Classical Thermodynamics as a Consequence of Spacetime Geometry

Jay R. Yablon
910 Northumberland Drive
Schenectady, New York 12309-2814
jyablon@nycap.rr.com

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Abstract: Just as Maxwell's magnetic equations emerge entirely from dd = 0 of exterior calculus applied to a gauge potential A, so too does the second law of thermodynamics emerge from applying dd=0 to a scalar potential s. If we represent this as dds = dU = 0, then when the Gauss / Stokes theorem is used to obtain the integral formulation of this equation, and after breaking a time loop that appears in the integral equation, we find that U behaves precisely like the internal energy state variable, and that the second law of thermodynamics for irreversible processes naturally emerges.

Contents

1. Introduction

Nowhere is the power of differential forms geometry to determine physical results in spacetime more apparent than for the magnetic monopole equation of classical electrodynamics. One postulates a gauge potential one-form $A = A_\mu dx^\mu$ with an energy-dimensioned vector, defines from this a field strength two-form $F = dA = \frac{1}{2!}\partial_{[\mu} A_{\nu]} dx^\mu dx^\nu$, and applies the fundamental result *dd*=0 of exterior calculus that the exterior derivative of an exterior derivative is zero, to obtain $dF = ddA = 0$ which contains Gauss' and Faraday's classical laws for magnetism. Then, one applies an open triple integral to the monopole equation three-forms, also applies the Gauss / Stokes theorem $\int_M dH = \oint_{\partial M} H$ where H is a generalized *p*-form and ∂M is the closed exterior boundary of a *p*+1-dimensional manifold, and thereby obtains $\iiint dF = \oiint F = 0 \left(= \iiint 0\right)$ which are the classical magnetic equations in integral form. Good reviews of the underlying exterior calculus and differential forms are provided, for example, in [1] Chapter 4 and [2] Chapter IV.4.

The result that *dd*=0 does not, however, stop with its use to obtain $ddA = 0$. It applies to any *p*-form of any rank. In this paper, we shall demonstrate that by starting with a dimensionless *scalar* potential *s* which is a zero-form, defining a one form $U \equiv ds$, next obtaining the two-form $dU = dds = 0$, and finally integrating with Gauss / Stokes via $\iint dU = \oint U = 0 \left(= \iint 0\right)$, the energy-dimensioned vector U_μ in $U = U_\mu dx^\mu$ turns out to behave like the internal energy of a thermodynamic system, and the resulting integral form equations when studied in detail, turn out to contain the laws of classical thermodynamics.

In a nutshell: just as *dd*=0 when applied to a one-form potential via $dF = ddA = 0$ and then integrated contains the classical Gauss and Ampere laws for magnetism, this same *dd*=0 when applied to a zero-form potential via $dU = dds = 0$ and then integrated contains the laws of classical thermodynamics.

2. The Reversible Entropy Equation

As just introduced, the equation from which we will proceed is the two form equation:

$$dU = dds = 0 \tag{2.1}$$

as well as its integral formulation

$$\iint dU = \oint U = 0 \tag{2.2}$$

which uses Gauss / Stokes. Let us start by developing (2.1).

First, we may expand the differential forms to extract the tensor equation:

$$\partial_\mu U_\nu - \partial_\nu U_\mu = \partial_\mu \partial_\nu s - \partial_\nu \partial_\mu s = 0 . \tag{2.3}$$

We define the four components of the prospective internal energy vector as $U^\sigma \equiv (U, \mathbf{u})$, and of course the spacetime gradient operator $\partial_\mu = (\partial_t, \nabla)$ with $\partial_t = \partial / \partial t$. We shall work throughout in flat Minkowski spacetime with the metric tensor $\mathrm{diag}(\eta_{\mu\nu}) = (1,-1,-1,-1)$ used to raise and lower indexes.

For the space components, with $\mu = 1$, $\nu = 2$ we obtain $\partial_1 U_2 - \partial_2 U_1 = \partial_1 \partial_2 \tau - \partial_2 \partial_1 \tau = 0$, and once all three components are obtained, this readily generalizes to:

$$\nabla \times \mathbf{u} = \nabla \times \nabla \tau = 0 \tag{2.4}$$

The latter $\nabla \times \nabla \tau = 0$ of course is the mathematical identity that the curl of the gradient of a scalar is zero. The latter contains the physical content $\nabla \times \mathbf{u} = 0$, which tells is that the curl of the prospective internal energy three-vector $\mathbf{u}$ is zero.

