Beginners guide to differential forms in thermodynamics

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Abstract

The purpose of this paper is to present derivation of basic thermodynamic relations made with differential forms. This approach is rarely mentioned in textbooks and usually without much of details provided. In this work I fill this gap and promote "thermodynamical" application of differential forms. No prior knowledge of differential forms is required from the Reader, but familiarity with three laws of thermodynamics is assumed. This article may be a good starting point for studying physical applications of differential forms and geometrical methods in physics.

Introduction

Every theory in theoretical physics begins from establishing a connection between real physical objects and abstract mathematical structures. In a sense abstract objects represent real physical substances and their qualities. But this represention is by no means unique — one may use different math entities to represent the same physics. Due to various reasons — simplicity of used math, historical, or any other — one way of mathematical description always prevails.

In current contribution I'll make a review of classical thermodynamics done with differential forms. This approach is not new [1], but it lacks solid exposition, because most books do not proceed beyond an outline. Since thermodynamics is a broad field, I will restrict myself to basic non-relativistic thermodynamics.

It will be shown, that using differential forms, one may obtain many relations of classical thermodynamics in a few lines of computation. Standard derivation of this relations needs introduction of derived thermodynamic potentials (H, F). On the contrary, I will use only primitive (P, V, ...) and basic (T, S, ...) properties. This may be seen as a utilisation of "Keep It Simple" principle. Derivation of Maxwell's relations is a great example when this approach simplifies and clarifies all calculations.

Of course, there are issues, otherwise any textbook on thermodynamics would start with differential forms. What makes this approach unpopular is that mathematical apparatus behind the scene needs some time to get used to. I'll try to smooth out this drawback by introducing a minimal number of used relations without getting much into mathematical details. For readers who are interested in diving deeper into this section of math, I would recommend the book [2].

The article is organized as follows. *Section 1* is devoted to mathematical apparatus and introduces differential forms and their properties. This article is physicists-oriented and I assume that Reader doesn't know anything about differential forms. In *section 1* I explain some of their properties starting from scratch.

"Mathematical part" is followed by "physical part". Section 2 introduces the method of derivation of thermodynamic relations via differential forms. Some of them are prominent like Maxwell's equations and relation connecting thermic and caloric equations of state, while others are not widely used. I hope You'll enjoy reading.

1 Mathematical notes

In this section I introduce differential forms and give a short list of their properties. This section has no objective of an exhaustive description — I just try to give the Reader some intuition about the subject. Thus, readers interested in "what's behind the scene" should refer to mathematical books on the theory of differential forms, e.g. [2].

First of all, let's develop an intuitive understanding of what a differential form is. Suppose we are in $\mathbb{R}^3$ space realm. These three constructions (α, β, γ) we will call 1-form, 2-form and 3-form respectively

$$\begin{aligned}
\alpha &= X(x;y;z)dx + Y(x;y;z)dy + Z(x;y;z)dz,\\
\beta &= A(x;y;z)dx\wedge dy + B(x;y;z)dy\wedge dz + C(x;y;z)dz\wedge dx,\\
\gamma &= f(x;y;z)dx\wedge dy\wedge dz.
\end{aligned}$$

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Capital letters stand here for arbitrary functions of three varibles (x, y, z). Symbol $\wedge$ denotes a new kind of product that is called "wedge product" or "exterior product". Its main difference from the regular product is that it throws minus sign every time adjacent multiplicants are transposed. We expect from product $dx\,dy = dy\,dx$, but for wedge product

$$dx \wedge dy = -dy \wedge dx$$

holds. It acts only on objects of the form d(something), ordinary functions don't even notice this wedge sign and may be permuted with other multiplicants as if $\wedge$ were an ordinary product

$$A(x;y;z)dx \wedge dy = dx \wedge A(x;y;z)dy = dx \wedge dy\, A(x;y;z).$$

It can be shown (Reader may check this with any of α, β or γ forms mentioned) that for every two forms — p-form and q-form — following equality holds

$$\underbrace{\omega}_{p-\text{form}} \wedge \underbrace{\eta}_{q-\text{form}} = (-1)^{pq}\eta \wedge \omega. \tag{P.1}$$

Property (P.1) is transposition law for any two forms.

