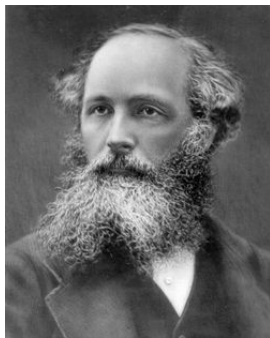


Classical Mechanics versus Thermodynamics



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Why do Hamilton's equations in classical mechanics:

$$\frac{dp}{dt} = -\frac{\partial H}{\partial q}$$

$$\frac{dq}{dt} = \frac{\partial H}{\partial p}$$

look so much like the Maxwell relations in thermodynamics?

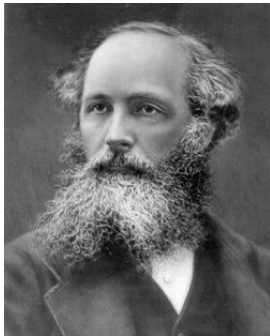
$$\left. \frac{\partial T}{\partial V} \right|_S = - \left. \frac{\partial P}{\partial S} \right|_V$$

$$\left. \frac{\partial S}{\partial V} \right|_T = \left. \frac{\partial P}{\partial T} \right|_V$$

William Rowan Hamilton discovered his equations describing classical mechanics in terms of *energy* around 1827. By 1834 he had also introduced *Hamilton's principal function*, which I'll explain later.



James Clerk Maxwell is most famous for his equations describing electromagnetism, perfected in 1865. But he also worked on thermodynamics, and discovered the “Maxwell relations” in 1871.



Hamilton's equations describe how the position q and momentum p of a particle on a line change with time t if we know the energy or **Hamiltonian** $H(q, p)$:

$$\frac{dp}{dt} = -\frac{\partial H}{\partial q}$$

$$\frac{dq}{dt} = \frac{\partial H}{\partial p}$$

Two of the **Maxwell relations** connect the volume V , entropy S , pressure P and temperature T of a system in thermodynamic equilibrium:

$$\left. \frac{\partial T}{\partial V} \right|_S = - \left. \frac{\partial P}{\partial S} \right|_V$$

$$\left. \frac{\partial S}{\partial V} \right|_T = \left. \frac{\partial P}{\partial T} \right|_V$$

Using this change of variables:

$$\begin{array}{ll} q \rightarrow S & p \rightarrow T \\ t \rightarrow V & H \rightarrow P \end{array}$$

Hamilton's equations:

$$\frac{dp}{dt} = -\frac{\partial H}{\partial q}$$

$$\frac{dq}{dt} = \frac{\partial H}{\partial p}$$

become these relations:

$$\frac{dT}{dV} = -\frac{\partial P}{\partial S}$$

$$\frac{dS}{dV} = \frac{\partial P}{\partial T}$$

These are *almost* like two of the Maxwell relations:

$$\frac{dT}{dV} = -\frac{\partial P}{\partial S}$$

$$\frac{dS}{dV} = \frac{\partial P}{\partial T}$$

But in thermodynamics we always use partial derivatives and say which variables are held constant:

$$\left. \frac{\partial T}{\partial V} \right|_S = - \left. \frac{\partial P}{\partial S} \right|_V$$

$$\left. \frac{\partial S}{\partial V} \right|_T = \left. \frac{\partial P}{\partial T} \right|_V$$

If we write Hamilton's equations in the same style as the Maxwell relations, they look funny:

$$\left. \frac{\partial p}{\partial t} \right|_q = - \left. \frac{\partial H}{\partial q} \right|_t$$

$$\left. \frac{\partial q}{\partial t} \right|_p = \left. \frac{\partial H}{\partial p} \right|_t$$

Can this possibly be right? *Yes!*

When we work out the analogy between classical mechanics and thermodynamics we'll see why.

We can get Maxwell's relations starting from this: the internal energy U of a system in equilibrium depends on its entropy S and volume V .

Temperature and pressure are derivatives of U :

$$T = \left. \frac{\partial U}{\partial S} \right|_V \quad P = - \left. \frac{\partial U}{\partial V} \right|_S$$

Maxwell's relations follow from the fact that mixed partial derivatives commute! For example:

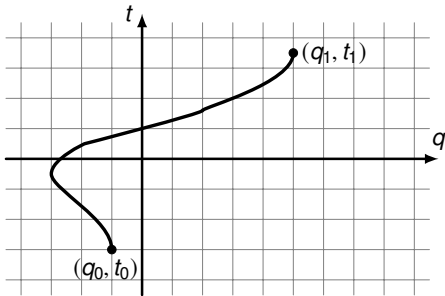
$$\left. \frac{\partial T}{\partial V} \right|_S = \left. \frac{\partial}{\partial V} \right|_S \left. \frac{\partial}{\partial S} \right|_V U = \left. \frac{\partial}{\partial S} \right|_V \left. \frac{\partial}{\partial V} \right|_S U = - \left. \frac{\partial P}{\partial S} \right|_V$$

To get Hamilton's equations the same way, we need a function W of the the particle's position q and time t such that

$$p = \left. \frac{\partial W}{\partial q} \right|_t \quad H = - \left. \frac{\partial W}{\partial t} \right|_q$$

Then we'll get Hamilton's equations from the fact that mixed partial derivatives commute!

