1

Fundamental notions of classical thermodynamics
and the

ZEROTH, FIRST & SECOND LAWS

Introduction. It is a familiar fact that classical mechanics is an implication of quantum mechanics—is quantum mechanics "in the limit that the quantum numbers are large" (formally: quantum mechanics in the limit $\hbar \downarrow 0$)—but should in this connection be emphasized that

- classical mechanics stands on its own feet as a *self-contained and logically complete theoretical structure*
- many problems are most usefully/efficiently addressed classically, without reference to quantum mechanics
- it is (as was emphasized by Bohr) *by classical experiments that we know all that we know about the quantum world*: it is classical mechanics which—observationally/theoretically—"supports" the quantum theory.

Nearly identical remarks pertain to the resonant relationship between classical thermodynamics[1] and statistical mechanics. Just as one might preface an

---

[1] Thermo*dynamics* might more appropriately be called "thermostatics." The "classical" is intended here to convey a distinction not from "quantum thermostatics" but from "*modern* thermodynamics"—that time-dependent recent generalization of the classical theory which takes
- relaxation processes
- self-organization in driven open systems
and related phenomena as its primary subject matter.

account of quantum mechanics with a review of the principles of classical mechanics, so do we proceed here to a review of the fundamentals of classical thermodynamics.

My objective in this introductory chapter will be to assemble concepts, language, principles—raw material for the more concrete and informatively detailed work undertaken in subsequent chapters. My approach will be "informally axiomatic," and I will allow myself to make unapologetic use of notions that on first encounter can be only imperfectly defined. We are, I assert, no more entitled here than elsewhere in physics to expect conceptual precision at the outset: we have no alternative but to build upon our tentatively-held intuitions, in the hope and expectation that the elaborated theory will serve ultimately and with ever-increasing clarity to illuminate its own foundations, to expose its own meaning. I cannot account for why that circumstance is felt to be more acutely embarrassing in the present context than it is in (say) mechanics (and I admit that by me it is): are we really entitled to suppose that our mechanical intuitions are that much sharper and secure than our thermal intuitions?

1. Thermal systems and their states. Let $\mathfrak{S}$ denote a "thermal system"—a finite glob of stuff, the internal constitution of which is such as to permit it to achieve states of thermal equilibrium (in short: to "thermalize")—and let real numbers $\xi_1, \xi_2, \ldots, \xi_N$ record the results of probing $\mathfrak{S}$ with devices ("gages") of the sorts standard to the thermodynamic laboratory. We agree to write $\boldsymbol{\xi} \equiv \{\xi_1, \xi_2, \ldots, \xi_n\}$ when those numbers comprise a <u>least set sufficient to determine the thermodynamic state of the system</u>.[2] Thus are we led (by instrumental procedures) to an identification of the form

$$\text{state of } \mathfrak{S} \quad \longleftrightarrow \quad \text{point } \boldsymbol{\xi} \text{ in } n\text{-dimensional state space } \Xi$$

Notice in this connection that

- the ξ-variables can be expected to be *dimensionally diverse*.
- it becomes natural to say that $\mathfrak{S}$ has "n thermodynamic degrees of freedom;" generally we can expect n to be small, but it will vary from case to case, and not principle supplies an *a priori* value in any particular case[3]
- thermodynamic state space Ξ is *not a metric space*: it is not possible to ascribe a natural meaning to "how far" state $\boldsymbol{\xi}_1$ lies from state $\boldsymbol{\xi}_2$.

We will find it essential to distinguish thermal systems of several types. Specifically, we will distinguish **open systems** from **closed systems** (Figure 1),

---

[2] "Determine" in the sense "identify: distinguish one from another."

