ON GEOMETRY OF PHENOMENOLOGICAL THERMODYNAMICS

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1. MOTIVATIONS

Thanks to works of Caratheodory [4] and Gibbs [5] phenomenological thermodynamics of equilibrium (PTE) has become a standard axiomatic theory. Formulated in the general way [11,3], it reveals the structure which is universal in the sense that the later statistical and quantum statistical mechanics have not replaced it but rather serve as models of the general scheme. [1]

Phenomenological thermodynamics is claimed to be a typical theory, the formalism of which could not be understood without the language of differential geometry. Nonetheless, in the traditional approach the geometric situation is often unclear, "differential calculus" used there is highly formal, without specified underlying manifolds often arbitrary and confusing.

Recently, thanks to some attempts [6,9,10] PTE occurred in the mainstream of the geometrization of physics. This presentation is intended to be such an attempt suggesting however alternate recognition of geometrical objects underlying the theory.

It can be assumed that in classical textbooks the basic manifold of PTE is that of n+1 extensive variables (like S, V, N, and U). [2] New attempts extend the above configuration space of PTE by including n intensive coordinates (like T, p, μ). Thus one obtains a universal space E (the phase space of PTE - according to [6,10]), where admissible states of a given theory form some submanifold $\Lambda \subset E$. The phase space E is provided with the distinguished Gibbs differential one-form θ, and an admissible submanifold Λ has to satisfy the Gibbs relation $\theta\big|_\Lambda = 0$. In [6,9,10] the space is *odd-*dimensional and θ constitutes a *contact* structure, and thus a *pre*-symplectic structure on E determined by the bi-form $d\theta$.

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[1] for models other than PT see e.g. [2] (cosmology of black holes).

[2] Caratheodory assumes even that each coordinate description of a given system demands independent treatment (space).

In this paper we would like to justify that the accurate geometrical description of PTE should be based on the assumption that the phase space of PTE is an *even*-dimensional manifold. Moreover, the internal energy U, no longer a basic coordinate, forms, together with other thermodynamical potentials, an algebraic lattice (Sec. 3). Thus,

> *PTE is a superposition of symplectic structure of the phase space and of lattice structure of thermodynamical potentials.*

Classical Mechanics vs Phenomenological Thermodynamics

Some authors (see e.g. [10]) stress the similarity between structure of PTE and that of classical mechanics (CM), whereas they should be rather contrasted.
Although both PTE and CM rely essentially on a manifold with a closed biform ω [(pre-)symplectic structure (Poisson bracket)], yet the one-form θ, $d\theta = \omega$, plays different roles in these theories:
● in CM θ is defined up to an external derivative of any function on the manifold of the phase space, i.e. the gauge $\theta \to \theta' = \theta + df$ does not change the classical equation of motion $X \lrcorner d\theta = dH$, since $d\theta = d\theta'$ (nor even quantum measurable effects [7]: the term df only shifts the global phase factor of the wave function);
● whereas in PTE things seem to be quite opposite: one of the one-forms (the Duhem-Gibbs form) generating the symplectic structure, say θ_o, is distinguished, and this fact is crucial for the theory. The equation for the submanifold Λ of admissible states, $\theta_o|_\Lambda = 0$, is not invariant under the gauge $\theta_o \to \theta_o + df$ (however the resulting Maxwell identity $d\theta_o|_\Lambda = 0$ is invariant).
And this is the source of importance of thermodynamical potentials in PTE.

Odd- vs Even-Dimensional Phase Space

Earlier approaches [6,9,10] assume for the phase space of PTE the odd-dimensional manifold routinely constructed from all variables appearing in the Gibbs relation $dU - TdS + pdV - \mu dN = 0$.
Unfortunately such an approach overlooks some important subtlety of the structure of PTE. If we take into account that the symplectic form $d\theta$ conjugates thermodynamical variables into pairs (T-S, P-V, μ-N,...) leaving internal energy U out, and the fact that U is actually of a different genre than above variables, having common features with other thermodynamical potentials rather, it should be obvious that the natural basic PHASE SPACE of PTE is an even-dimensional symplectic manifold. Then U becomes a distin-- guished function on the space (i.e. of 2n variables (e.g. T, S, P, V, μ, N)), as well as other potentials.
In fact it will appear, that the function U is natural in terms of the geometry of phase space, i.e. can be constructed in the coordinate-free manner (see Sec. 2).