With $\mu = 0$, $\nu = k = 1,2,3$ we obtain $\partial_0 U_k - \partial_k U_0 = \partial_0 \partial_k \tau - \partial_k \partial_0 \tau = 0$, which becomes:

$$-\partial_t \mathbf{u} - \nabla U = \frac{\partial}{\partial t} \nabla \tau - \nabla \frac{\partial \tau}{\partial t} = 0 . \tag{2.5}$$

The latter equation is simply the commutator identity $[\partial_t, \nabla] \tau = 0$, which together with $\nabla \times \nabla \tau = 0$ is the expansion of $dd\tau = 0$.

Putting (2.4) and (2.5) together showing only U^σ gives us the pair of differential equations which analogize via the differential form to $\nabla \cdot \mathbf{B} = 0$ and $\partial_t \mathbf{B} + \nabla \times \mathbf{E} = 0$, namely:

$$\begin{cases} \nabla \times \mathbf{u} = 0 \\ \partial_t \mathbf{u} + \nabla U = 0 \end{cases} . \tag{2.6}$$

Now let's turn to the integral equation (2.2).

Expanding the forms in (2.2)

$$\iint \tfrac{1}{2!} \left(\partial_\mu U_\nu - \partial_\nu U_\mu \right) dx^\mu dx^\nu = \oint U_\sigma dx^\sigma = 0 . \tag{2.7}$$

Separating space and time components and accounting for all index permutations we obtain:

$$\begin{aligned}&\iint\left(\partial_0 U_k-\partial_k U_0\right)dx^0dx^k\\&+\iint\left(\partial_1 U_2-\partial_2 U_1\right)dx^1dx^2+\iint\left(\partial_2 U_3-\partial_3 U_2\right)dx^2dx^3+\iint\left(\partial_3 U_1-\partial_1 U_3\right)dx^3dx^\nu\ .\\&=\oint U_0 dx^0+\oint U_k dx^k=0\end{aligned}\tag{2.8}$$

The covariant (lower-indexed) $U_k=\left(U,-\mathbf{u}\right)$, and of course the differential elements anticommute $dx^\mu dx^\nu=-dx^\nu dx^\mu$. So separating the time integral from the space integral in the top line and being careful with the signs, this may be written as:

$$\int\left(\int\left(\partial_t\mathbf{u}+\nabla U\right)\cdot\mathrm{d}l\right)\mathrm{d}t-\iint\left(\nabla\times\mathbf{u}\right)\cdot\mathrm{d}\mathbf{S}=\oint U\mathrm{d}t-\oint\mathbf{u}\cdot\mathrm{d}l=0\,.\tag{2.9}$$

Now, let us spend a moment on the term $\oint U\mathrm{d}t$, which is something of an oddity because it represents a *closed loop line integral over* *<u>time</u>* of the prospective state variable for internal energy. We of course know that the ability to travel a closed time loop is fictive in the natural world, but so too is a reversible thermodynamic process. So let's follow this through: The integral $\oint U\mathrm{d}t$ says that we start with the prospective internal energy U at time t=0, then move forward in time, but then eventually loop around and come back to t=0. So whatever we do between the first time 0 and the second time 0 will be reversed, because we arrive right back at time 0. *So the integral* $\oint U\mathrm{d}t$ *is, in many ways, the very definition of a reversible process.* And this, of course, is fictive, because time is only experienced in one direction. This is the first indication we have of some thermodynamic possibilities. Shortly, we shall break this time loop to establish Eddington's "arrow of time," but before we do so, we will want to make a connection to entropy S while (2.9) still represents a reversible process, because in a reversible process, $T\mathrm{d}S=\delta Q$ is an equality rather than an inequality, where T is the temperature, Q is the heat, and δ which operates on heat is an inexact differential which means that the heat upon which it operates is not a thermodynamic state function. Once the process becomes irreversible, then the entropy law becomes $T\mathrm{d}S\geq\delta Q$, but this inequality should be naturally supplied by the spacetime geometry, not inserted by hand.