[3] Recall that it took many years to discover how many degrees of freedom to ascribe to an electron, or to an atom (*i.e.*, to discover "spin"), and that when this was finally accomplished it was by tinkering with theory until it conformed to the experimental facts.
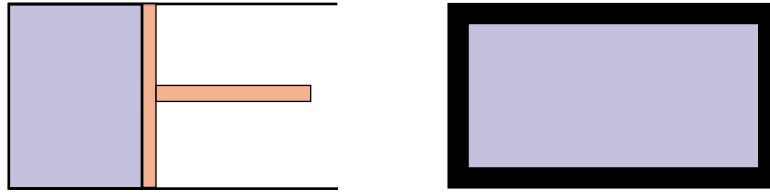
FIGURE 1: *At left: a system* **open** *to interaction—in this instance: to* energetic *interaction—with external agents. At right: a* **closed** *system: idealized walls prevent mass, energy and other kinds of exchange with exterior agents of systems.*
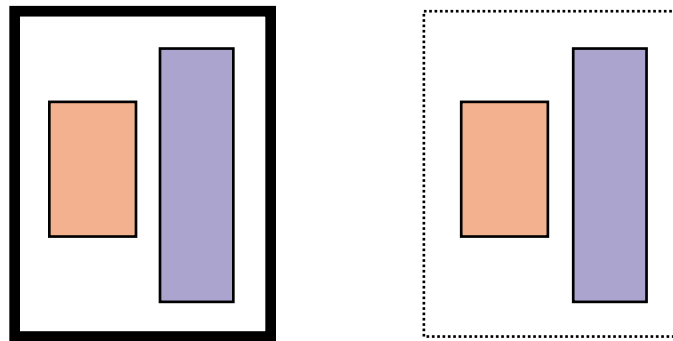

FIGURE 2: *At left: the physically isolated compose of two systems. At right: the merely* mental *compose.*
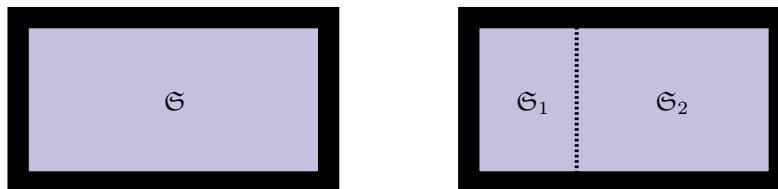

FIGURE 3: *A frequently useful trick: compare the thermodynamics of a closed system (left) with that of its "mental resolution into a pair of subsystems" (right).*

and **solitary systems** from **composite systems** (Figure 2). It is evident that an expanded set $\{\boldsymbol{\xi}_1, \boldsymbol{\xi}_2\}$ of variables will be needed to describe the state of the composite system $\mathfrak{S} = \mathfrak{S}_1 \oplus \mathfrak{S}_2$. Figure 3 alludes to a non-obvious application of the composite system idea of which we will have occasion to make fundamental use.

2. State transitions: processes. Thermalized systems—when tickled, kicked or allowed to interact in this way or that with other systems—typically respond by moving out of equilibrium ... and coming to rest finally in a state different from the one from which they departed. The point to notice (see Figure 4) is that during the temporal interval

$$\boldsymbol{\xi}_{\text{initial}} \xrightarrow{\text{succession of hard-to-describe microstates}} \boldsymbol{\xi}_{\text{final}}$$

(which is typically—though by no means invariably—quite brief) the system, since disequilibrated, <u>cannot be said even to possess</u> state variables $\boldsymbol{\xi}_{\text{transitional}}$, cannot be associated with a "moving point $\boldsymbol{\xi}(t)$ in state space."

This is in sharp contradistinction to the situation in classical dynamics (also in quantum dynamics, up until the time of the next "measurement"), where it is fundamental that the progress

$$\text{initial state} \longrightarrow \text{final state}$$

proceeds always through a smooth t-parameterized continuum of intermediate states, as described by the equations of motion.

It is, however, possible to imagine—and to realize in the laboratory—processes that proceed $\boldsymbol{\xi}_{\text{initial}} \longrightarrow \boldsymbol{\xi}_{\text{final}}$ *via* an arbitrarily large number of arbitrarily proximate intermediate states. Such **quasi-static processes** might take arbitrarily long to accomplish (though in practice can be actually quite brisk), but they possess the property that, by tickled design and intent, $\mathfrak{S}$ is *never detectably far from equilibrium.* Quasic-static processes *can* be represented (Figure 5) by <u>curves (if "pointillistic" curves) drawn on state space.</u> Thermodynamics recognizes—attaches importance to—before-after distinctions ("time's arrow"), so *directionality* can/should be assigned to such curves. But thermodynamics is blind to "time's measure:" it assigns no importance to, and has nothing to say about ... the temporal *rate of progress* along such a curve.