Legendre vs Gauge Transformations

The appearance of different potentials in PTE is often referred to the Legendre transformation (justifying parallelity of structures of CM and PT). Legendre transformation in CM is essentially the map between tangent and cotangent bundles over configuration space $TQ \leftrightarrow T^*Q$ so that the induced transformation sends the symplectic form $d(\partial_q L) \wedge dx$ defined by the Lagrangian L on TQ to the canonical form $dp \wedge dx$ on T^*M (Darboux variables) [1]. Whereas

this context does not appear in PT, where the (pre-)symplectic form $d\theta =$ $dT \wedge dS + dV \wedge dp + d\mu \wedge dN$ has already the canonical form. The potentials appear when one would like to express the same θ in another basis of differentials on M (like e.g. $TdS = -SdT + d(TS)$).

In order to geometrize the notion of potentials one has to extend the manifold of phase space M^{2n} to a real linear fiber bundle E over M and reinterpret the Gibbs form in terms of the connection structure on E, so that the potentials, interpreted as sections of the fiber bundle, refer to different "gauges" of the connection, as shown in the Section 4.

On the other hand, if the manifold M^{2n} has a distinguished splitting into (Lagrangian) subspaces of intensive and extensive variables, the potentials, as functions on M, constitute the lattice structure shown in Section 3.

2. PHASE SPACE OF PTE

Let us state the general definitions constituting PTE.

● By THERMODYNAMICAL PHASE SPACE we will understand the pair (M,α), where M is a 2n-dimensional manifold and $\alpha \in \Lambda^1 M$ is a distinguished differential 1-form of the maximal rank. The form α will be called the Gibbs form.

It follows from the definition that the phase space is a symplectic manifold, since the bi-form $\omega =: d\alpha$ is nondegenerate.

● A STATE is a point in M.

● A PROCESS is a curve $c: \mathbb{R} \to M$ (not all are admissible).

The one-form α has a physical sense of the work $W[c]$ one has to put into the system to carry out the process c:

$$W[c] = \int_c \alpha \tag{1}$$

A THEORY (or a SYSTEM) is a submanifold Λ of the phase space with an embedding

$$\iota : \Lambda \longrightarrow M \tag{2}$$

such that

$$\iota^*\alpha = 0. \tag{3}$$

Eq. (2) is called the EQUATION OF STATE.

Eq. (3) is called the GIBBS-DUHEM RELATION and means that the directions tangent to Λ lie in the kernel of α, i.e. that α restricted to Λ vanishes, $\alpha|_\Lambda = 0.$

Cor. Since the external derivative commutes with ι^*, it immediately follows from (3) that

$$\iota^*d\alpha = 0, \tag{4}$$

i.e. that Λ is a Lagrangian submanifold of M (of course, eq. (3) are more restrictive conditions for Λ).
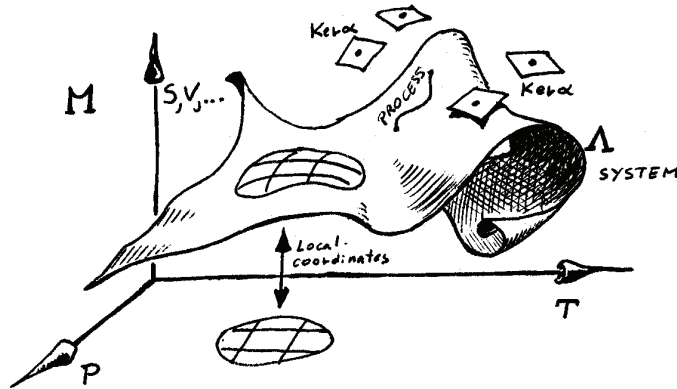
FIG. 1

Cor. The dimension of Λ is at most $\frac{1}{2}\dim M$.

Eq. (4) is called a MAXWELL IDENTITY and is, in fact, the integrability condition on Λ (it is an analog of the Hamilton-Jacobi equation in CM).

● By the SPECIAL PHASE SPACE we will understand the cotangent bundle over the linear space Q

$$M = T^*Q \cong \mathbb{R}^{2n}$$
$$\downarrow \pi$$
$$Q \cong \mathbb{R}^n$$

(5)

The form $-\alpha$ is here defined as the natural Liouville form of the cotangent bundle. Q will be named INTENSIVE SPACE (analogously to the intensive parameters of PTE).

