+k\ln\left[\frac{(V_1-Nb)^N}{N!}\left(\frac{2m\pi kT_1}{h^2}\right)^{3N/2}\right],\\ p_1&=p(1)=p_0+\frac{N^2kT_1b}{V_1(V_1-Nb)}-\frac{N^2a}{V_1^2}=\frac{NkT_1}{V_1-Nb}-\frac{N^2a}{V_1},\\ T_1&=T(1)=T_0,\end{aligned}$$

where the initial values $(U_0,V_0,S_0,p_0,-T_0)$ fulfill the relations

$$\begin{aligned}U_0&=\tfrac{3}{2}NkT_0,\\ S_0&=\tfrac{3}{2}Nk+k\ln\left[\frac{V_0^N}{N!}\left(\frac{2m\pi kT_0}{h^2}\right)^{3N/2}\right],\\ p_0V_0&=NkT_0,\end{aligned} \tag{4.9}$$

valid for the ideal gas. Let us stress, in particular, that the equation for p_1 reproduces the standard van der Waals equation of state,

$$\left(p_1+\frac{aN^2}{V_1^2}\right)(V_1-Nb)=NkT_1.$$

In what follows, we will omit the subscript 1, keeping in mind that all thermodynamic quantities for the final system are evaluated at $t=1$.

Using the flow of the contact field (4.8), we are able to transform not only thermodynamic variables but also relations including them. For example, it is easy to map the specific heat

$$c_V = T\left(\frac{\partial S}{\partial T}\right)_V. \tag{4.10}$$

Indeed, Eq. (4.10) differentiated in t leads to

$$\dot{c}_V = T\left(\frac{\partial \dot{S}}{\partial T}\right)_V = T\left(\frac{\partial}{\partial T} Nk \ln \frac{V-Nb}{V}\right)_V = 0, \tag{4.11}$$

and we conclude that c_V remains constant during the evolution. The value of c_V is then the same as for the ideal gas and equals $\frac{3}{2}Nk$.

According to Eq. (3.8) we get a continuous family of van der Waals-like systems described by the partition functions

$$Z_{(t)}(T,V;N) = \frac{V^{N(1-t)}(V-Nb)^{Nt}}{N!}\left(\frac{2m\pi kT}{h^2}\right)^{3N/2} \exp\left(\frac{atN^2}{kTV}\right),$$

which lead to the equations of state

$$U = \tfrac{3}{2}NkT - \frac{taN^2}{V},$$

$$\left(p + \frac{N^2at}{V^2}\right)(V-Nb) = NkT\left(1 + \frac{Nb}{V}(t-1)\right).$$

The first one represents the slightly modified energy of the van der Waals model while the second introduces corrections to the van der Waals pVT equation.

Example 2: Deformation into a nonideal gas

This example concerns the contact flow that introduces a deformation of an equilibrium submanifold of the ideal gas into an appropriate submanifold of the gas of N interacting particles.

Let us assume that a mechanical Hamiltonian describing the system,

$$\mathcal{H}_N = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + \sum_{i<j} V(|\mathbf{q}_i - \mathbf{q}_j|), \tag{4.12}$$

contains a two-particle potential V dependent only on distances between particles. It is easy to show by calculating the partition function (4.3) with the Hamiltonian (4.12) that

$$Z(T,V;N) = Z_0(T,V;N)\,Q_N(T,V),$$

where $Z_0(T,V;N)$ is the canonical partition function (4.5) and $Q_N(T,V)$ is a configuration integral,

$$Q_N(T,V) = \frac{1}{V^N}\int_{V^N \subset \mathbb{R}^{3N}} \exp\left(-\frac{1}{kT}\sum_{i<k} V(|\mathbf{q}_i - \mathbf{q}_k|)\right) \times d\mathbf{q}_1 \cdots d\mathbf{q}_N, \tag{4.13}$$

which contains all information about the interaction. Due to Eq. (4.4) the contact Hamiltonian that transforms the Legendre submanifold of an ideal gas into the equilibrium submanifold of a gas with interacting particles takes the form

$$f(T,V;N) = -kT \ln \frac{Z(T,V;N)}{Z_0(T,V;N)} = -kT \ln Q_N(T,V). \tag{4.14}$$