As we proceed we will acquire means and reason to refine our "catalog of process types."

3. Heat and work. Thermals physics is mainly concerned with the **energetics** of systems—with the distribution of energy within systems, with the exchange of energy among interactive systems, with the injection/extraction of energy by external agents. It is occasionally remarked[4] that the methods of statistical

---

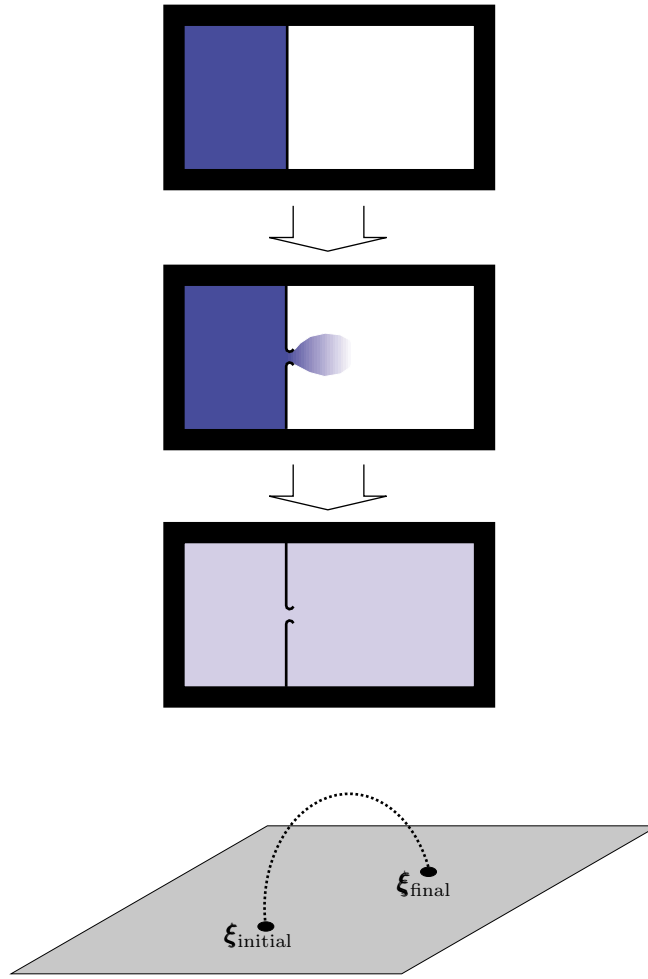[4] See, for example, E. Schrödinger, *Statistical Thermodynamics* (2$^{\text{nd}}$ edition 1952), page 1.

FIGURE 4: JOULE FREE EXPANSION: *a thermalized gas is initially separated from an evacuated chamber by a diaphram. The diaphram is punctured, the gas spills into the expanded volume, and eventually equilibrates. During the interval, the gas cannot be said to possess a thermodynamic state.*