If $\{x'^i\}$ are any linear coordinates on Q, and $\{p_i\}$ induced coordinates on T^*Q, called EXTENSIVE PARAMETERS, then

$$\alpha = -p_i \, d \, x^i$$

(6)

and $\omega = d\alpha = -dp_i \wedge dx^i.$ $(x^i =: x'^i \circ \pi)$

The above geometry (5) of the special phase space distinguishes the natural function defined in coordinate-independent way:

● The INTERNAL ENERGY is the function $U \in FM$

$$T^*Q \ni \quad p \longmapsto U(p) =: p(V_{\pi(p)})$$
$$\equiv \quad p(K_{\pi(p)} \circ \pi \, p)$$

(7)

where $V \in XQ$ is the natural Liouville vector field on the intensive space, K is the natural canonical isomorphism on linear spaces $K_q: Q \longmapsto T_qQ \quad \forall q \in Q$, and p as a point of T^*Q is a differential form on Q.

In the coordinates (6) $U = p_i x^i,$

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and, since $dU = p_i dx^i + x^i dp_i$, the Gibbs form may be written in the more familiar form:

$$\alpha = x^i dp_i - dU \tag{8}$$

so that the Gibbs relation (3) is

$$\iota *(x^i dp_i - dU) = 0 \tag{9}$$

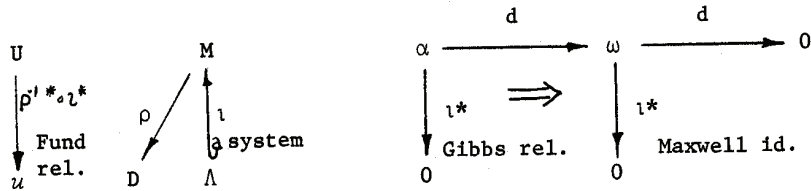i.e. $(x^i \circ \iota) d(p_i \circ \iota) - d(U \circ \iota) = 0$.

Since we have the distinguished function U on M, another possibility of description of the system Λ in M appears. Let ρ be a projection on some manifold D of dim $D \leq \frac{1}{2} \dim M$. We can set the problem: for a given function $u \in FD$ find the submanifold $\iota: \Lambda \to M$ such that

$$\iota *U = (\rho \circ \iota)*u \tag{10}$$

Eq. (10) is called the FUNDAMENTAL RELATION. Often ρ and D are π and Q of (5). In this case (10) is equivalent to (2).

Let us call u a DEFINING FUNCTION of internal energy. It ought to be clearly distinguished from the function of internal energy $U \in FM$. The function $u \circ \iota$ is the INTERNAL ENERGY OF THE SYSTEM ι.

Summarizing this section:

The standard model is 6-dimensional:

$x^1 = T$ —temperature $\qquad p_1 = S$ —entropy

$x^2 = -P$ —pressure $\qquad p_2 = V$ —volume $\hfill (11)$

$x^3 = \mu$ —chemical potential $\quad p_3 = N$ —number of molecules

The Gibbs form is

$$\alpha = -SdT + VdP - Nd\mu \tag{12}$$

$$= TdS - PdV + \mu dN - dU$$

where

$$U = ST - PV + \mu N. \tag{13}$$

The embedding ι of a system (2) may be set by "constraints" of the type $pV^\alpha = $ const. T, etc., or - equivalently - by the fundamental relation. Let e.g. $u \in FQ$, i.e. $u = u(T,P,\mu)$. Thus eq. (10) is an equation for such an embedding $S \circ \iota = S(T,P,\mu)$, $V \circ \iota = V(T,P,\mu)$ and $N \circ \iota = N(T,P,\mu)$ that

$$u(T,P,\mu) = S(T,P,\mu) \cdot T - V(T,P,\mu) \cdot P + N(T,P,\mu) \cdot \mu. \tag{14}$$