The trick is to let W be "Hamilton's principal function".

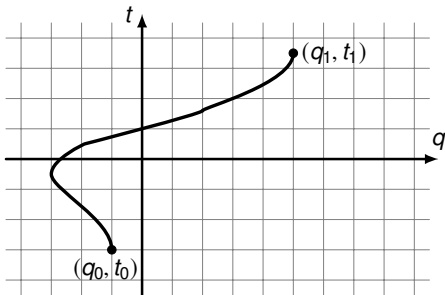


The **action** of a particle's path is

$$\int_{t_0}^{t_1} L(q(t), \dot{q}(t)) dt$$

where L is the **Lagrangian**:

$$L(q, \dot{q}) = p\dot{q} - H(q, p)$$



The particle always takes a path from (q_0, t_0) to (q_1, t_1) that's a critical point of the action. Let's assume it's a *minimum*. We can derive Hamilton's equations from this fact.

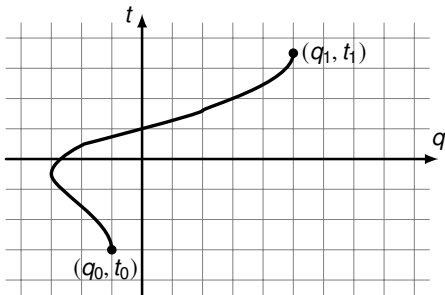
The least action for any path from (q_0, t_0) to (q_1, t_1) is called **Hamilton's principal function**:

$$W(q_0, t_0, q_1, t_1) = \min_{q \text{ with } q(t_0)=q_0, q(t_1)=q_1} \int_{t_0}^{t_1} L(q(t), \dot{q}(t)) dt$$

A beautiful fact: if we differentiate Hamilton's principal function, we get back the energy H and momentum p :

$$\frac{\partial}{\partial q_0} W(q_0, t_0, q_1, t_1) = -p(t_0) \quad \frac{\partial}{\partial t_0} W(q_0, t_0, q_1, t_1) = H(t_0)$$

$$\frac{\partial}{\partial q_1} W(q_0, t_0, q_1, t_1) = p(t_1) \quad \frac{\partial}{\partial t_1} W(q_0, t_0, q_1, t_1) = -H(t_1)$$



$$\begin{aligned}\frac{\partial}{\partial t_0} W(t_0, q_0, t_1, q_1) &= -H(t_0) & \frac{\partial}{\partial q_0} W(t_0, q_0, t_1, q_1) &= p(t_0) \\ \frac{\partial}{\partial t_1} W(t_0, q_0, t_1, q_1) &= H(t_1) & \frac{\partial}{\partial q_1} W(t_0, q_0, t_1, q_1) &= -p(t_1)\end{aligned}$$

You can prove these equations using

$$L = p\dot{q} - H$$

which implies that

$$W(q_0, t_0, q_1, t_1) = \int_{q_0}^{q_1} p dq - \int_{t_0}^{t_1} H dt$$

where we integrate along the minimizing path.

Now let's fix a starting-point (q_0, t_0) for our particle, and say its path ends at (q, t) . Think of Hamilton's principal function as a function of just (q, t) :

$$W(q, t) = W(q_0, t_0, q, t)$$

Then the particle's momentum and energy when it reaches (q, t) are:

$$p = \left. \frac{\partial W}{\partial q} \right|_t \quad H = - \left. \frac{\partial W}{\partial t} \right|_q$$

This is just what we wanted. Hamilton's equations now follow from the fact that mixed partial derivatives commute!

Classical Mechanics	Thermodynamics
action $W(q, t)$	internal energy $U(V, S)$
position q	entropy S
momentum $p = \frac{\partial W}{\partial q}$	temperature $T = \frac{\partial U}{\partial S}$
time t	volume V
energy $H = -\frac{\partial W}{\partial t}$	pressure $P = -\frac{\partial U}{\partial V}$
$dW = pdq - Hdt$	$dU = TdS - PdV$

What's really going on in this analogy? Let's dig deeper.