mechanics—whence also of thermodynamics—could, in principle, be adjusted so that instead of fixating on energy (a constant of the internal microscopic motion, however complex that motion may be) they fixate on other constants of the motion (momentum? angular momentum?), but efforts to pursue that idea have not borne useful fruit. The practical fact of the matter is that it is mainly—but, on the evidence of the preceding figure, by no means exclusively—by energy injection/extraction that we tickle, prod and kick thermal systems.
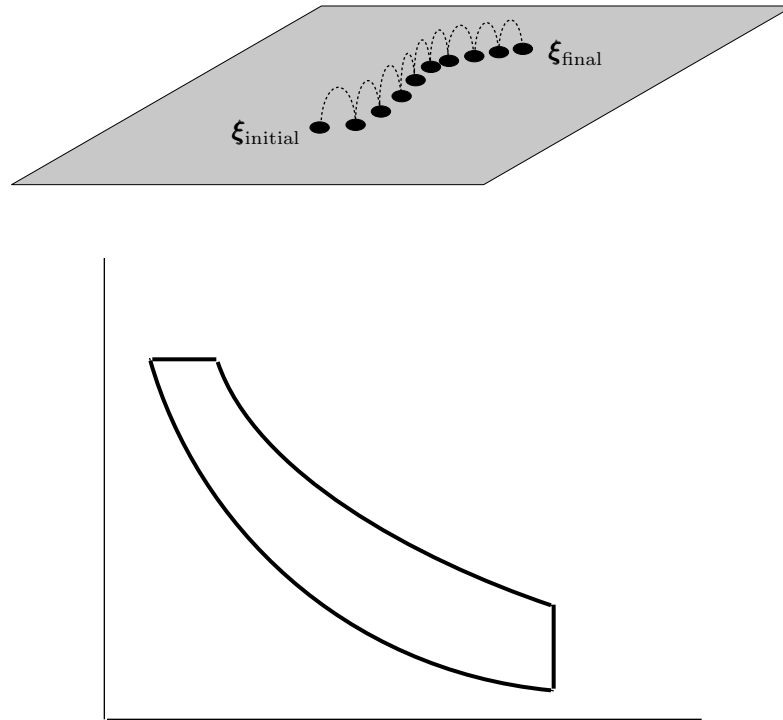
FIGURE 5: *Above: schematic representation of quasi-static process. It is intended that the sequential state adjustments are to be made finer and finer (but they become soon too fine to draw). Below: a cycle inscribed on state space, of the sort encountered in discussions of the theory of refrigerators and engines.[5] Such figures evidently allude to quasi-static processes, and can pertain successfully to the real physics of engines (which operate typically at thousands of cycles per minute) only if the thermal equilibration of the working fluid is quite rapid.*

Thermodynamics recognizes the existence of two and only two modes of energy injection:
- one can **heat** the system, or
- one can **do mechanical work upon** it.

The discovery (Count Rumford [Benjamin Thompson] 1798; James Prescott Joule 1842) that heat has not the nature of a "substance," has not to do with a hypothetical "flow of caloric," but with *energetics* ... marks a watershed in the

---

[5] See, for example, Halliday, Resnick & Walker, *Fundamentals of Physics* (5th edition 1997) Figure 21-8 on page 516; D. C. Giancoli, *Physics for Scientists & Engineers* (3rd edition 2000) Figure 20-5 on page 521.

prehistory of thermodynamics, but does not in itself cast any light upon this seldom-asked question: *Why do heat and work exhaust the possibilities*?

Essential insight into the issue is provided by a look to some of the most rudimentary aspects of the underlying microdynamics... which, for the purposes of this discussion, I will assume to be classical. The short of it:

- "Heating" refers to energy injection by "flicking" the system from one solution of the equations of micromotion to a *higher-energy solution of those same equations*.
- "Working on" involves *adjusting the parameters that control the <u>design</u> of the equations of micromotion*: during that process the former solution of the old equations "tracks" to a higher-energy solution of the new equations. *Which* solution of the new equations depends critically upon details of the adjustment process.

"Heating" is, in this light, the easier of the two processes to comprehend (see Figure 6), though it is by no means mechanically obvious that if one reaches into a thermalized system and "flicks" some of its constituent parts the system as a whole will then "re-thermalize;" *i.e.*, that it will relax again to an (elevated) equilibrated state.

To grasp the meaning of "work" in its thermodynamic usage one must recognize that the Hamiltonian (which steers the micromotion) is a function of

- dynamical variables (lots of x's and p's);
- system parameters that describe the gross design of the physical system (things like the size of the box, the strength of the impressed magnetic field) and that—typically—are under the control of the experimenter: we will adopt the generic notation $\alpha_1, \alpha_2, \ldots$ to describe such things, which are invariably few in number;
- constants: things like e, m, the parameters that enter into the description of the intermolecular potential. Those numbers are *not* under the control of the experimenter; it is therefore natural to omit them from our notation, writing something like

$$H(\boldsymbol{p}, \boldsymbol{x}; \alpha_1, \alpha_2, \ldots)$$

to describe the Hamiltonian.