We start with the first law of thermodynamics which we shall write as

$$dU=\delta Q-\delta W\ .\tag{2.10}$$

The exact differential form for internal energy is $dU=\frac{1}{2!}\left(\partial_\mu U_\nu-\partial_\nu U_\mu\right)dx^\mu dx^\nu$ which we can compact using a commutator to $dU=\frac{1}{2}\partial_{[\mu}U_{\nu]}dx^\mu dx^\nu$, while δQ and δW are the inexact differential forms for heat and work and therefore are not state functions. We can write these in expanded form as $\delta Q=\frac{1}{2}\delta_{[\mu}Q_{\nu]}dx^\mu dx^\nu$ and $\delta W=\frac{1}{2}\delta_{[\mu}W_{\nu]}dx^\mu dx^\nu$. By putting a negative sign in front of the work differential in (2.10) we are representing systems which gain heat, but perform work on (lose work energy to) the environment. To represent the components of the contravariant heat and work four-vectors we may employ $Q^\mu \equiv (Q, \mathbf{q})$ and $W^\mu \equiv (W, \mathbf{w})$. The exact differential as already noted is $\partial_\mu \equiv (\partial_t, \nabla)$. And we shall use $\delta_\mu \equiv (\delta_t, \boldsymbol{\delta})$ to represent the components of the inexact differentials. So expanding $\mathrm{d}U = \delta Q - \delta W$ and using the foregoing, we may write the first law in tensor format as:

$$\partial_{[\mu} U_{\nu]} = \delta_{[\mu} Q_{\nu]} - \delta_{[\mu} W_{\nu]} . \tag{2.11}$$

The 0k components of the above, contrast (2.5), are:

$$\partial_0 U_k - \partial_k U_0 = \delta_0 Q_k - \delta_k Q_0 - \left(\delta_0 W_\nu - \delta_k W_0\right) = -\partial_t \mathbf{u} - \nabla U = -\delta_t \mathbf{q} - \boldsymbol{\delta} Q + \delta_t \mathbf{w} + \boldsymbol{\delta} W . \tag{2.12}$$

The 12 components of (2.11) are $\partial_1 U_2 - \partial_2 U_1 = \delta_1 Q_2 - \delta_2 Q_1 - \delta_2 W_1 + \delta_1 W_2$ and this generalizes to:

$$-\nabla \times \mathbf{u} = -\boldsymbol{\delta} \times \mathbf{q} + \boldsymbol{\delta} \times \mathbf{w} . \tag{2.13}$$

We then use (2.12) and (2.13) in (2.9) to obtain:

$$\int \left(\int \left(\delta_t \mathbf{q} + \boldsymbol{\delta} Q - \delta_t \mathbf{w} - \boldsymbol{\delta} W \right) \cdot \mathrm{d}l \right) \mathrm{d}t - \iint \left(\boldsymbol{\delta} \times \mathbf{q} - \boldsymbol{\delta} \times \mathbf{w} \right) \cdot \mathrm{d}\mathbf{S} = \oint U \mathrm{d}t - \oint \mathbf{u} \cdot \mathrm{d}l = 0 . \tag{2.14}$$

Now that we have a reversible equation which contains $\delta_t \mathbf{q} + \boldsymbol{\delta} Q$ we turn to entropy. As already noted after (2.9), whenever a process is reversible as is (2.14) because of the closed time loop in $\oint U \mathrm{d}t$, the entropy is related to heat and temperature by the differential forms:

$$T dS = \delta Q . \tag{2.15}$$

Here, the entropy $S = S_\mu dx^\mu$ is also a one-form with four-vector components that we shall write as $S^\mu = (S, \mathbf{s})$. From the above we extract the tensor expression:

$$T \partial_{[\mu} S_{\nu]} = \delta_{[\mu} Q_{\nu]} . \tag{2.16}$$

The 0k relationship is then:

$$T \left(\partial_0 S_k - \partial_k S_0 \right) = \delta_0 Q_k - \delta_k Q_0 = -T \left(\partial_t \mathbf{s} + \nabla S \right) = -\delta_t \mathbf{q} - \boldsymbol{\delta} Q , \tag{2.17}$$

while the 12 index equation $T \left(\partial_1 S_2 - \partial_2 S_1 \right) = \delta_1 Q_2 - \delta_2 Q_1$ generalizes for all space indexes to:

$$-T \nabla \times \mathbf{s} = -\boldsymbol{\delta} \times \mathbf{q} . \tag{2.18}$$