I said we could get Maxwell's relations from the fact that mixed partials commute, and gave one example:

$$\left. \frac{\partial T}{\partial V} \right|_S = \left. \frac{\partial}{\partial V} \right|_S \left. \frac{\partial}{\partial S} \right|_V U = \left. \frac{\partial}{\partial S} \right|_V \left. \frac{\partial}{\partial V} \right|_S U = - \left. \frac{\partial P}{\partial S} \right|_V$$

But to get the other Maxwell relations we need to differentiate other functions — and there are *four* of them!

U **internal energy**

$U - TS$ **Helmholtz free energy**

$U + PV$ **enthalpy**

$U + PV - TS$ **Gibbs free energy**

This has annoyed students of thermodynamics for over a century. Is there some other way? Yes!

In 1958 David Ritchie showed we can get all four Maxwell relations from one equation! Start here:

$$dU = TdS - PdV$$

Integrate around a loop γ :

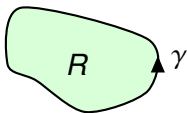
$$\oint_{\gamma} TdS - PdV = \oint_{\gamma} dU = 0$$

so

$$\oint_{\gamma} TdS = \oint_{\gamma} PdV$$

The **heat** added to a system equals the **work** it does in this cycle.





Green's theorem implies that if a loop γ encloses a region R ,

$$\oint_{\gamma} T dS = \int_R dT dS$$

Similarly

$$\oint_{\gamma} P dV = \int_R dP dV$$

But we know these are equal!

Since

$$\int_R dT dS = \int_R dP dV$$

for any region R enclosed by a loop, we must have

$$dT dS = dP dV$$

In fact, all of Maxwell's relations are hidden in this one equation!

Mathematicians call something like $dT dS$ a **2-form** and write it as $dT \wedge dS$. It's an "oriented area element", so

$$dT dS = -dS dT$$

$$dT dS = dP dV$$

We can choose any coordinates X, Y and get

$$\frac{dT dS}{dX dY} = \frac{dP dV}{dX dY}$$

$$dT dS = dP dV$$

We can choose any coordinates X, Y and get

$$\frac{dT dS}{dX dY} = \frac{dP dV}{dX dY}$$

(Yes, this is mathematically allowed.)

$$dT dS = dP dV$$

We can choose any coordinates X, Y and get

$$\frac{dT dS}{dX dY} = \frac{dP dV}{dX dY}$$

If we take $X = V, Y = S$ we get

$$\frac{dT dS}{dV dS} = \frac{dP dV}{dV dS}$$

$$dT dS = dP dV$$

We can choose any coordinates X, Y and get

$$\frac{dT dS}{dX dY} = \frac{dP dV}{dX dY}$$

If we take $X = V, Y = S$ we get

$$\frac{dT dS}{dV dS} = -\frac{dV dP}{dV dS}$$

$$dT dS = dP dV$$

We can choose any coordinates X, Y and get

$$\frac{dT dS}{dX dY} = \frac{dP dV}{dX dY}$$

If we take $X = V, Y = S$ we get

$$\frac{dT dS}{dV dS} = -\frac{dV dP}{dV dS}$$

$$dT dS = dP dV$$

We can choose any coordinates X, Y and get

$$\frac{dT dS}{dX dY} = \frac{dP dV}{dX dY}$$

If we take $X = V, Y = S$ we get

$$\frac{dT dS}{dV dS} = - \frac{dV dP}{dV dS}$$

and thus

$$\left. \frac{\partial T}{\partial V} \right|_S = - \left. \frac{\partial P}{\partial S} \right|_V$$

(Yes, this is mathematically justified!)

$$dT dS = dP dV$$

We can choose any coordinates X, Y and get

$$\frac{dT dS}{dX dY} = \frac{dP dV}{dX dY}$$

If we take $X = T, Y = V$ we get

$$\frac{dT dS}{dT dV} = \frac{dP dV}{dT dV}$$

$$dT dS = dP dV$$

We can choose any coordinates X, Y and get

$$\frac{dT dS}{dX dY} = \frac{dP dV}{dX dY}$$

If we take $X = T, Y = V$ we get

$$\frac{dT dS}{dT dV} = \frac{dP dV}{dT dV}$$

$$dT dS = dP dV$$

We can choose any coordinates X, Y and get

$$\frac{dT dS}{dX dY} = \frac{dP dV}{dX dY}$$

If we take $X = T, Y = V$ we get

$$\frac{dT dS}{dT dV} = \frac{dP dV}{dT dV}$$

or

$$\left. \frac{\partial S}{\partial V} \right|_T = \left. \frac{\partial P}{\partial T} \right|_V$$

$$dT dS = dP dV$$

We can choose any coordinates X, Y and get

$$\frac{dT dS}{dX dY} = \frac{dP dV}{dX dY}$$

If we take $X = T, Y = V$ we get

$$\frac{dT dS}{dT dV} = \frac{dP dV}{dT dV}$$

or

$$\left. \frac{\partial S}{\partial V} \right|_T = \left. \frac{\partial P}{\partial T} \right|_V$$

Other choices of X, Y give two more Maxwell relations.