Procedures that involve <u>averaging over phase space</u> (by whatever yet-to-be-described protocol) will yield expressions

$$U(\alpha_1, \alpha_2, \ldots) \equiv \langle H(\boldsymbol{p}, \boldsymbol{x}; \alpha_1, \alpha_2, \ldots) \rangle$$

from which the x's and p's have disappeared but in which the α's (also the surpressed constants) survive as arguments. It becomes at this point possible/natural to write

$$dU = \sum_i \frac{\partial U}{\partial \alpha_i} d\alpha_i$$

to describe the <u>adjusted system energy that results from tickling the control</u>
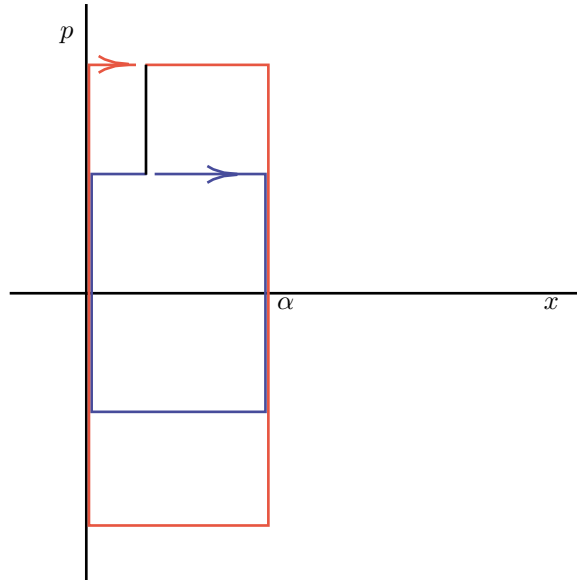
FIGURE 6: *Attempt to illustrate energy injection by a "heating" process. Our system has been taken to be a gas—specifically, a "gas" consisting of a single molecule confined to a box of length α. The cartoon is unfortunately too simple to capture the meaning of "thermal equilibrium." Initially the molecule bounces back and forth with energy E. After being "flicked" it moves with energy $E > E$.*

parameters α. It is tempting to think of the objects

$$\mathcal{F}_i(\boldsymbol{\alpha}) \equiv -\frac{\partial U(\boldsymbol{\alpha})}{\partial \alpha_i}$$

as "thermodynamic forces," though they are dimensionally as diverse as the α's

$$[\mathcal{F}_i][\alpha_i] = \text{energy}$$

and the conventions of the field require that we hold that terminology in reserve.

To summarize: "work," as the term is used in thermodynamics, refers to energy injection (or extraction) by controlled manipulation of global system parameters, and is quantified by devices standard to the mechanics laboratory. "Heat," on the other hand, refers to energy injection/extraction "by reaching in and flicking." Of course, "flicking" amounts also to "doing work," but in a micromechanical sense, and is never subject to detailed control. Heat is quantified its own distinct set of operational procedures and devices, the stuff of *calorimetry*.[6]

---

[6] The word has recently been commandeered by experimental particle physicists (accelerator people), who use it to refer to *energy measurement in general, by any means.*
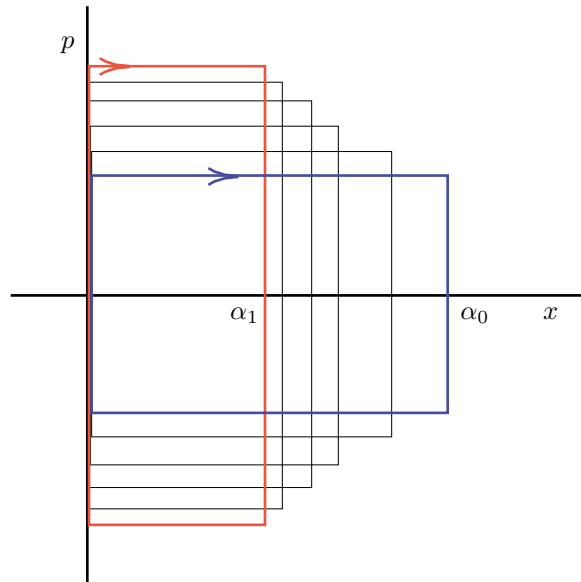
FIGURE 7: *The "one-dimensional gas" particle moves initially on a low energy trajectory within a box of length α_0. The box is slowly compressed $\alpha_0 \longrightarrow \alpha_1 < \alpha_0$ by an external agent. Every time the particle hits the advancing wall its speed is increased. It ends up tracing a shorter trajectory with increased energy $E > E$.*

Recall, in the latter connection, the definition of the *calorie*: it is "the amount of heat required to raise the temperature of 1 gram of water from $14.5°$ to $15.5°$C at a constant pressure of 1 standard atmosphere."[7] The apparatus alluded to (thermometer stuck into a beaker of water, sitting on a hotplate) is not to be found among the clocks, metersticks and spring scales in a mechanics laboratory, but that the number produced has to do with energy in the standard mechanical sense is enshrined in the statement

$$1 \text{ calorie} = 4.1855 \pm 0.0005 \text{ joules}$$

that quantifies the *mechanical equivalence of heat*.