What remains is to determine $Q_N(T,V)$. To this end, let us assume that particles behave like hard balls and the interaction potential has a cutoff at the distance d. Moreover, we take into account rare gases so that the probability of a simultaneous collision of three or more particles is negligible. These assumptions imply that the configuration integral is [21]

$$Q_N(T,V) = \prod_{r=1}^{N} \left(1 + (r-1)\frac{a(T)}{V}\right), \tag{4.15}$$

where

$$a(T) = \int_0^d 4\pi q^2 \left(e^{-V(q)/kT} - 1\right) dq. \tag{4.16}$$

Because of Eq. (4.14) the contact Hamiltonian turns out to be

$$f(T,V;N) = -kT \sum_{r=1}^{N} \ln\left(1 + (r-1)\frac{a(T)}{V}\right). \tag{4.17}$$

If $(N/V)a(T) \ll 1$ for the whole temperature interval is assumed, then

$$\begin{aligned} f(T,V;N) &= -kT\frac{a(T)}{V}\sum_{r=1}^{N}(r-1) \\ &= -kT\frac{a(T)}{V}\frac{N-1}{2}N \\ &\cong -kT\frac{a(T)}{V}\frac{N^2}{2}. \end{aligned}$$

The function $f(T,V;N)$ generates the following vector field [see Eq. (4.1)]:

$$\dot{U} = \frac{kT^2N^2}{2V}a'(T),$$

$$\dot{V} = 0,$$

$$\dot{S} = \frac{kN^2}{2V}[a(T) + Ta'(T)] = \frac{kN^2}{2V}\frac{d}{dT}[Ta(T)],$$

$$\dot{p} = -\frac{kTN^2}{2V^2}a(T),$$

$$\dot{T}=0.$$

Because of Eq. (4.9) we get the set of thermodynamic relations for the final system,

$$U=\tfrac{3}{2}NkT+\frac{kT^2N^2}{2V}a'(T),$$

$$S=\tfrac{3}{2}Nk+k\ln\left[\frac{V^N}{N!}\left(\frac{2m\pi kT}{h^2}\right)^{3N/2}\right]+\frac{kN^2}{2V}\frac{d}{dT}[Ta(T)],$$

$$p=\frac{NKT}{V}-\frac{kTN^2}{2V^2}a(T)=\frac{NkT}{V}\left(1-\frac{N}{2V}a(T)\right),$$

where we omit the subscript 1. Let us stress that the equation for p has the well-known form of a virial expansion,

$$\frac{p}{kT}=\frac{N}{V}\left[1-\frac{1}{2}\left(\frac{N}{V}\right)a(T)\right].$$

Similarly to Eq. (4.11), we are able to calculate the relation for c_V for the final system,

$$\dot{c}_V=T\left(\frac{\partial\dot{S}}{\partial T}\right)_V=T\frac{kN^2}{2V}\frac{d^2}{dT^2}[Ta(T)],$$

which gives, after integration, the formula

$$c_V=\tfrac{3}{2}Nk+\frac{kN^2}{2V}T\frac{d^2}{dT^2}[Ta(T)],$$

where $\frac{3}{2}Nk$ originates from the initial condition and corresponds to the value of c_V for an ideal gas.