We then use (2.17) and (2.18) to replace all the heat in (2.14) with entropy, thus advancing to:

$$\int\left(\int T\left(\left(\partial_t \mathbf{s}+\nabla S\right)-\delta_t \mathbf{w}-\boldsymbol{\delta} W\right)\cdot \mathrm{d}l\right)\mathrm{d}t-\iint\left(T\nabla\times\mathbf{s}-\boldsymbol{\delta}\times\mathbf{w}\right)\cdot \mathrm{d}\mathbf{S}=\oint U\mathrm{d}t-\oint \mathbf{u}\cdot \mathrm{d}l=0 . \tag{2.19}$$

Now that we have included the reversible entropy relationship in this reversible equation, it is time to see what happens when we make the above irreversible.

3. The Irreversible Entropy Equation

As we observed at (2.9), the integral $\oint U\mathrm{d}t$ which still appears in (2.19) informs us that this equation is for a fictive reversible process. This is why we able to properly utilize the reversible entropy relationship $TdS=\delta Q$ of (2.15) in (2.19). Now let us break this time loop, and establish an arrow of time. Specifically, let us now replace $\oint U\mathrm{d}t \rightarrow \int_0^t U\mathrm{d}t$ with an *irreversible* time integral. What can we say about $\oint U\mathrm{d}t$ and $\int_0^t U\mathrm{d}t$ in relation to 0 and to one another? If U represents internal energy, then given that energies are always represented as positive or zero, $U(t)\geq 0$ at all times t. However, in $\oint U\mathrm{d}t$ we are starting at a given time t=0, moving somewhere else in time, and then fictively returning to the same time t=0 at which we started. So the time loop integral $\oint U\mathrm{d}t=\int_0^0 U\mathrm{d}t=0$, irrespective of the energy. On the other hand, if the definite time t at the upper bound in $\int_0^t U\mathrm{d}t$ is greater than or equal to zero, i.e., if $t\geq 0$, then so too, $\int_0^t U\mathrm{d}t\geq 0$. Therefore:

$$\int_0^t U\mathrm{d}t \geq \oint U\mathrm{d}t=0 . \tag{3.1}$$

So if we now substitute $\oint U\mathrm{d}t \rightarrow \int_0^t U\mathrm{d}t$ with $t\geq 0$ into (2.19), then the term on the right will become greater than or equal to 0, and to capture this, we need to *simultaneously* replace the final $=0$ with a ≥ 0. Doing so, we obtain:

$$\int\left(\int\left(T\left(\partial_t \mathbf{s}+\nabla S\right)-\delta_t \mathbf{w}-\boldsymbol{\delta} W\right)\cdot \mathrm{d}l\right)\mathrm{d}t-\iint\left(T\nabla\times\mathbf{s}-\boldsymbol{\delta}\times\mathbf{w}\right)\cdot \mathrm{d}\mathbf{S}=\int_0^t U\mathrm{d}t-\oint \mathbf{u}\cdot \mathrm{d}l\geq 0 . \tag{3.2}$$

Now, we have an expression which expressly includes entropy terms, and by breaking the time loop and into an arrow of time, we have some expressions involving these entropy terms being ≥ 0. So we need to see if the second law relations $T\mathrm{d}S\geq \delta Q$ and / or $dS\geq 0$ are included in (3.2) in some clear form. First, as is done at this stage of developing for Maxwell's integral from differential forms, let us multiply through all of (3.2) by d/dt, thus:

$$d\int\left(\int\left(T\left(\partial_t \mathbf{s}+\nabla S\right)-\delta_t \mathbf{w}-\boldsymbol{\delta} W\right)\cdot \mathrm{d}l\right)-\frac{d}{dt}\iint\left(T\nabla\times\mathbf{s}-\boldsymbol{\delta}\times\mathbf{w}\right)\cdot \mathrm{d}\mathbf{S}=\frac{d}{dt}\int_0^t U\mathrm{d}t-\frac{d}{dt}\oint \mathbf{u}\cdot \mathrm{d}l\geq 0 . \tag{3.3}$$