Heating $\mathfrak{S}$, working on $\mathfrak{S}$... are extrinsic procedures that serve to *alter the state* of $\mathfrak{S}$, so deserve to be called "processes." An **adiabatic process** is one that entails no injection/extraction of heat, a process that proceeds under the presumption that $\mathfrak{S}$ has been wrapped round and isolated from the rest of the universe by ideal insulation. Processes that proceed under the complementary presumption that no work is done on/by $\mathfrak{S}$ are encountered often enough, but appear to have no distinctive name.

---

[7] *McGraw-Hill Dictionary of Scientific & Technical Terms* (2nd edition 1978).

4. Process initiation by relaxation of a constraint. I want now to describe a point of view, and associated language, that will permit us to speak in a unified way about a broad class of thermodynamic processes and issues. The viewpoint I advocate will sometimes seem entirely natural, but sometimes seem at first to be a bit contrived and artificial. I start with an instance of the latter:

In our laboratory—which is thermally isolated (a closed system)—we have equipped ourselves with
- an sealed ampule of salt, placed within
- an open beaker of water, which is suspended over an unlit burner that has been connected to
- a closed tank of flamable gas and
- a closed tank of oxygen.

Having assured ourselves that those systems are at thermal equilibrium, both individually and collectively,

□1 We break the ampule; *i.e.*, we "*relax the constraint* that the salt and water be separated." The process

$$\text{salt} + \text{water} \longrightarrow \text{saltwater}$$
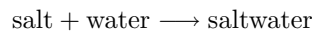
runs to thermalized completion.

□2 We turn the valves on the gas tanks; *i.e.*, we "*relax the constraint* that the oxygen and fuel be separated." They come together, spontaneously combust, the flame heats the water, which evaporates. Ultimately we recover our salt crystals, but they are in thermal equilibrium with an atmosphere that can be described now as hot, steamy smog.

The claim is that thermodynamic processes—at least those that take place (or can be considered to take place) within a closed composite system—can always be said to have been initiated by the relaxation of a constraint. Or, more precisely, by the sequential relaxation of a series of constraints (see Figure 8).

Contraints are maintained by real/idealized **partitions**. We will have need mainly of
- partitions that are opaque to the matter but transparent to heat (such partitions are called **diathermal walls**)
- partitions that are opaque to the heat but transparent to matter