In short, Maxwell's relations all follow from one simple equation:

$$dT dS = dP dV$$

Similarly, Hamilton's equations follow from this equation:

$$dp dq = dH dt$$

All calculations work in *exactly* the same way!

We can get these equations efficiently using the identity $d^2 = 0$ and the product rule for d :

$$dU = TdS - PdV \Rightarrow d^2U = d(TdS - PdV)$$

$$\Rightarrow 0 = dT dS - dP dV$$

$$\Rightarrow dT dS = dP dV$$

Now start with \mathbb{R}^4 with coordinates (S, T, V, P) , treating P and V as independent from S and T . This 2-form on \mathbb{R}^4 :

$$\omega = dT dS - dP dV$$

is called a **symplectic structure**.

Choosing the internal energy $U(S, V)$, we get this 2d **surface of equilibrium states**:

$$\Lambda = \left\{ (S, T, V, P) : T = \left. \frac{\partial U}{\partial S} \right|_V, P = - \left. \frac{\partial U}{\partial V} \right|_S \right\} \subset \mathbb{R}^4$$

Since

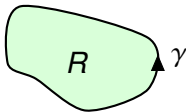
$$\omega = dT dS - dP dV$$

we know

$$\int_R \omega = 0$$

for any region in the surface Λ , since on this surface $dU = TdS - PdV$ and our old argument applies.

This fact encodes the Maxwell relations! Physically: for any cycle on the surface of equilibrium states, the heat flow in equals the work done.



Similarly, in classical mechanics we can start with \mathbb{R}^4 with coordinates (q, p, t, H) , treating p and H as independent from q and t . This 2-form on \mathbb{R}^4 :

$$\omega = dH dt - dp dq$$

is a symplectic structure. Hamilton's principal function $W(q, t)$ defines a 2d surface

$$\Lambda = \left\{ (q, p, t, H) : p = \left. \frac{\partial W}{\partial q} \right|_t, H = - \left. \frac{\partial W}{\partial t} \right|_q \right\} \subset \mathbb{R}^4$$

We have $\int_R \omega = 0$ for any region R in Λ . And this fact encodes Hamilton's equations!

SUMMARY

In thermodynamics, any 2d region R in the surface Λ of equilibrium states has

$$\int_R \omega = 0$$

This is equivalent to the Maxwell relations.

In classical mechanics, any 2d region R in the surface Λ of allowed (q, p, t, H) 4-tuples for particle trajectories through a single point (q_0, t_0) has

$$\int_R \omega = 0$$

This is equivalent to Hamilton's equations.

These facts generalize when we add extra degrees of freedom, e.g. the particle number N in thermodynamics:

$$\omega = dT dS - dP dV + d\mu dN$$

or more dimensions of space in classical mechanics:

$$\omega = dp_1 dq_1 + \cdots + dp_{n-1} dq_{n-1} - dH dt$$

We get a vector space \mathbb{R}^{2n} with a 2-form ω on it, and a **Lagrangian submanifold** $\Lambda \subset \mathbb{R}^{2n}$: a n -dimensional submanifold such that

$$\int_R \omega = 0$$

for any 2d region $R \subset \Lambda$.

EVERYTHING IS A LAGRANGIAN SUBMANIFOLD

— Alan Weinstein

MAXWELL'S RELATIONS VERSUS HAMILTON'S EQUATIONS

$$\left. \frac{\partial T}{\partial V} \right|_S = - \left. \frac{\partial P}{\partial S} \right|_V \qquad \left. \frac{\partial p}{\partial t} \right|_q = - \left. \frac{\partial H}{\partial q} \right|_t$$

$$\left. \frac{\partial S}{\partial V} \right|_T = \left. \frac{\partial P}{\partial T} \right|_V \qquad \left. \frac{\partial q}{\partial t} \right|_p = \left. \frac{\partial H}{\partial p} \right|_t$$

$$\left. \frac{\partial V}{\partial T} \right|_P = - \left. \frac{\partial S}{\partial P} \right|_T \qquad \left. \frac{\partial t}{\partial p} \right|_H = - \left. \frac{\partial q}{\partial H} \right|_p$$

$$\left. \frac{\partial V}{\partial S} \right|_P = \left. \frac{\partial T}{\partial P} \right|_S \qquad \left. \frac{\partial p}{\partial H} \right|_q = \left. \frac{\partial t}{\partial q} \right|_H$$