The Inglorious History of Thermodynamics

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Lisez Euler, lisez Euler, c'est nous maiître à tous!

Pierre-Simon Laplace

Abstract. Usually, physics students don't like thermodynamics: it is incomprehensible. They commonly get told to get used to it. Later on, as an expert, they'll find that the thermodynamic calculations come with surprises: sometimes evil, sometimes good. That can mean only one thing: The theory is inconsistent. In here, it will be shown where that is.

1. Lisez Euler

Laplace meant what he said, and he knew what Daniel Bernoulli and Leonhard Euler worked out in Basel and Saint Petersburg 30-60 years ago: His theory of gravitation introduced hydrodynamics and Euler's methods into classical mechanics - a fact that was well-understood by Lyapunow in Russia, but completely overlooked in the rest of the world.

In order to shed a bit of light on Bernoulli's and Euler's doings: Newton's axioms surely were a lovely set of mathematical statements for one or two particles, but noone ever succeeded to calculate three or more interacting particles with that. At that point, Bernoulli radically cut down the hindering $3N$ location coordinates of an N-particle system to three location coordinates which allowed to describe the flow of myriads of particles altogether, which made up the hydromechanics. Euler's path however was a more subtle one: He noticed that generally (i.e.: in case the forces are the differential of a potential energy V), the equations of motion of an N-particle system could be described as the extremal paths of a function $L = T - V$ of $3N$ location coordinates q_j, their velocities $\dot{q}_j$, and the time coordinate t, where T denotes the kinetical energy of the system. (The function L now is oddly called Lagrange function, and the equations are termed the Euler-Lagrange equations.) The hindsight with these extremal equations is that the conjugates of all coordinates, which the Lagrange function does not explicitly depend upon, drop out as integration constants. And, for the most parts, a coordinate system

can be chosen, such that the new coordinates are constant along the path of motion. Hence, the equations of many N-particle systems can be solved, which previously were held to be insolvable. (What in Göttingen was termed to be Noether's theorem at the beginning of the 20th century, was nothing new: it was Euler's well-understood, common practice since at least 1750.)

We'll pick up with Euler later. For now, let's summarize that Bernoulli and Euler had set the theoretical foundation for a possible theory of heat.

2. Steam Engine

The steam engine was invented in England at lifetime of both Euler and Bernoulli by Thomas Newcomen and enhanced by James Watt, and it became the driving force for its industrialization. It is highly uneffient (by design), but just because it was the "ideal" machine for the forthcoming thermodynamics, it is necessary to describe its working shortly: heated water vapor was let in to a cylinder with a moveable, airtight piston, then cold water was sprayed into the cylinder, extracting the vapor molecules the warm condensed water, rinsing into the cool water basin, and the cooled down gas contracted, pulling in the piston, which would do work against an external system. It was clear from scratch that the "heat" Q in the hot vapor containing cylinder was energy, and the transfer of much of that to the cool water basin meant a tremendous loss of unused energy. So, the very first problem to answer should have been: is that loss by design, or is it by principle? - However, the evolving thermodynamics took as granted to be by principle:

3. Beginnings of Thermodynamics

The big industrial success of the Watt's machine towards the end of the 18th century drew considerable attention to the then leading French physics community, reviving the theory of gas with its formost theorem, the law of Boyle-Mariotte (then 100 years old), and it was in line with these, that Lazar N. Carnot and his sun Sadi Carnot engaged themselves in the physical understanding of the steam engine, and in the year 1824, Sadi published a summarizing book on that, [1], which became famous, not because of its rocksolid physical contents, but because it was unavailable for nearly 70 years, and it was constantly referred to it indirectly. (Therefore, I highly recommend reading that book, althemore, since it was finally re-published 1892 by Ostwald, the foremost advocate of a felt supremacy of thermodynamics over "atomism", governing the 19th century in Germany.)
Remarkably, Carnot's book does not mention a cycle, not really touches on the reversibility, and there is no mention of the engine's efficiency, so no notion of what relates to the entropy.