3. SEVEN (OR ∞) POTENTIALS OF PTE

The Gibbs form α of the phase space can always be expressed in the canonical coordinates as $\alpha = p_i dx^i$ (Darboux theorem). If for any reason we would like to have a term $x^{\overset{k}{\cdot}} dp_{\overset{\cdot}{k}}$ (the dot designs no summation over k) instead of $p_{\overset{\cdot}{k}} dx^k$ for some k, then the external derivative of $p_{\overset{\cdot}{k}} x^{\overset{k}{}}$ must appear:

$$\alpha = p_i dx^i = \sum_{i \neq k} p_i dx^i - x^{\overset{k}{}} dp_{\overset{\cdot}{k}} + d(p_{\overset{\cdot}{k}} x^{\overset{k}{}}) \tag{15}$$

Such a "coordinate flip" can be done for any such pair of conjugated canonical variables. Although the above coordinate trick in the general case of M has an underlying geometry in the case of the special phase space, let us simplify it here to the statement, that for distinguished 2n coordinates on M each subset J of I =: $\{1,2,\ldots,n\}$ is related to one of n! distinguished functions:

$$f_J =: \sum_{k \in J} p_k x^k, \qquad\qquad f_\emptyset =: 0 \tag{16}$$

called the Jth POTENTIAL, so that the Gibbs form can be expressed

$$\alpha = \sum_{i \in I \setminus J} p_i dx^i - \sum_{k \in J} x^k dp_k + df_J. \tag{17}$$

For the coordinates (11) we have 7 nonzero potentials which form a lattice structure isomorphic with the lattice of subsets of a set $I = \{1,2,3\}$
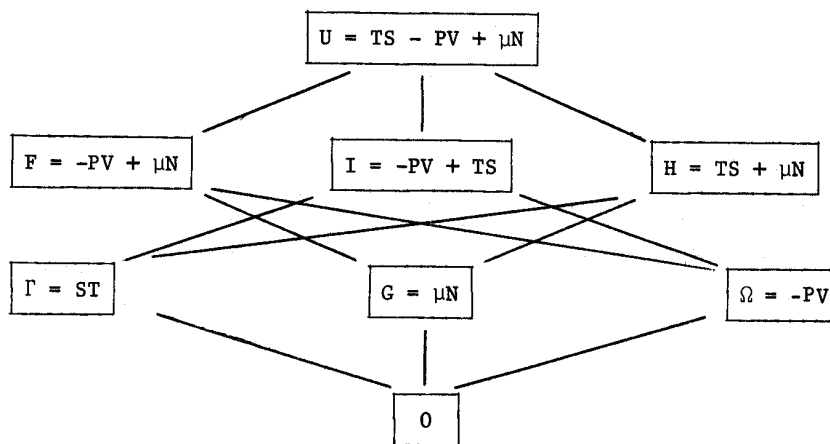

FIG. 2

where the functions are called:

U	–	internal energy	Γ –	nameless
F	–	Helmhotz free energy	G –	Gibbs potential
I	–	nameless	Ω –	grand potential
H	–	enthalpy	0 –	just zero! (unrecognized trivial potential)

In fact, the geometry of the special phase space allows us to define thermodynamical potentials in coordinate-independent way:

Each linear decomposition A of Q into two subspaces

$$Q = A \oplus B, \qquad\qquad \pi_A: Q \to A \qquad\qquad (18)$$

determines the function $f_A \in FM$ (cf. (7))

$$f_A(p) =: p(\kappa_{\pi p} \circ \pi_A \circ \pi p) \qquad\qquad (19)$$

called the THERMODYNAMICAL POTENTIAL for the splitting A.

Thus we have the infinite lattice L of thermodynamical potentials with the structure induced from the natural lattice of subspaces A, B of the linear space Q. The maximal element in the lattice, U, corresponds to the trivial decomposition $Q = Q \oplus \emptyset$. The minimal element of the decomposition $Q = \emptyset \oplus Q$ is the constant null function.
The lattice in Fig. 2 is a finite sublattice of L.

NOTE 1: If the euclidean structure is introduced to Q, then π_A is determined by only one subspace and the orthogonal projection on it. Thus the lattice L is isomorphic to the Grassman lattice of all subspaces of Q.

NOTE 2: Decomposition (18) induces a decomposition of M into the symplectic spaces $M = T^*A \oplus T^*B$. This shows the way to generalize Def. (19) to the case of the general phase space.

Generally for a potential $f \in FM$ we will write

$$\alpha \equiv \alpha_f - df. \qquad\qquad (20)$$

In fact, for the special phase space (5) the statement (1) concerns the integral of α_U rather.