In what is now $(d/dt)\int_0^t U\mathrm{d}t$ we have an offsetting $\mathrm{d}t/\mathrm{d}t=1$. And we may also apply $d\int=1$ to both this and the first term. So we then have:

$$\int\left(T\left(\partial_t\mathbf{s}+\nabla S\right)-\delta_t\mathbf{w}-\delta W\right)\cdot\mathrm{d}l-\frac{d}{dt}\iint\left(T\nabla\times\mathbf{s}-\delta\times\mathbf{w}\right)\cdot\mathrm{d}\mathbf{S}=U-\frac{d}{dt}\oint\mathbf{u}\cdot\mathrm{d}l\geq 0\,. \tag{3.4}$$

Now let's look at the terms to the left of the equal sign. On the right we have an integral $\iint\left(T\nabla\times\mathbf{s}-\delta\times\mathbf{w}\right)\cdot\mathrm{d}\mathbf{S}$ over an *open* surface. The open surface is bounded by a closed loop, yet the line integral $\int\left(T\left(\partial_t s+\nabla S\right)-\delta_t\mathbf{w}-\delta W\right)\cdot\mathrm{d}l$ on the left is also taken over an *open* path. So this does not match up. What do we do? The same situation is encountered in Maxwell's equations. For example, Gauss' Law for magnetism $\oiint\mathbf{B}\cdot\mathrm{d}\mathbf{S}=0$ is defined over a closed surface. But if one actually develops Faraday's law from the differential forms $\iiint dF=\oiint F=0$, the equation one first arrives at is $\oint\mathbf{E}\cdot\mathrm{d}l=-(d/dt)\oiint\mathbf{B}\cdot\mathrm{d}\mathbf{S}$ containing the same $\oiint\mathbf{B}\cdot\mathrm{d}\mathbf{S}$. But the boundaries are mismatched. So to match them up we convert the closed surface to an open surface, and thereby obtain $\oint\mathbf{E}\cdot\mathrm{d}l=-(d/dt)\iint\mathbf{B}\cdot\mathrm{d}\mathbf{S}$ which is Faraday's law. Then, the path of the closed line integral can be identified with the boundary of the open two-dimensional surface through which the magnetic field is flowing. The same exercise occurs when developing Ampere's law. So in (3.4), we need to match up the perimeter of the open boundary in $\iint\left(T\nabla\times\mathbf{s}-\delta\times\mathbf{w}\right)\cdot\mathrm{d}\mathbf{S}$ with a closed loop in $\int\left(T\left(\partial_t s+\nabla S\right)-\delta_t\mathbf{w}-\delta W\right)\cdot\mathrm{d}l$. Here, we need to turn the open line integral into a closed line integral. Making this boundary change, (3.4) now becomes:

$$\oint\left(T\left(\partial_t\mathbf{s}+\nabla S\right)-\delta_t\mathbf{w}-\delta W\right)\cdot\mathrm{d}l-\frac{d}{dt}\iint\left(T\nabla\times\mathbf{s}-\delta\times\mathbf{w}\right)\cdot\mathrm{d}\mathbf{S}=U-\frac{d}{dt}\oint\mathbf{u}\cdot\mathrm{d}l\geq 0\,. \tag{3.5}$$

Because there are now closed loop integrals on *both sides* of the above equality following the change in (3.5), we need to see if any terms might mutually cancel. At this point, let us backtrack a bit. Writing (2.12) as $-\delta_t\mathbf{w}-\delta W=-\delta_t\mathbf{q}-\delta Q+\partial_t\mathbf{u}+\nabla U$, we replace the work terms in the loop integral and use $\partial_t=\partial/\partial t$ to obtain:

$$\oint\left(T\left(\partial_t\mathbf{s}+\nabla S\right)-\delta_t\mathbf{q}-\delta Q+\frac{\partial}{\partial t}\mathbf{u}+\nabla U\right)\cdot\mathrm{d}l-\frac{d}{dt}\iint\left(T\nabla\times\mathbf{s}-\delta\times\mathbf{w}\right)\cdot\mathrm{d}\mathbf{S}=U-\frac{d}{dt}\oint\mathbf{u}\cdot\mathrm{d}l\geq 0\,. \tag{3.6}$$

Surely enough, the time-dependent $\oint(\partial/\partial t)\mathbf{u}\cdot\mathrm{d}l$ term now on the left of the equality is the same as the term $(d/dt)\oint\mathbf{u}\cdot\mathrm{d}l$ on the right of the equality. But because of the inequality ≥ 0, we need to be careful how we work with this equivalence.