Ten years after, in the year 1834, E. Clapyeron wrote his famous paper [3], pointing to Carnot's book [1] as his principal source. That paper included nearly all of what was to become the thermodynamics, from the cycle, later

incorrectly attributed to Carnot (see figure 1 below), the irreversibility considerations, the calculation of energy consumption of (reversible) steam engines, to the introduction of entropy.

It also included a sad mathematical error of confusing the path integration over the cycle with the calculation of the encircled area (see: next section), which will turn out to be the cause of much of the cumbersome energy and reversibility discussion within thermodynamics. Historically, R. Clausius' book [2] from 1850 is understood to have been the next milestone for thermodynamics. (Unfortunately, I was not able to note essential changes in contents compared to [3]: Both, Carnot and Clapyeron already state, that the flow of heat was only from high to low temperature. Clausius later expressed that as the 2nd law of thermo-

FIGURE 1. Carnot cycle.

dynamics, while the very nature of heat was left unqualified as some kind of energy. As to Clausius, the 15th edition of Encyclopedia Britannica says: (He) "is credited with making thermodynamics a science".)

Strangely neither Carnot, nor in succession Clapyeron, Clausius, Meyer, Helmholtz, Ostwald do mention Euler and Bernoulli at all. Both, Euler and Bernoulli, simply had been forgotten.
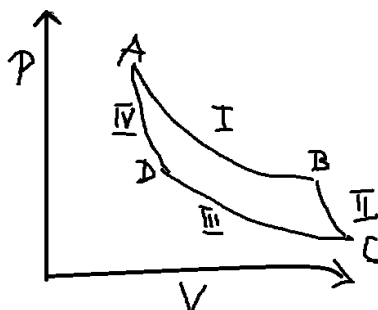
4. Comprenez Euler

What the beginning thermodynamics had missed out, is elucidated by a short citation from Euler's popular lecture notes on physics (see: [4, p.137]) on heat and combustion from 1761:

> *Wenn nämlich die natürlichen Sonnenstrahlen auf einen Körper fallen, so bringen sie dessen kleinste Theilchen zum Erzittern oder in eine schwingende Bewegung, welche ihrerseits neue Strahlen hervorzurufen vermag, wodurch eben der Körper sichtbar wird. Ein Körper ist überhaupt nur erleuchtet und sichtbar, insofern seine eigenen Theile in eine so rasche schwingende Bewegung versetzt werden, daß er imstande ist, im Aether neue Strahlen hervorzurufen... Denn wenn ein Körper brennbar ist, wie das Holz, so wird die Trennung seiner kleinsten Theilchen, verbunden mit der heftigsten Bewegung einen großen Theil derselben in Form von Rauch in die Luft treiben, während die größeren Theile als Asche zurückbleiben. Schmelzbare Körper, wie Metalle, werden durch die Trennung ihrer kleinsten Theilchen flüssig, und man kann hieraus begreifen wie das Feuer auf die Körper wirkt.*

In particular, what Euler a.o. wrote is: Heat is kinetic energy of the N-particle body (which is a statement, commonly attributed to Robert Mayer, a century later). As easy as it is to derive energy conservation from the Euler-Lagrange equation for a not explicitly time dependent potential field, it seems unlikely that Euler, the master of cyclic coordinates, did not know about energy conservation. As of today still one third of Eulers work has not yet been published, which comprises much of his papers late of age.