Notice that applying this property to the same form yields a strange thing. For example, $dx \wedge dx = dx \wedge dx$, but appliying (P.1) one gets $dx \wedge dx = -dx \wedge dx$. Actually that's fine, it just means $dx \wedge dx = 0$. Moreover, it can be proven, that for any form of odd order $p = 1, 3, 5, \ldots$

$$\omega \wedge \omega = 0. \tag{P.2}$$

This property will often be used in the next section.

Now it's time to switch gears to the d symbol I've used without any explanation. This differential is the generalisation of the ordinary differential that can be applied not only to functions but to differential forms as well. It is called "exterior differential" and has some extra properties compared to the d we are used to.

Let's explore how d behaves in different cases. For the sake of simplicity I'll use $\mathbb{R}^2$ space instead of $\mathbb{R}^3$ that I used before. First of all, let's apply exterior differential to the regular function

$$dA(x;y) = \frac{\partial A}{\partial x}dx + \frac{\partial A}{\partial y}dy,$$

and note that it acts like the ordinary differential. Things get more interesting when you try to differentiate differential form. This is done according to few simple rules.

- First, no matter how complicated the form is, d can be applied separately to every summand (it is linear like the regular differential).
- Second, no matter how much wedge products there are (if there are any) in the expression $f(x;y;z;t;\ldots)dx \wedge dy \wedge dz \ldots$, one should apply d to the functions only and put wedge product in appropriate places (between differentials).

Let's try some simple example

$$d\left(A(x;y)dx + B(x;y)dy\right) = d(A(x;y)) \wedge dx + d(B(x;y)) \wedge dy = \left(\frac{\partial A}{\partial x}dx + \frac{\partial A}{\partial y}dy\right) \wedge dx + \left(\frac{\partial B}{\partial x}dx + \frac{\partial B}{\partial y}dy\right) \wedge dy.$$

In the last expression parenthesis can be expanded and constructions like $dx \wedge dx$ and $dy \wedge dy$ set to zero with (P.2). We will get

$$d\left(A(x;y)dx + B(x;y)dy\right) = \frac{\partial A}{\partial y}dy \wedge dx + \frac{\partial B}{\partial x}dx \wedge dy = \left(\frac{\partial B}{\partial x} - \frac{\partial A}{\partial y}\right) dx \wedge dy.$$

This sort of transformations will be frequently used in the next section.

It should be noticable that differentiation adds some sort of "balance" to the expression

$$d(f(x;y;z;t;\ldots)dx \wedge \text{whatever follows}) = \underbrace{\left(\frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy + \ldots\right)}_{\text{all variables are present}} \wedge dx \wedge \text{whatever}.$$

Let's add "more balance" and perform differentiation once more. This leads to

$$d^2(f(x;y;z;t;\ldots)dx \wedge \text{whatever}) = \underbrace{\left(\overbrace{\frac{\partial^2 f}{\partial x^2}dx \wedge dx + \frac{\partial^2 f}{\partial y \partial x}dy \wedge dx + \ldots}^{\text{comes from } \partial f/\partial x\, dx} + \overbrace{\frac{\partial^2 f}{\partial y^2}dy \wedge dy + \frac{\partial^2 f}{\partial x \partial y}dx \wedge dy}^{\text{comes from } \partial f/\partial y\ dy} + \ldots\right)}_{\text{all combinations are present}} \wedge dx \wedge \text{whatever},$$

but we already know that $dx \wedge dx = dy \wedge dy = \cdots = 0$ and $dx \wedge dy + dy \wedge dx = 0$ (and other similar combinations give zero as well). Keeping this in mind and simplifying last expression, we extend this property and the double differentiation law raises

$$d(d\omega) = d^2\omega = 0, \tag{P.3}$$

which is true for any differential form ω.

