Philosophical Foundations of Thermal Physics

James Wills

January 19, 2023

Lamentations

"There can be no doubt, I think, that the average physicist is made a little uncomfortable by thermodynamics. He is suspicious of its ostensible generality, and he doesn't quite see how anybody has a right to expect to achieve that kind of generality. He finds much more congenial the approach of statistical mechanics, with its analysis reaching into the details of those microscopic processes which in their larger aggregates constitute the subject matter of thermodynamics. He feels, rightly or wrongly, that by the methods of statistical mechanics and kinetic theory he has achieved a deeper insight." (Bridgman)

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"Mathematicians who take a professional interest in thermodynamics usually find themselves exasperated at the obscurity and imprecision which bedevil traditional ways of presenting that subject." (Day)

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> *"The presence of temperature distinguishes thermodynamics from other macroscopic branches of science, such as geometrical optics, mechanics, or electricity and magnetism." (Zemansky and*

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"Orthodox thermodynamics is an approach associated with the names of Clausius, Kelvin, and Planck. Here, one aims to describe the thermal properties of macroscopic bodies while deliberately avoiding commitment to any hypothesis about the microscopic entities that might constitute the bodies in question." (Uffink)

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> *A thermodynamic system is that portion of the universe which we select for investigation. (Adkins)*

What is thermodynamics about?

A couple of suggestions, to be made more precise later. Thermodynamics is . . .

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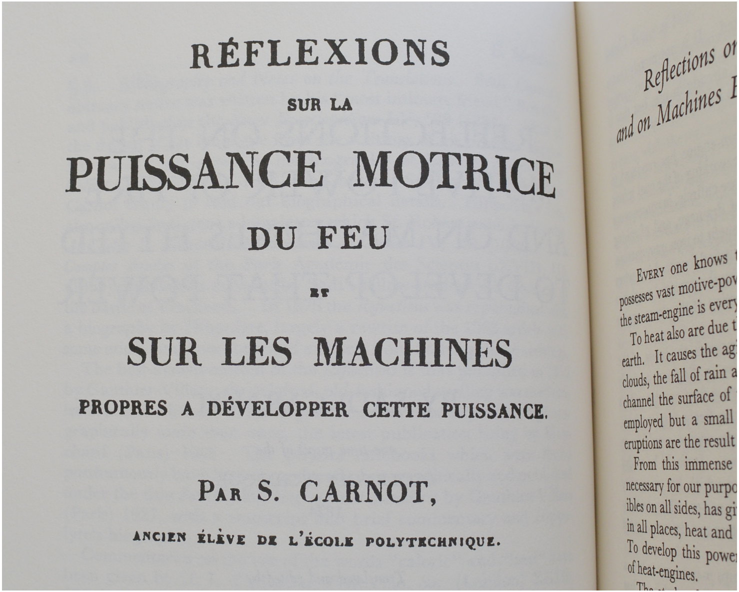
Heat/Work



RÉFLEXIONS
SUR LA
PUISSANCE MOTRICE
DU FEU
ET
SUR LES MACHINES
PROPRES A DÉVELOPPER CETTE PUISSANCE.

PAR S. CARNOT,
ANCIEN ÉLÈVE DE L'ÉCOLE POLYTECHNIQUE.

Reflections o
and on Machines

EVERY one knows
possesses vast motive-po
the steam-engine is every
To heat also are due t
earth. It causes the ag
clouds, the fall of rain a
channel the surface of
employed but a small
eruptions are the result
From this immense
necessary for our purpo
ibles on all sides, has gi
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Carnot's Insight

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"In order to consider in the most general way the principle of the production of motion by heat, it must be considered independently of any mechanism or any particular agent. It is necessary to establish principles applicable not only to steam-engines but to all imaginable heat-engines, whatever the working substance and whatever the method by which it is operated." (Carnot)

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Work can only be extracted when there is a temperature gradient

Theories of Heat

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No change in what thermodynamics was fundamentally about: Still there remained a fundamental distinction between heat and work and ‘flow’ of the former could generate the latter.

Orthodox Thermodynamics: First and Second Laws

First Main Principle

"In all cases where work is produced by heat, a quantity of heat consumed is proportional to the work done; and inversely, by the expenditure of the same amount of work the same quantity of heat may be produced."