Even more, conservative N-particle systems would just fit into his view of mechanics: For one, his mechanical world could always be expressed through the single function $L(q, \dot{q}, t) = T - V$ of a vector of location coordinates $q = (q_1, \ldots, q_{3N})$, the velocity vector $\dot{q} = (\dot{q}_1, \ldots, \dot{q}_{3N})$, and a time parameter $t \in \mathbb{R}$, which means that the overall force must be integrable to a scalar potential field $V(q, \dot{q}, t)$. The motion of all N particles then is nothing but a (time) curve starting from some vector q_0 with velocity $\dot{q}_0$ at time t_0 to some other end location vector q_0' at end time t_0'. And, knowing that time is completely decoupled from location coordinates, for a mathematician there is nothing more natural than to always start from time zero and end at time 1. The very first scratch of an idea would therefore be to demand time translation invariance for time, as a second postulate, to be allowed to always start from time 0. And the third postulate would be that a scaling of time $t \mapsto \lambda t$ for any positive $\lambda > 0$ would map the the given dynamic system into an equivalent one, which I call "scale covariance", since that would allow to set the end time equal to 1, always.

And indeed, the time-translation invariance demands that V will no longer be explicitly depending on time (as is well-known), and the scale postulate likewise implies V not to be explicitly dependent of the velocities. Plus, looking at the Euler-Lagrange equations $\partial L / \partial q + \frac{d}{dt} \frac{\partial}{\partial \dot{q}} L = 0$, where V is only a function of q, we see that the scaling of time $t \mapsto \lambda t$ is equivalent to the scaling of the potential energy by the factor λ^{-1}. That is the desired covariance: A scaling of time by a factor λ can be compensated by scaling the potential energy by λ^{-1}.

That would make $E := E_0 + T + V$ a cyclic (invariant) coordinate, where E_0 is an arbitrary, yet properly to pick integration constant for the system. Summarizing: if at all the Carnot cycle is telling us a story from Euler's view, then it is hiding us the rest of the energy, which is a rest mass E_0 and a potential $V(q)$, whereas the sum E, the total energy will have to be conserved at all times on a dynamically possible path of particle motion!

5. Integrating the Carnot cycle

What Euler did with $6N$ coordinates, that can also be done with two, namely the pressure P and the volume V, shown in the above graph 1: the curve is composed of 4 smooth curves $I, \ldots, IV$, so the result will be the sum of path integration of these four curves. Let $\omega : [t_0, t_1] \mapsto (\omega_P(t), \omega_V(t)) \in \mathbb{R}^2$ be any one of these curves, where $[t_0, t_1]$ denotes the (closed) time interval

from t_0 to t_1. The function to integrate is $L(P,V) := PV$, so path integral is $\int L d\omega = \int_{t_0}^{t_1} \omega_P(t)\omega_V(t)\|\frac{d\omega(t)}{dt}\|dt$. Adding all four values up, we get zero. Why? Because the entire path is closed, is piecewise continuously differentiable, and L is continuous and well-defined throughout $\mathbb{R}^2$. Zero action means zero loss or gain in energy, which of course becomes trivial, when demanding the whole system to be energy preserving.

Now, let us define a system to be reversible, if the Euler-Lagrange equations are invariant w.r.t. time reflection $t \mapsto -t$. Obviously, conservation of energy implies reversibility. The opposite direction, however, is untrue: reversibility does not imply conservation of energy, but if energy would not be conserved, then the system would not be invariant w.r.t. time translation. And of an engine, in particular, we would expect it to work the same today as tomorrow. That said, we can replace the reversibility demand of the Carnot engine with the demand of conserving energy. Let's now look a little closer at this machine: It has two distinct modes, an idle mode and a load mode. In idle mode, we don't feed it with any energy, there will be no energy in and no energy out.