And just to mention (I'll not use it in a such a complicated form), the differentiation law

$$d(\underbrace{\omega}_{p-\text{form}} \wedge \underbrace{\eta}_{q-\text{form}}) = d\omega \wedge \eta + (-1)^p \omega \wedge d\eta. \tag{P.4}$$

Apparatus presented at this level is more than enough to understand the next section. If Reader feels need in more rigour, he can consult [2], which starts with simple examples and leads to understanding differential form as "alternating multilinear map from tangent space of some smooth manifold at some point to real numbers".

2 Thermodynamics of gases

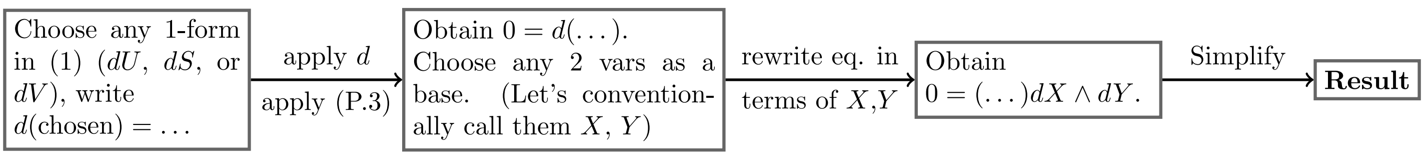
Now we get to the physical part. Thermodynamics is based on three postulates (laws of thermodynamics) that can be merged into following equality

$$dU = TdS - PdV. \tag{1}$$

If you are interested in its derivation please refer to any textbook in thermodynamics, e.g. [1].

And now differential forms come into play. Let's treat d as an exterior derivative and suppose that dU, dS and dV are 1-forms. Now we can use properties of differential forms (mentioned in the previous section) to obtain a bunch of thermodynamic identities.

The method for deriving these identities may be formalised as follows.



Maybe this is not the clearest explanation of what is going to happen, but treating the first example will make it self-evident.

Let's choose dU at the first step and express it in terms of other differential forms. In fact (1) is already in the form we need. Now we can apply exterior differentiation to both sides of the relation to get

$$0 = ddU = dT \wedge dS - dP \wedge dV,$$

or in a more convenient form

$$dT \wedge dS = dP \wedge dV.$$

There are 6 possible pairs of 1-forms we can choose (any two of dT, dS, dP and dV). For the beginning we limit ourselves with 4 different pairs of presented variables — $(S;V)$, $(S;P)$, $(T;V)$ and $(T;P)$ (easy mnemonic — one is chosen from the left side of the equality sign and the other — from the right). For every pair let's rewrite the last equation in terms of these variables. By this I mean to treat other variables as functions of the chosen two and expand their differentials in appropriate form (P.4)

$$\left[\left(\frac{\partial T}{\partial S}\right)_V dS + \left(\frac{\partial T}{\partial V}\right)_S dV\right] \wedge dS = \left[\left(\frac{\partial P}{\partial S}\right)_V dS + \left(\frac{\partial P}{\partial V}\right)_S dV\right] \wedge dV$$
$$\left[\left(\frac{\partial T}{\partial S}\right)_P dS + \left(\frac{\partial T}{\partial P}\right)_S dP\right] \wedge dS = dP \wedge \left[\left(\frac{\partial V}{\partial S}\right)_P dS + \left(\frac{\partial V}{\partial P}\right)_S dP\right]$$
$$dT \wedge \left[\left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV\right] = \left[\left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV\right] \wedge dV$$
$$dT \wedge \left[\left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP\right] = dP \wedge \left[\left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP\right]$$

There are two minor remarks to do. First, if one is confused which pair was chosen in every case, he needs to check variables at d sign and this should be the answer. And second, I gave reference to (P.4) in some sence "formally", it's better to refer to example of differentiating a regular function (example in previous section). For example, equation contains dT and $(S;V)$ were chosen as "basic". Then one can say $T = T(S;V)$ and thus $dT = (\partial T/\partial S)_V dS + (\partial T/\partial V)_S dV$.