The same considerations as in Example 1 can be applied when we choose as variables the thermodynamic densities $u=U/N$, $v=V/N$, and $s=S/N$, i.e., we parametrize thermodynamic phase space by $(u,v,s,p,-T)$. When we select (v,T) as independent variables and consider the free energy per particle $\phi(v,T)$ as a generating function, it is immediately clear that such a model is suitable to describe statistical systems in the thermodynamic limit $N\rightarrow\infty$ while $v=V/N$ remains constant. Suppose that the system has $Z(V,T;N)$ as a partition function. Then

$$\phi(v,T)=-kT\lim_{N\rightarrow\infty}\frac{1}{N}\ln Z(V,T;N). \tag{4.18}$$

Theorem 1 implies that the contact Hamiltonian deforming the initial submanifold into the final one has the form

$$f(v,T)=\Phi_{(1)}(v,T)-\phi_0(v,T).$$

Example 3: van der Waals model in the thermodynamic limit

Using Eqs. (4.5) and (4.6) for the calculation of the free energy (4.18) in the thermodynamic limit we obtain the following contact Hamiltonian:

$$f(v,T)=-kT\ln\frac{v-b}{v}-\frac{a}{v}.$$

As in Eq. (4.8) we get the contact field and thermodynamic relations for the van der Waals gas,

$$\dot{u}=-\frac{a}{v},\quad u=u_0-\frac{a}{v_0},$$

$$\dot{v}=0,\quad v=v_0,$$

$$\dot{s}=k\ln\frac{v-b}{v},\quad s=s_0+k\ln\frac{v_0-b}{v_0},$$

$$\dot{p}=\frac{kTb}{v(v-b)}-\frac{a}{v^2},\quad p=p_0+\left(\frac{kT_0b}{v_0(v_0-b)}-\frac{a}{v_0^2}\right),$$

$$\dot{T}=0,\quad T=T_0,$$

where (u_0,v_0,s_0,p_0,T_0) represent the initial conditions of the dynamics. Again we conclude that the thermodynamic relations for the van der Waals gas are reproduced.

B. Spin systems

Any other choice of independent variables in Z consistent with Theorem 1 can be made; in particular, magnetic systems can be taken into account. As an illustration we recall two magnetic systems, the one-dimensional Ising model and the Curie-Weiss model, for which partition functions are known [22,23]. The appropriate thermodynamic phase space is similar to that previously used, where one changes the contact variable $p\rightarrow-H$ (magnetic field intensity) and $v\rightarrow m$ (magnetization), i.e., we assume a contact vector field of the form

$$X_f=\left(f-H\frac{\partial f}{\partial H}-T\frac{\partial f}{\partial T}\right)\frac{\partial}{\partial u}-\frac{\partial f}{\partial H}\frac{\partial}{\partial m}-\frac{\partial f}{\partial T}\frac{\partial}{\partial s}+\left(H\frac{\partial f}{\partial u}-\frac{\partial f}{\partial m}\right)\frac{\partial}{\partial H}+\left(T\frac{\partial f}{\partial u}+\frac{\partial f}{\partial s}\right)\frac{\partial}{\partial T}. \tag{4.19}$$

As a generating function we use the Gibbs thermodynamic potential per spin,

$$\mathbf{f}(H,T)=-kT\lim_{N\rightarrow\infty}\frac{1}{N}\ln Z(H,T;N), \tag{4.20}$$

which implies according to Theorem 1 that the contact Hamiltonian is

$$f(H,T)=\mathbf{f}_{(1)}(H,T)-\mathbf{f}_{(0)}(H,T), \tag{4.21}$$

where the contact flow deforms the initial submanifold of the system of noninteracting spins (but interacting with the external magnetic field) into a system of spins where interactions are present.

Example 4: Short interaction model

Let us consider first the case of a one-dimensional cyclic spin chain in a magnetic field of intensity H, where each spin interacts with its nearest neighbors (the Ising model). We denote by J the parameter of interaction and assume the Gibbs potential in the following form [22]:

$$\mathbf{f}(H,T)=-J-kT\ln\left(\cosh\left(\frac{H}{kT}\right)+\sqrt{\cosh^2(H/kT)-2e^{-2J/kT}\sinh(2J/kT)}\right),$$

which simplifies for noninteracting spins to

$$\mathbf{f}_{(0)}(H,T)=-kT\ln[2\cosh(H/kT)].$$

Due to Eq. (4.21) the contact Hamiltonian turns out to be

$$f(H,T)=-J-kT\ln\left(\frac{1}{2}+\frac{1}{2}\times\frac{\sqrt{\cosh^2(H/kT)-2e^{-2J/kT}\sinh(2J/kT)}}{\cosh(H/kT)}\right). \tag{4.22}$$