The best approach is to now separate (3.6) into its two inequalities with the time-derivative outside each integral, and then to isolate this matching term in each, thus:

$$\begin{cases} \oint \frac{\partial}{\partial t}\mathbf{u}\cdot \mathrm{d}l \geq -\oint \left(T\left(\partial_t \mathbf{s}+\nabla S\right)-\delta_t \mathbf{q}-\delta Q+\nabla U\right)\cdot \mathrm{d}l+\frac{d}{dt}\iint \left(T\nabla\times\mathbf{s}-\boldsymbol{\delta}\times\mathbf{w}\right)\cdot \mathrm{d}\mathbf{S} \\ U\geq \frac{d}{dt}\oint \mathbf{u}\cdot \mathrm{d}l \end{cases}. \tag{3.7}$$

Then, we may once again recombine these two inequalities as such:

$$U\geq \frac{d}{dt}\oint \mathbf{u}\cdot \mathrm{d}l \geq -\oint \left(T\left(\partial_t \mathbf{s}+\nabla S\right)-\delta_t \mathbf{q}-\delta Q+\nabla U\right)\cdot \mathrm{d}l+\frac{d}{dt}\iint \left(T\nabla\times\mathbf{s}-\boldsymbol{\delta}\times\mathbf{w}\right)\cdot \mathrm{d}\mathbf{S}\,. \tag{3.8}$$

Then, we use $T\left(\partial_t s+\nabla S\right)=\delta_t \mathbf{q}+\delta Q$ from (2.17) to backtrack and further cancel terms, thus:

$$U\geq \frac{d}{dt}\oint \mathbf{u}\cdot \mathrm{d}l \geq -\oint \nabla U\cdot \mathrm{d}l+\frac{d}{dt}\iint \left(T\nabla\times\mathbf{s}-\boldsymbol{\delta}\times\mathbf{w}\right)\cdot \mathrm{d}\mathbf{S}\,. \tag{3.9}$$

Next, the term containing $\iint \left(T\nabla\times\mathbf{s}-\boldsymbol{\delta}\times\mathbf{w}\right)\cdot \mathrm{d}\mathbf{S}$ above originated in and is equal to the term $\iint \left(\nabla\times\mathbf{u}\right)\cdot \mathrm{d}\mathbf{S}$ in (2.9). But in (2.4) we found that by mathematical identity, $\nabla\times\mathbf{u}=\nabla\times\nabla\tau=0$. So this term

$$\frac{d}{dt}\iint \left(T\nabla\times\mathbf{s}-\boldsymbol{\delta}\times\mathbf{w}\right)\cdot \mathrm{d}\mathbf{S}=\frac{d}{dt}\iint \left(\nabla\times\mathbf{u}\right)\cdot \mathrm{d}\mathbf{S}=\iint \left(T\nabla\times\mathbf{s}-\boldsymbol{\delta}\times\mathbf{w}\right)\cdot \mathrm{d}\mathbf{S}=\iint \left(\nabla\times\mathbf{u}\right)\cdot \mathrm{d}\mathbf{S}=0 \tag{3.10}$$

is always zero by $\nabla\times\nabla\tau=0$, in all places at all times. We could have zeroed this out back at (2.9), but kept this in place so that we would be able to obtain these entropy and work identities and properly match up all the integral boundaries. So returning the remaining ∂_t to inside the line integral, this further simplifies (3.9) to:

$$U\geq \oint \partial_t \mathbf{u}\cdot \mathrm{d}l \geq -\oint \nabla U\cdot \mathrm{d}l\,. \tag{3.11}$$

Finally, we forward track again. From (2.12) we may separate the time-dependent relationship $\partial_t \mathbf{u}=\delta_t \mathbf{q}-\delta_t \mathbf{w}$ from the space-dependent $-\nabla U=-\delta Q+\delta W$ to rewrite the above:

$$U\geq \oint \left(\delta_t \mathbf{q}-\delta_t \mathbf{w}\right)\cdot \mathrm{d}l \geq \oint \left(-\delta Q+\delta W\right)\cdot \mathrm{d}l\,. \tag{3.12}$$