Now open parenthesis and simplify everything we can (here (P.2) and (P.1) are handy). As a result we get **Maxwell's relations**

$$\boxed{\begin{aligned}\left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial P}{\partial S}\right)_V,\\ \left(\frac{\partial T}{\partial P}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_P,\\ \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial P}{\partial T}\right)_V,\\ \left(\frac{\partial S}{\partial P}\right)_T &= -\left(\frac{\partial V}{\partial T}\right)_P.\end{aligned}} \tag{2}$$

We have just derived Maxwell's relations in a few lines of computations. Moreover— no additional thermodynamic potentials were introduced. "Standard" approach implies extra potentials (H, F), and after lengthy computations gets relations that do not contain these potentials. George Berkeley would have called them "Ghosts of Departed Thermodynamic Potentials" [3]. They come from nowhere and disappear into nowhere, they do not have any meaning from Maxwell's relations perspective. These potentials prove useful in many problems, but here they appear as some sort of math-o-magic, a trick. Anyway, I think it's great to have derivation that does not introduce any additional variables. I don't expect everyone to share my excitement, but definitely this approach should be valued from methodological point of view.

Now let's proceed with two more possible pairs— $(T;S)$ and $(P;V)$. They produce two following equations

$$\begin{aligned}dT\wedge dS &= \left[\left(\frac{\partial P}{\partial T}\right)_S dT + \left(\frac{\partial P}{\partial S}\right)_T dS\right]\wedge\left[\left(\frac{\partial V}{\partial T}\right)_S dT + \left(\frac{\partial V}{\partial S}\right)_T dS\right],\\ dP\wedge dV &= \left[\left(\frac{\partial T}{\partial P}\right)_V dP + \left(\frac{\partial T}{\partial V}\right)_P dV\right]\wedge\left[\left(\frac{\partial S}{\partial P}\right)_V dP + \left(\frac{\partial S}{\partial V}\right)_P dV\right].\end{aligned}$$

Simplification yields some sort of themodynamical invariants

$$\boxed{\begin{aligned}1 &= \left(\frac{\partial P}{\partial T}\right)_S\left(\frac{\partial V}{\partial S}\right)_T - \left(\frac{\partial P}{\partial S}\right)_T\left(\frac{\partial V}{\partial T}\right)_S,\\ 1 &= \left(\frac{\partial T}{\partial P}\right)_V\left(\frac{\partial S}{\partial V}\right)_P - \left(\frac{\partial T}{\partial V}\right)_P\left(\frac{\partial S}{\partial P}\right)_V.\end{aligned}} \tag{3}$$

We are now done with "dU" case. But there are two more 1-forms in equation (1) that could be used in exactly the same way.

Let's choose dS as our next target for differentiation and rewrite (1) for conveniency

$$dS = \frac{dU}{T} + \frac{PdV}{T}.$$

Performing exterior differentiation one gets

$$0 = ddS = d\left(\frac{1}{T}dU + \frac{P}{T}dV\right) = -\frac{1}{T^2}dT\wedge dU + \frac{1}{T}dP\wedge dV - \frac{P}{T^2}dT\wedge dV,$$

or in a simplified form

$$T\ dP\wedge dV = dT\wedge dU + P\ dT\wedge dV.$$

It seems that we should check all combinations of 2 variables, but in fact three pairs (T,P), (T,V), and (U,V) lead to the same result. That's why there is actually no need for checking them all. Let's consider the pair that yields result with minimum algebraic transformations— (T,V)

$$T\left[\left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV\right]\wedge dV = dT\wedge\left[\left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV\right] + P\ dT\wedge dV.$$

After simplification we get **relation between thermic and caloric equations of state**

$$\boxed{T\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial U}{\partial V}\right)_T + P.} \tag{4}$$

Once again, we have a valuable physical result with almost no effort.