The integral curve of the vector field (4.19) passing through a point (u_0,s_0,T_0,H_0,m_0) has the form

$$u(t)=u_0+\left(f-H\frac{\partial f}{\partial H}-T\frac{\partial f}{\partial T}\right)t,$$

$$s(t)=s_0-\frac{\partial f}{\partial T}t,$$

$$T(t)=T_0,$$

$$H(t)=H_0,$$

$$m(t)=m_0-\frac{\partial f}{\partial H}t. \tag{4.23}$$

Because of the complicated form of the partial differentials of f, we explicitly give only the relation for magnetization at $t=1$. Taking into account that for noninteracting spins $m_0=\tanh(H/kT)$, we get

$$m(H,T)=\frac{\sinh(H/kT)}{\sqrt{\cosh^2(H/kT)-2e^{-2J/kT}\sinh(2J/kT)}}. \tag{4.24}$$

Using Eq. (4.22) we can easily obtain the magnetic susceptibility per spin,

$$\chi(H,T)=\frac{\partial m(H,T)}{\partial H},$$

transforming it from the noninteracting system. Indeed, according to $T=\text{const}$, $H=\text{const}$, and taking the differential of t in the last equation, we get

$$\dot{\chi}(H,T)=\frac{\partial \dot{m}(H,T)}{\partial H}=-\frac{\partial^2 f}{\partial H^2}.$$

Keeping in mind the initial condition $\chi(0)=\chi_0(H,T)=[\cosh^2(H/kT)]^{-1}$, one can obtain

$$\chi(H,T)=-\frac{\cosh(H/kT)[2e^{-2J/kT}\sinh(2J/kT)-1]}{kT[\cosh^2(H/kT)-2e^{-2J/kT}\sinh(2J/kT)]^{3/2}},$$

which is in agreement with relations one gets using statistical methods.

Example 5: Long interaction model

This example concerns the contact Hamiltonian that generates the flow transforming the Legendre submanifold of noninteracting spins into the set of equilibrium states of the Curie-Weiss model. Let us assume that spins are located on a lattice and each spin interacts with the mean field generated by other spins. We describe the system by the spin Hamiltonian [22]

$$\mathcal{H}(\mathbf{s})=-\frac{J}{N}\sum_{1\leqslant i<j\leqslant N}s_is_j-H\sum_{i=1}^{N}s_i,$$

where $\mathbf{s}=(s_1,\ldots,s_N)$ denotes the spin configuration of N particles. It can be shown [22] that the Gibbs function per spin $\mathbf{f}(\beta,H)$ $[\beta=(kT)^{-1}]$ in the thermodynamic limit takes the form

$$\mathbf{f}(\beta,H)=-\frac{1}{\beta}[\ln 2-\tfrac{1}{2}\beta J\eta_0^2+\ln\cosh(\beta J\eta_0+\beta H)], \tag{4.25}$$

where η_0 is the greatest solution of the equation

$$\eta_0=\tanh(\beta J\eta_0+\beta H). \tag{4.26}$$

In the case of $H=0$ it is well known that Eq. (4.26) has only one solution $\eta_0=0$ for $\beta<\beta_c=1/J$, i.e., above the critical temperature, and three solutions for $\beta>\beta_c$, but only the greatest one that is nonzero maximizes the Gibbs function (4.25). Such a phenomenon is called a phase transition. In the case of nonzero intensity of the magnetic field there can be 1–3 solutions, but there always exists a positive solution which, as is suggested by numerical simulations, maximizes the Gibbs function. There is no phase transition in the system.