And from (2.17) we may also separate the time-dependent $\delta_t \mathbf{q}=T\partial_t \mathbf{s}$ from the space dependent $\delta Q=T\nabla S$ and return the entropy terms back into (3.12), thus:

$$U\geq \oint \left(T\partial_t \mathbf{s}-\delta_t \mathbf{w}\right)\cdot \mathrm{d}l \geq \oint \left(-T\nabla S+\delta W\right)\cdot \mathrm{d}l\,. \tag{3.13}$$

It will be seen that all of these terms were originally in (3.5) before we backtracked and then returned. Indeed, with the exception of U which still remains, all these terms were in $\oint\left(T\left(\partial_t\mathbf{s}+\nabla S\right)-\delta_t\mathbf{w}-\delta W\right)\cdot \mathrm{d}l$, and everything else has dropped out while in the process the irreversible inequality has been resituated. The above is a precise restatement of the original reversible $\iint dU=\oint U=0$ of (2.2) following full development and cancellation of terms, and after replacing the time loop integral with an arrow of time integral via $\oint U\mathrm{d}t\rightarrow\int_0^t U\mathrm{d}t$. If one were to revert the inequalities in the above back to equalities, then this would be completely the same as $\iint dU=\oint U=0$, and (3.13) would then describe a fictive reversible process.

4. The Second Law of Thermodynamics

At this point, let us focus on the latter inequality in (3.13), and move everything to the left side, thus:

$$\oint\left(T\partial_t\mathbf{s}+T\nabla S-\delta_t\mathbf{w}-\delta W\right)\cdot \mathrm{d}l\geq 0\,. \tag{4.1}$$

Also, let's return spacetime indexes so we can examine covariant behaviors in spacetime and using $\mathrm{diag}\left(\eta_{\mu\nu}\right)=\left(1,-1,-1,-1\right)$ to make sure the signs are correct. This yields:

$$\oint\left(-T\partial_0 S_k+T\partial_k S_0+\delta_0 W_k-\delta_k W_0\right)\cdot dx^k=\oint\left(T\partial_{[k}S_{0]}-\delta_{[k}W_{0]}\right)\cdot dx^k=\oint\left(T\partial_{[\mu}S_{0]}-\delta_{[\mu}W_{0]}\right)\cdot dx^\mu\geq 0\,. \tag{4.2}$$

Now let's compact this into the differential one-form equation. This is a bit different from a usual differential form, because there is one loose (uncontracted) time index. The expression $\partial_{[\mu}S_{0]}$ is a time component (and really, the time bivector) of a second rank antisymmetric tensor. Similarly for $\delta_{[\mu}W_{0]}$, except this contains an inexact differential. In general, if we only contract one index of such a tensor $S_{\mu\nu}=-S_{\nu\mu}$, then $S_\nu=S_{\mu\nu}dx^\mu$ and therefore $S_0=S_{\mu 0}dx^\mu$ is the time component of a four-vector of differential forms. So with that, (4.2) compacts fully to:

$$\oint\left(TdS_0-\delta W_0\right)\geq 0\,. \tag{4.3}$$

When the inexact work differential $\delta W_0=0$, this reduces to:

$$\oint dS_0\geq 0\,. \tag{4.4}$$

And this is the *second law of thermodynamics for an irreversible process*. At no point along the way did we have to put this inequality into this equation by hand. This inequality was a natural result of developing the differential form equation $dU=dds=0$ (2.1) in the integral form

$\iint dU = \oint U = 0$ of (2.2) and converting the resulting reversible time loop that emerged to an arrow of time, $\oint U\mathrm{d}t \to \int_0^t U\mathrm{d}t$. Were we to turn $\int_0^t U\mathrm{d}t$ back to $\oint U\mathrm{d}t$, everything would again become reversible, and (4.4) would become the fictive $\oint dS_0 = 0$.

5. Conclusion

Just as Maxwell's classical magnetic equations emerge entirely from *dd*=0 of exterior calculus applied to a gauge potential *A*, so too does classical thermodynamics emerge from applying *dd*=0 to a scalar potential *s*. If we represent this as $dds = dU = 0$, then U behaves precisely as the internal energy state variable, and after breaking a time loop that appears in the integral equation $\iint dU = \oint U = 0$ to make the this equation irreversible, we obtain the second law of thermodynamics in the form $\oint dS_0 \geq 0$, which governs the entropy state variable S_0 for an irreversible system.

References

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