Two different combination of variables (T, U) and (P, V) produce two more pretty relations. First, one can do a minor rearrangement to make less calculations later

$$\begin{aligned}(T\ dP - P\ dT) \wedge dV = dT \wedge dU,\\ dT \wedge (dU + P\ dV) = T\ dP \wedge dV,\end{aligned}$$

and rewrite this equations in terms of chosen variables

$$\begin{aligned}\left[T\left(\frac{\partial P}{\partial T}\right)_U dT + T\left(\frac{\partial P}{\partial U}\right)_T dU - P\ dT\right] \wedge \left[\left(\frac{\partial V}{\partial T}\right)_U dT + \left(\frac{\partial V}{\partial U}\right)_T dU\right] = dT \wedge dU,\\ \left[\left(\frac{\partial T}{\partial P}\right)_V dP + \left(\frac{\partial T}{\partial V}\right)_P dV\right] \wedge \left[\left(\frac{\partial U}{\partial P}\right)_V dP + \left(\frac{\partial U}{\partial V}\right)_P dV + P\ dV\right] = T\ dP \wedge dV.\end{aligned}$$

Last equations can be simplified by expanding and using properties of differential forms

$$\begin{aligned}T\left(\frac{\partial P}{\partial T}\right)_U\left(\frac{\partial V}{\partial U}\right)_T - T\left(\frac{\partial P}{\partial U}\right)_T\left(\frac{\partial V}{\partial T}\right)_U - P\left(\frac{\partial V}{\partial U}\right)_T = 1,\\ \left(\frac{\partial T}{\partial P}\right)_V\left(\frac{\partial U}{\partial V}\right)_P + P\left(\frac{\partial T}{\partial P}\right)_V - \left(\frac{\partial T}{\partial V}\right)_P\left(\frac{\partial U}{\partial P}\right)_V = T.\end{aligned}$$

After rearrangement, let's multiply first equation by $(\partial U/\partial V)_T$, second by $(\partial P/\partial T)_V$, and use equation (4)

$$\begin{aligned}T\left(\frac{\partial P}{\partial T}\right)_U - T\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_U = \left(\frac{\partial U}{\partial V}\right)_T + P = T\left(\frac{\partial P}{\partial T}\right)_V,\\ \left(\frac{\partial U}{\partial V}\right)_P - \left(\frac{\partial T}{\partial V}\right)_P\left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial P}{\partial T}\right)_V - P = \left(\frac{\partial U}{\partial V}\right)_T,\end{aligned}$$

this yields two following neet relations

$$\boxed{\begin{aligned}\left(\frac{\partial P}{\partial T}\right)_U - \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_U,\\ \left(\frac{\partial U}{\partial V}\right)_P - \left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial T}{\partial V}\right)_P\left(\frac{\partial U}{\partial T}\right)_V.\end{aligned}} \tag{5}$$

The only unused combination is now (P, U), but I'll spoil that equations (4) and (5) are equivalent to what we get by considering this pair. Thus, it's better to skip them and proceed to the next 1-form that is dV.

Let's follow the scheme and perform rearrangement in (1)

$$dV = \frac{TdS}{P} - \frac{dU}{P},$$

with subsequent exterior differentiation

$$0 = ddV = d\left(\frac{T}{P}dS - \frac{1}{P}dU\right) = \frac{1}{P}dT \wedge dS - \frac{T}{P^2}dP \wedge dS + \frac{1}{P^2}dP \wedge dU,$$

and minor simplification to get more convenient expression

$$T\ dP \wedge dS = P\ dT \wedge dS + dP \wedge dU.$$

Now it's time for choosing pairs. Let me spoil again — pairs (T, P), (P, S), and (S, U) lead to equivalent expressions; there is no need to check them all. I chose $(P; S)$ pair as a basis. So, let's rearrange summands in a following way