These considerations allow us to deduce that there is a single function $\mathbf{f}(\beta,H)$ that generates the submanifold of equilibrium states as long as the magnetic intensity is nonzero, and there are two such functions when $H=0$. Keeping that in mind, we can give the contact Hamiltonian,

$$f(T,H,\eta_0(T,H))=\tfrac{1}{2}J\eta_0^2(T,H)-kT\ln\times\frac{\cosh[J/kT\,\eta_0(T,H)+H/kT]}{\cosh(H/kT)}, \tag{4.27}$$

where we take into account that the Gibbs function for noninteracting spins has the form $\mathbf{f}_{(0)}(T,H)=-kT[\ln 2+\ln\cosh(H/kT)]$. The analytical form of $\eta_0=\eta_0(T,H)$ is, of course, unknown, but in spite of that we can calculate the magnetization. According to Eq. (4.23) we should calculate $\partial f/\partial H$ but now $f=f(T,H,\eta_0(T,H))$ is a composite function of T and we are obliged to modify Eq. (4.23),

$$m(t)=m_0-\frac{df}{dH}t=m_0-\left(\frac{\partial f}{\partial H}+\frac{\partial f}{\partial \eta_0}\frac{\partial \eta_0}{\partial H}\right)t.$$

Since

$$\frac{\partial f}{\partial \eta_0}=\frac{\partial \mathbf{f}}{\partial \eta_0}-\frac{\partial \mathbf{f}_{(0)}}{\partial \eta_0}=\frac{\partial \mathbf{f}}{\partial \eta_0}=0,$$

we finally get

$$\begin{aligned}
m&=m_0-\frac{\partial f}{\partial H}\\
&=\tanh(\beta H)-\frac{\partial}{\partial H}\left(\frac{1}{2}J\eta_0^2-\frac{1}{\beta}\ln\cosh(\beta J\eta_0+\beta H)\right.\\
&\qquad\left.+\frac{1}{\beta}\ln\cosh(\beta H)\right)\\
&=\tanh(\beta H)+\tanh(\beta J\eta_0+\beta H)-\tanh(\beta H)\\
&=\tanh(\beta J\eta_0+\beta H)=\eta_0 .
\end{aligned}$$

Example 6: Scaling

Let us choose the intensive parameters $(p,T,\mu_1,\ldots,\mu_r)$ in the r-component system as independent variables. Then from Theorem 1 we get

$$f(p,T,\mu_1,\ldots,\mu_r)=\Phi_{(1)}(p,T,\mu_1,\ldots,\mu_r)-\Phi_{(0)}\times(p,T,\mu_1,\ldots,\mu_r). \tag{4.28}$$

Let additionally $\Phi_{(1)}=\chi\Phi_{(0)}$, where χ is some non-negative constant. This corresponds to the rescaling of the submanifold and leads to the homogeneous decrease $(\chi<1)$ or increase $(\chi>1)$ of extensive parameters $(V,S,N_1,\ldots,N_r)$ and internal energy U:

$$\begin{aligned}
V_{(1)}&=\frac{\partial\Phi_{(1)}}{\partial p}=\chi\frac{\partial\Phi_{(0)}}{\partial p}=\chi V_{(0)},\\
S_{(1)}&=-\frac{\partial\Phi_{(1)}}{\partial T}=-\chi\frac{\partial\Phi_{(0)}}{\partial T}=\chi S_{(0)},\\
N_m^{(1)}&=-\frac{\partial\Phi_{(1)}}{\partial\mu_m}=-\chi\frac{\partial\Phi_{(0)}}{\partial\mu_m}=\chi N_m^{(0)},\quad m=1,\ldots,r,
\end{aligned} \tag{4.29}$$

$$U_{(1)}=\Phi_{(1)}-p\frac{\partial\Phi_{(1)}}{\partial p}-T\frac{\partial\Phi_{(1)}}{\partial T}-\sum_{m=1}^{r}\mu_m\frac{\partial\Phi_{(1)}}{\partial\mu_m}=\chi U_{(0)} .$$

We can interpret

$$f(p,T,\mu_1,\ldots,\mu_r)=(\chi-1)\Phi_{(0)}(p,T,\mu_1,\ldots,\mu_r) \tag{4.30}$$

as the function generating the process that does not change any physical properties of the initial system. The final system can be treated as a rescaled initial one by multiplying the control parameters by χ.

