Applications of differential forms in thermodynamics

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I. INTRODUCTION

Thermodynamics is an universal physical theory that describes the equilibrium states of a generic system determined by the surroundings with which they can coexist and which can be described by a few macroscopic parameters. These parameters are usually its internal energy (U), pressure (P) entropy (S), temperature (T), volume (T) etc. Depending on the complexity of the system, these parameters will be differently correlated, and the number of independent parameters is called the number of degrees of freedom of the system. The simplicity of this description allows the theory to hold in a plethora of different physical systems, such as heat engines, refrigeration systems, metabolism, or even black holes.

A very important notion to have in mind while studying thermodynamics is that of equilibrium - it refers to a condition in which a system has settled into a stable, unchanging configuration concerning its macroscopic properties under given external conditions. It's a state where observable properties such as temperature, pressure, volume, and chemical composition remain constant over time.

The mathematical theory of thermodynamic systems focuses on one such system, and describes geometrically the set of equilibrium states it can have. The allowed modes of interaction with the surroundings define the equilibrium.

II. MATHEMATICAL FOUNDATIONS OF THERMODYNAMICS

We start by defining the manifold $\mathcal{M}$ as the set of equilibrium states of a thermodynamic system. The dimension of $\mathcal{M}$ will be the number of degrees of freedom, defined above. It is worth to mention that this number may depend on the time scale of the system that we are interested in.

A path in a $\mathcal{M}$ is a differentiable one-parameter family of points defined by a continuous function ϕ that maps an interval in the real numbers to points in $\mathcal{M}$. In thermodynamics such path is called quasistatic locus because every point on the path is in equilibrium state, and it is a good example of a process that occurs on time scales that are slower than the equilibrium time of the system.

Recalling the definition of tangent vectors at a given point (or state) in manifolds, they can be thought of as n-tuples of the time derivatives of the coordinate charts at a point. Thus a tangent vector represents any path that has the same instantaneous values of all these derivatives. By the chain rule, a tangent vector assigns a time derivative to any function of state. For example, if we have a simple system where the two independent parameters are entropy and pressure and we want to write the derivative of a function of state f, we have:

$$\frac{df}{dt} = \frac{\partial f}{\partial S}\frac{\partial S}{\partial t} + \frac{\partial f}{\partial P}\frac{\partial P}{\partial t},$$

where the derivative was assigned by the tangent vector $(\frac{dS}{dt}, \frac{dP}{dt})$.

As tangent vectors at a point can be thought of as equivalence classes of paths along which a set of coordinate functions changes at the same rate, the cotangent vector at a point is an equivalence class of functions where two functions are said to be equivalent if their derivatives are the same along every tangent vector at the point. This may be identified at a each point (S_0, P_0) with the differential of any F in the equivalence class:

$$dF = f dS + g dP.$$

As tangent vectors form a vector space called tangent space, the cotangent vectors also form a vector space, that is the dual of the tangent space. Thus the cotangent vectors are linear functionals that map tangent vectors to $\mathbb{R}$.

With both the notions of tangent and cotangent vectors in mind, come the notions of vector field and differential form. The development of thermodynamics can me made using one of this prescriptions, but typically one uses differential forms. Important examples of differential forms are work W and heat Q.

To delve deeper to the important results, the notions of exterior derivative and wedge product are needed, highlighting the antisymmetry of this product.

III. LAWS OF THERMODYNAMICS

The first law of thermodynamics can be written as:

$$dU = Q + W \tag{1}$$

where U is the internal energy of the system. When the differential forms Q and W are written in coordinates, this equation becomes a Pfaffian differential equation, and the Frobenius and Darboux theorems are the main results concerning these equations.

To obtain relevant results from this equations explicitly, one is interested in taking the differential or exterior derivative of (1). The set of differential forms with the wedge product form a ring. If one rewrites (1) as

$$dU - Q - W = 0,$$

one may notice that this is equivalent to finding a 1-form that vanishes on the solution submanifold, so the set of these differential forms must form an ideal. The fact that these ideals must be closed under the operation of taking a differential, yields the extension of the d(.) operator to higher order differentials:

- $d(.)$ of a function gives the differential, $d(d(f)) = 0$, and:

$$d(v \wedge w) = dv \wedge w + (-1)^k v \wedge dw,$$

where w is a k-form and v any form. The celebrated Maxwell relations can now be readily obtained: take $Q = TdS$ (2nd law of thermodynamics) and $W = -PdV$ (work done by the surroundings on the system), plug this in (1) and take the differential. Applying the prescription $d(d(f)) = 0$ one gets:

$$0 = dT \wedge dS - dP \wedge dS. \tag{2}$$

Expanding dT in coordinates $(S, V) : dT = \frac{\partial T}{\partial S} dS + \frac{\partial T}{\partial V} dV$, doing the same with dP and evoking antisymmetry of the wedge product one gets:

$$\left(\left(\frac{\partial T}{\partial V} \right)_S + \left(\frac{\partial P}{\partial S} \right)_V \right) dV \wedge dS = 0$$

which yields:

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V,$$

where the subscript in the partial derivatives denotes that the derivative is taken leaving that parameter constant. The other Maxwell relations can be obtained from (2) expanding the different differentials in different coordinates.

We saw a particular case of a solution of (1), but can this equation always be integrated? Frobenius's theorem guarantees that for every system of differential form equations:

$$w_j = 0, \; j = 1, ..., N$$

where each w_j is an 1-form on $\mathcal{M}$, there is a differential ideal of forms generated by w_j which must vanish on any solution of the equation. Specifically, it is an ideal in which the exterior derivative of any form in the ideal is still in the ideal.

If one wants to solve a single equation of the form $w = 0$, one can take differentials and wedge products of the equation successively:

$$dw, w \wedge dw, dw \wedge dw, w \wedge dw \wedge dw, ... \tag{3}$$

On any solution of the equation, every single one of this differentials must vanish, but some of them may be identically zero in $\mathcal{M}$. If one is zero, all the subsequent ones are zero. Suppose that the first identically zero terms appears in the position r of the sequence (3): then r is the minimum number of variables needed to express w.

Furthermore, suppose that the parameters are labeled by X_i, Y_i and Z. Darboux's theorem states that these smooth independent functions exist and for r given by:

- $r = 2n : \; w = \sum_i^n Y_i dX_i$
- $r = 2n + 1 : \; w = dZ + \sum_i^n Y_i dX_i$.

And the dimension of the maximal solutions of $w = 0$ is n.

These theorems can be applied to (1), to obtain $r = 5$ and thus the maximal solutions of the equation are two dimensional. As mentioned before, the equilibrium states that are obtained solving (1) live in a n dimensional manifold, and one can think of a thermodynamic system as a submanifold of a $2n+1$ manifold equipped with a differential form Ω such that $\Omega \wedge (d\Omega)^n \neq 0$. These are so called contact manifolds that arise frequently in classical mechanics.

Finally, it is noteworthy to mention that in our case, $\Omega = dU - TdS + PdV$ so the set of dependent variables is (U, T, S, P, V). However, one can always perform Legendre transform to other variables, that preserve the form $w = dZ + \sum_i^n Y_i dX_i$.