Using the universal gas law, $PV = NkT$ (which Clapyeron derived from the laws of Boyle- Mariotte and Gay-Lussac (see: [3, p.164])), we see that Clapyeron designed path I as the hyperbola $P(V) = (const)/V$ of points (P,V) of constant heat quantity PV. Since the total energy is constant and that heat quantity is constant on that path, so must be the potential energy U (which we now have to give the different symbol U in order not to clash with the volume V). So, everything of dynamical relevance is constant on path I, and the analogous holds for path III. These two paths do nothing, they are completely uninteresting and useless. It's only path II and path IV, where something is happening, and they are doing just the reverse of eachother: the path -IV from point A to D is equivalent to path II: on it, the heat drops from a high value to a low value, and that means that as the heat drops, an additional potential energy must increase from 0 to the energy difference between high and low heat. So, the whole system turns out to be a harmonic oscillator, where heat is nothing but the system's kinetic energy - as proposed by Euler!
But there is more: The oscillator deviates around the average temperatur $T_{av} = \frac{1}{2}(T_{hot} - T_{cold})$ (where T_{hot} is the temperature on path I and T_{cold} that of path III), which determines the oscillation energy per period to be $E_{osc} = \frac{nk}{\sqrt{2\pi}}T_{av}$.

Now, how can that energy-conserving oscillator machine do work on an external system? The answer is: it cannot. But it can transform energy coming in into equal energy going out: each time the oscillator converted the maximum kinetic energy into potential energy (of either sign), which means, when the oscillator reached either path I or III, we may exchange the particles of the same total energy with minimal potential energy and an appropriately higher kinetic energy. And the potential energy of the expelled

particles are usable for doing work! In all, although the total energy is maintained throughout, the Carnot engine would be able to "import" heat and convert it into usable potential energy. (Note: if we exchanged the particles only at the low temperature, then we'd get an ideal Newcomen machine, and with an exchange at both high and low temperature points, that's what's making it an ideal Watt's machine.)

6. Entropy and Irreversibility

Clausius followed Clapyeron in his interpretation of the area between curve III and the V-axis (defined by $P \equiv 0$) to be a measure of inefficiency of the (reversible) Carnot engine. That said, translating the system along the positive P-axis, the Carnot engine would become steadily more inefficient. It is a curious idea, because the heat consumption only depends on the difference of the temperature, not on the temperature or pressure itself. Anyhow, the ratio of the enclosed area of the Carnot cycle by the area under the path I was calculated, and it was found to be the simple formula $W := Q_{eff}/Q_{total} = 1 - \frac{T_{cold}}{T_{hot}}$, see e.g. [5, eq. 44.14]. That led to a factor Q/T that was conserved in a (reversible) Carnot cycle. The entropy S then is defined as the indefinite integral $S = \int \frac{dQ}{T}$, which exists as an up to a constant defined function in the cone $\{(T, V) \in \mathbb{R}^2 | T, V > 0\}$, see: [5, Sec. 4-6]: it's just the same argument as for the Carnot circle: if the (real-valued) function is defined throughout that cone (which is convex) and is continuous therein, then the path integral over any closed, (piecewise) continuously differentiable paths is zero. That's why that integral is defined up to a constant. (Out of the box, that indefinite integral is logarithmic of nature, so it never can be extended to a point, where the denominator T vanishes. But Walter Nernst could: he simply declared it to be zero, when T is zero, which would fix the additive constant of S. He called this then a theorem.)

So, what is the physical meaning of entropy? Assuming that the number of particles N in the system is constant, the universal gas law gives: $dQ/T = d(PV)/T = NkdT/T$, so $S = ln(T) + Const$, and is monotone increasing with T. So, with the assumption that an irreversible dynamic system will strictly heat up the system, then it would follow that the entropy increases. However, that is not the case:
The classic experiment to show irreversibility is a closed container with a wall that separates two volumes A and B say which are filled with two gasses G_A and G_B at temperature T_1 and T_2, say. So, the heat Q_1 of G_A is given by $Q_1 = N_1 k T_1$, and analogously $Q_2 = N_2 k T_2$ is that of G_B, where N_1 and N_2 are the numbers of particles in either gas.
The irreversible observation now is: Not depending from the values Q_1 and Q_2, G_A and G_B will always change in positive time direction such that their temperatures become equal.