Introduced potentials enables to express the Gibbs relation (3) in a way described here in coordinates (11). If a neighborhood U of Λ is projectible on some subspace of M, then coordinates of the subspace can be used (by pull-back, $\iota^*p_i =: p_i \circ \iota$, ι^*x_i) to parametrize $U \subset \Lambda$ (see Fig. 1). Each choice of those coordinates brings through (3) the "definitions" of the rest. E.g. if the variables T,V,N on Λ are chosen, then the convenient expression for the form α on M is

$$\alpha = -SdT + PdV + \mu dN - dF \qquad\qquad (21)$$

and thus

$$\iota^*\alpha = -S(T,V,N)dT - P(T,V,N)dV + \mu(T,V,N)dN - dF(T,V,N) \qquad\qquad (22)$$

so $\iota^*\alpha = 0$ means:

$$\iota^*S = S(T,V,N) = -\left.\frac{\partial F \circ \iota}{\partial T}\right|_{V,N}$$

$$P(T,V,N) = -\left.\frac{\partial F \circ \iota}{\partial V}\right|_{T,N} \qquad\qquad (23)$$

$$\mu(T,V,N) = \left.\frac{\partial F \circ \iota}{\partial N}\right|_{P,T}$$

For other choices of coordinates e.g. entropy can be expressed similarly:

$$\imath * S = -\left.\frac{\partial G}{\partial T}\right|_{P,N} = -\left.\frac{\partial \Omega}{\partial T}\right|_{N,\mu} = \left.\frac{\partial \Gamma}{\partial T}\right|_{\mu,P} \tag{24}$$

By analogy, all other of 3·7 such relations can be expressed.

4. GAUGE INTERPRETATION OF PTE

Let $\{E,\pi,M\}$ be a real linear fiber bundle over thermodynamical phase space M, with a projection

$$\pi: E \to M, \qquad\qquad \pi^{-1}(m) \cong \mathbb{R} \quad \forall m \in M \tag{25}$$

Def. The Gibbs connection on E is the connection ∇ defined by the vector-valued one-form

$$\boldsymbol{\alpha} =: \partial_u \otimes \alpha \tag{26}$$

The curvature of the connection is

$$Curv(\nabla) \equiv \boldsymbol{\omega} =: \partial_u \otimes d\alpha \tag{27}$$

Thus a system is defined now as a submanifold Λ of M such that curv ∇ on the subbundle $(\pi^{-1}(\Lambda),\pi,\Lambda)$ vanishes.
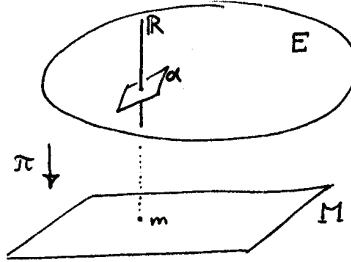

FIG. 3

Now a potential is a section of the fiber bundle

$$\Gamma(E,\pi,M) \ni \quad f: M \to E, \qquad \pi \circ f = id_M \tag{28}$$

Each such section induces a differential one-form α_f on M (see (20)) by the formula:

$$\Gamma(E,\pi,M) \ni \quad f \longmapsto \alpha_f =: \nabla f \tag{29}$$

$$\text{i.e.} \quad \alpha_f(v) = \nabla_v f \qquad \forall v \in TM.$$

Thus the known potentials correspond to convenient "choices of gauge" of the Gibbs connection $\boldsymbol{\alpha}$.

REMARK: If the connection (26) is built rather as $\boldsymbol{\alpha} =: \partial_v \otimes \alpha_U$, then it has a clear physical sense: if $\gamma: I \to M$ is a process in the phase space, then the curve $\tilde{\gamma}$ lifted through the connection rises by the energy put into the system.

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CONCLUSIONS

The geometrization of PTE in terms of even-dimensional symplectic space seems to be more profound than the usually suggested odd-dimensional contact manifold approach. [An interesting inverse shift may be noted: CM is usually presented in terms of symplectic geometry, whereas here the odd-dimensional contact formulation seems to be more profound [8] as reflecting the particle-wave duality in Lagrangian description.]

Such an approach is supported by the fact that now thermodynamical potentials can be defined in a rigorous geometrical way and they reveal the structure of a lattice.

The phase space may be extended by one more dimension by the use of the fiber bundle technique. Then, PTE may be reinterpreted in terms of "gauge theory".

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