V. CONCLUDING REMARKS

Let us note finally that another choice of independent variables might be (T,V,μ) and we would have in that case a direct connection with the partition function $Z(T,V,\mu)$ of the grand canonical ensemble. It turns out that the form

$$\Phi(T,V,\mu)=-kT\ln Z(T,V,\mu)$$

of the generating function leads to correct equations for the equilibrium manifold of the system in the grand canonical ensemble. The contact Hamiltonian f depends now on (T,V,μ) and is associated with $Z(T,V,\mu)$ in the same way as in Eq. (4.4), i.e.,

$$f(T,V,\mu)=-kT\ln\frac{Z_1(T,V,\mu)}{Z_0(T,V,\mu)}.$$

The above considerations dealt with the inverse problem, i.e., we were looking for the generating function assuming that we knew the initial and final systems. But the results can also be used when we know (or predict the form of) the generating function and want to investigate how the flow generated by X_f deforms the initial manifold, i.e., how it modifies thermodynamic functions such as energy, entropy, or pressure. This will be the subject of further investigations.

ACKNOWLEDGMENTS

The author is indebted to Darek Chruściński and to Professor R. Mrugala for many stimulating conversations.

[1] F. Weinhold, J. Chem. Phys. **63**, 2479 (1975); **63**, 2484 (1975); **63**, 2488 (1975); **63**, 2496 (1975).

[2] G. Ruppeiner, Phys. Rev. A **20**, 1608 (1979).

[3] G. Ruppeiner, Phys. Rev. A **44**, 3583 (1991).

[4] G. Ruppeiner, Phys. Rev. E **57**, 5135 (1998).

[5] H. Janyszek, J. Phys. A **23**, 477 (1990).

[6] D. Brody and N. Rivier, Phys. Rev. E **51**, 1006 (1995).

[7] H. Janyszek and R. Mrugala, J. Phys. A **23**, 467 (1990).

[8] H. Janyszek and R. Mrugala, Rep. Math. Phys. **27**, 145 (1989).

[9] R. Hermann, *Geometry, Physics, and Systems* (Dekker, New York, 1973).

[10] R. Mrugala, J. D. Nulton, J. Ch. Schön, and P. Salamon, Rep. Math. Phys. **29**, 109 (1991).

[11] R. Mrugala, Rep. Math. Phys. **33**, 149 (1993).

[12] R. Mrugala, J. D. Nulton, J. Ch. Schön, and P. Salamon, Phys. Rev. A **41**, 3156 (1990).

[13] G. Hernández and E. A. Lacomba, Diff. Geom. Applic. **8**, 205 (1998).

[14] V. I. Arnold, *Mathematical Methods of Classical Mechanics* (Springer, New York, 1983).

[15] P. Libermann and Ch. Marle, *Symplectic Geometry and Analytical Mechanics* (Reidel, Dordrecht, 1987).

[16] Y. Choquet-Bruhat, C. DeWitt-Morette, and M. Dillard-Bleick, *Analysis, Manifolds and Physics* (North-Holland, Am-

sterdam, 1982).
[17] J. Jurkowski, Rep. Math. Phys. **41**, 351 (1998).
[18] J. F. Cariñena, L. A. Ibort, G. Marmo, and A. Stern, Phys. Rep. **263**, 153 (1995).
[19] L. Benayoun, Ph.D. thesis, Grenoble INPG, 1999 (in French).
[20] H. B. Callen, *Thermodynamics and an Introduction to Thermostatics* (Wiley, New York, 1985).
[21] A. I. Anselm, *Introduction to Statistical Physics and Thermodynamics* (Nauka, Moscow, 1973) (in Russian).
[22] C. J. Thompson, *Mathematical Statistical Mechanics* (Princeton University Press, Princeton, NJ, 1979).
[23] H. Janyszek and R. Mrugala, Phys. Rev. A **39**, 6515 (1989).