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$$\oint dW = \oint dQ \implies \oint dW - dQ = 0. \tag{1}$$

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Thus $dW - dQ$ is a state function. We define:

$$dU := dW - dQ \tag{2}$$

Orthodox Thermodynamics: First and Second Laws

Second Main Principle

"A passage of heat from a colder to a hotter body cannot take place without compensation."

To show that this implies the existence of a state function is a lot of work and Clausius shows in (pp. 69–107) Clausius (1879) that it implies the existence of the entropy:

$$dS := dQ/T \tag{3}$$

The Q/W distinction

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But both are some form of motion:

> *"On the kinetic theory of heat, when a body is heated, the total kinetic energy of its molecules is increased, so, for body A to heat body B, parts of A must interact with parts of B to change their state of motion. When A does work on B, it is again the case that parts of A act on parts of B to change their state of motion." (Myrvold)*

So what grounds the distinction?

Means-relativity

Myrvold advocates a ‘Maxwellian’ view

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Means-relativity: whether energy counts as heat or as work depends on the means we have available to us to manipulate the system and extract useful work.

An Alternative View (Adkins)

"[A]lthough its application had at first been restricted to thermal engineering, its laws were soon recognized to be of such great generality as to be useful and important in many other branches of science also. Thermodynamics sets out to describe and correlate the directly observable properties of substances: the volume of a gas, the expansion of a wire, the polarization of a dielectric. The laws of thermodynamics enable us to interrelate the macroscopic quantities without making any microscopic assumptions at all. The great generality of thermodynamics is a direct consequence of this. It is precisely because it avoids microscopic theories that it is so valuable." (Adkins)

An Alternative View (Burke)

"A thermodynamic system is a homogeneous assembly that includes a very large number of unexamined and mutually interacting subparts. The energy shared among the unmeasured degrees of freedom of these subparts is called heat. Think, for instance, of a sample of gas. The atoms are subparts with translational degrees of freedom whose kinetic energy is shared among them. In addition, a thermodynamic system has some degrees of freedom (or combinations) that are measured, such as its volume, magnetization, electric charge, and number of particles. These aggregate variables are called extensive variables. . . The state space for the system consists of all the preceding extensive variables, plus one aggregate variable for the unexamined degrees of freedom. This aggregate variable is called entropy." (Burke)

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- Thus anthropocentric considerations are not what is fundamental.
- What is fundamental is a distinction between different types of degrees of freedom.

Geometric Thermodynamics

Postulate

The states of the thermodynamic system are represented by points in the *configuration space*: a $(k+1)$-dimensional smooth real manifold M with global coordinates $(X_0, X_1, X_2..., X_k)$ known as *extensive variables*, where $U := X_0$ is called the *internal energy* and $S := X_1$ is called the *entropy*.

Geometric Thermodynamics

Postulate

There exists a smooth function f between the extensive variables

$$U = f(S, X_2, ..., X_k) \tag{4}$$

defining a k-dimensional surface in M with the following properties:

- ⓐ f is a first-order homogeneous function of $S, X_2, ..., X_k$:

$$f(\lambda S, X_2..., \lambda X_k) = \lambda f(S, X_2..., X_k) \tag{5}$$

  for every positive real number λ and for all $S, X_2 \ldots, X_k$.
- ⓑ U is a monotonically increasing, surjective function from S to the real numbers, all other variables held fixed.
- ⓒ U is a convex function of its arguments.

Thermodynamic System

Thermodynamic System

A *thermodynamic system* is the pair (M, f), where M is a $(k+1)$-dimensional manifold with global coordinates $U, S, X_2, ..., X_k$ and $U = f(S, X_2, ..., X_k)$ where U is a first-order homogeneous function of its arguments, is a monotonically increasing function of S and is convex.

Concrete Example

The fundamental relation of the ideal gas is:

$$S = \left(\frac{3}{2}R\frac{N}{U}\right)U + \left(\frac{NR}{V}\right)V - \left(R\ln\left[\frac{N^{5/2}}{VU^{3/2}}\right] - K\right)N.$$

Some Questions

- Why are we just assuming the existence of the entropy variable?
- How can we recover the ‘orthodox’ first and second laws?
- What does ‘extensive’ mean?
- How are energy and entropy singled out as ‘special’ configuration variables?