Now we can calculate, what that final temperature T_{final} will be: The whole box is a closed system, and we assume G_A and G_B don't contain potential energy that could become active, transforming into kintic energy and faking the experiment. Then we have $T_{final} = \Delta T_1 + T_1 = \Delta T_2 + T_2$ and $Nj_1 k\Delta T_1 = -N_2 k\Delta T_2$ (from $\Delta Q_1 + \Delta Q_2 = 0$). The result is $\Delta T_1 = \frac{N_2}{N_1+N_2}(T - 1 - T_2)$, and, deciding for $T_1 < T_2$, we can calculate the entropy from this: $S = \int_{T_1}^{T_{final}} \frac{dQ}{T} + C_1 + \int_{T_{final}}^{T_2} \frac{dQ}{T} + C_2 = ln(\frac{T_2}{T_1}) + C_1 + C_2$, where C_1, C_2 are the entropy values of gas G_A and G_B at their initial temperatures T_1, T_2, respectively. We write that sum as $S = S_1 + S_2$. However, neither S_1 nor S_2 are well defined, because N_1, nor N_2, need to be independent fom temperature: G_A could have been water vapour starting at $T_1 = -10^0 C$ and ending with water vapor at $T_{final} = 15^0 C$. If it was water vapour throughout, then N_1 was constant throughout, fine. But, that water vapour on its tour from T_1 to T_{final} could have intermediately accumulated into snow flakes. Then the number of particles changes with temperature, $n : T \mapsto n(T)$, say, where we still have $N_1 = n(T_1) = n(T_{final})$. Consequently, $S_1' := \int_{T_1}^{T_{final}} k\frac{d(n(k)T)}{T} + C_1$ will become unequal to $S_1 = \int_{T_1} N_1 k T_{final} \frac{dT}{T} + C_1$. And now we have the problem that there are two processes with different entropy starting in the very same state and ending in the same state.

So, the entropy not only fails to describe that irreversibility, it is inconsistent!

Historically, what followed Nernst's theorem, was that a machinery set in: the entropy S was taken as if it was a time parameter, and an analogue of a Legendre transformation was carried out, which leads to the enthalpy $H(S, P)$... I'll leave that out and turn to statistical physics:

We saw above that the entropy is not capable to describe the obvious irreversibility of dynamic systems. Interestingly, statistical nearly physics was: It was James Clerk Maxwell, who started out to answer the daring question, what the distribution of the particles in the atmosphere must be like so that they withstand gravitation and don't just all fall to the ground like rain. And he succeeded (with the fortunate assistance from Ludwig Boltzmann from Austria): He found that, although the particle density drops exponentially with height, the distribution of the mean kinetic energy of the particles was independent from height.
That had to mean something: Because the earth's atmosphere is so enourmously stable, that macro state of the atmosphere must be attracted by a force. And, as was then shown by Boltzmann, it just needs that distribution of kinetic energy to explain, what the final state of equal temperature is about, given the above situation of two gases at different temperatures.
So, Maxwell and Boltzmann had achieved something that is strictly out of range for thermodynamics and was held to be uncalculatable by the methods

of Newtonian mechanics, either. Boltzmann then saw himself under cross-fire: From side of the Newtonian guards, his former teacher Loschmidt publically criticized Boltzmann for introducing an irreversibility into classical mechanics, for which there was no appropriate force. And from side of the thermodynamics favouring physicists, he was attacked for not being able to integrate his results into the concept of a monotonously growing entropy to full satisfaction of thermodynamics. For the latter, we saw why: the concept of entropy does not hold its promise. As to Newtonian mechanics, Loschmidt clearly was right in that a reversibility breaking law was missing. But it also was an unjust verdict, because Newtonian mechanics (at that time) was not able even to prove the stability of the solar system.

The 19th century saw a bad end for Boltzmann, even more for physics, and foremost for mankind, who steered right into world war I with the consciousness, that if entropy was to steadily increase over time, everything will go to ashes some day - a credo that still prevails today.

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