$$dP \wedge (TdS - dU) = P\ dT \wedge dS.$$

We can express all variables in terms of P and S

$$dP \wedge \left(TdS - \left(\frac{\partial U}{\partial P}\right)_S dP - \left(\frac{\partial U}{\partial S}\right)_P dS\right) = P\left(\left(\frac{\partial T}{\partial P}\right)_S dP + \left(\frac{\partial T}{\partial S}\right)_P dS\right) \wedge dS,$$

expand everything and simplify. As result we will get something similar to relation connecting caloric and termic state equations

$$\boxed{T - \left(\frac{\partial U}{\partial S}\right)_P = P\left(\frac{\partial T}{\partial P}\right)_S.} \tag{6}$$

There are three more possible pairs of thermodynamic variables. Let's consider two of them — $(T; S)$ and $(P; U)$. It seems to be convenient rewrite equation as follows

$$\begin{aligned} dP \wedge (T\ dS - dU) &= P\ dT \wedge dS, \\ (T\ dP - P\ dT) \wedge dS &= dP \wedge dU. \end{aligned}$$

Now we expand all summands in terms of chosen variables

$$\begin{aligned} \left(\left(\frac{\partial P}{\partial T}\right)_S dT + \left(\frac{\partial P}{\partial S}\right)_T dS\right) \wedge \left(TdS - \left(\frac{\partial U}{\partial T}\right)_S dT - \left(\frac{\partial U}{\partial S}\right)_T dS\right) &= P\ dT \wedge dS, \\ \left(TdP - P\left(\frac{\partial T}{\partial P}\right)_U dP - P\left(\frac{\partial T}{\partial U}\right)_P dU\right) \wedge \left(\left(\frac{\partial S}{\partial P}\right)_U dP + \left(\frac{\partial S}{\partial U}\right)_P dU\right) &= dP \wedge dU, \end{aligned}$$

open parenthesis and cancel out exterior products of differential forms

$$\begin{aligned} T\left(\frac{\partial P}{\partial T}\right)_S - \left(\frac{\partial P}{\partial T}\right)_S \left(\frac{\partial U}{\partial S}\right)_T + \left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial U}{\partial T}\right)_S &= P, \\ T\left(\frac{\partial S}{\partial U}\right)_P - P\left(\frac{\partial T}{\partial P}\right)_U \left(\frac{\partial S}{\partial U}\right)_P + P\left(\frac{\partial T}{\partial U}\right)_P \left(\frac{\partial S}{\partial P}\right)_U &= 1. \end{aligned}$$

Multiplying first equation by $(\partial T/\partial P)_S$, second by $(\partial U/\partial S)_P$, and applying equation (6) to both of them we get

$$\boxed{\begin{aligned} \left(\frac{\partial U}{\partial S}\right)_T - \left(\frac{\partial U}{\partial S}\right)_P &= \left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial U}{\partial P}\right)_S, \\ \left(\frac{\partial T}{\partial P}\right)_U - \left(\frac{\partial T}{\partial P}\right)_S &= \left(\frac{\partial T}{\partial S}\right)_P \left(\frac{\partial S}{\partial P}\right)_U. \end{aligned}} \tag{7}$$

The only untreated combination is (T, U), but it yields relation that may be reduced to equations (6) and (7) and thus does not contain any new information.

Now let's move to revision and conclusions.

Conclusions

This article gives the short review of classical thermodynamic relations derived with the help of differential forms. This approach has its pros and cons: unorthodox math apparatus may seem strange though proves rewarding. The article gives unified algorithm to derive many thermodynamic relations including Maxwell's relations and connection between thermic and caloric equations of state. Compared to the ordinary approach, presented method is much shorter and has a pleasing minimalistic feature of using only those variables that appear in the final result.

Here are few books for further reading.

Aknowledgements

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