but partitions with other transmission properties are imaginable. A partition opaque to *both* matter and heat can be fabricated by "stacking" partitions of
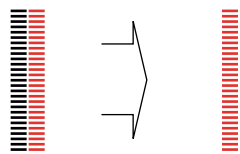
the sorts described above, and the essential idea admits of many variations. "Relaxation of a constraint" might then refer to removal of one but not the other of the elements of a composite partition, as illustrated. But the phrase might equally well refer to "removing the nails that hold the partitions in place," that lend *shape* to a system: we might, for example, want to release a piston (opaque to both matter and heat) so that it can seek the point where the pressure on its two faces has become equalized.
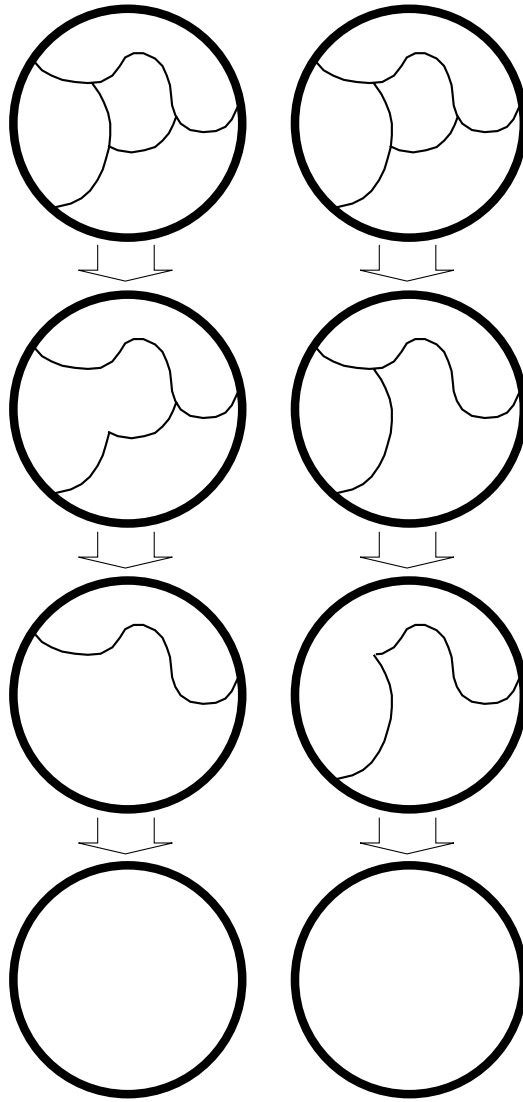
FIGURE 8: *A closed composite system (top) is subjected (at left) to a sequence of constraint relaxations, and (at right) to a different sequence of constraint relaxations. Both sequences happen here to proceed until no constraints remain to be relaxed. The question arises: Is the endstate independent of the relaxation sequence, if the latter is pursued to completion?* The "contraint relaxation" idea will turn out later to provide valuable insight into the essential drift of the 2nd Law (growth of entropy).

5. Zeroth law of thermodynamics: emperical temperature. Imagine that we possess a collection of all possible thermodynamic systems, each in all possible states. Imagine each system in the collection to be outfitted with gages sufficient to indicate the state of the system. The gages can be expected to differ in number from case to case, and we will allow them to be arbitrarily callibrated in each individual case. They therefore tell us nothing useful about the actual state of the system to which they refer, but do (we assume) serve to tell us whether or not the state changes when we interact with the system.

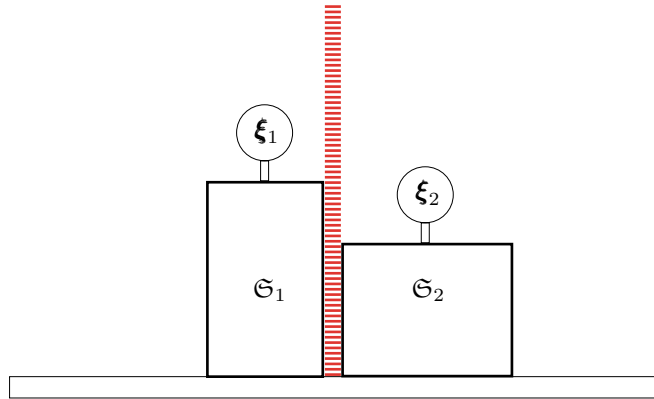FIGURE 9: *The* **diathermal wall test** *lends an idealized operational meaning to the question* Does anything happen when systems $\mathfrak{S}_1$ and $\mathfrak{S}_2$ are brought into diathermal contact? *The immobile diathermal partition is transparent to heat, but opaque to all else: it insures that* $\mathfrak{S}_1$ *and* $\mathfrak{S}_2$ *cannot do work on each other, exchange matter, etc.*

Select two systems, $\mathfrak{S}_1$ and $\mathfrak{S}_2$, and arrange (see the figure) that they be permitted to interact by heat exchange, but in no other way. What happens? One finds that

- either the states of *both $\mathfrak{S}_1$ and $\mathfrak{S}_2$ remain unaltered*, which we will record by writing $\mathfrak{S}_1 \sim \mathfrak{S}_2$, or

- *both states change*, which we record by writing $\mathfrak{S}_1 \not\sim \mathfrak{S}_2$. One never observes a change in the state of one system which is unaccompanied by a change in the state of the other ...though "thermostats" ("heat baths"), created by making one system very much more massive than the other, are designed to approximate such behavior. One finds, moreover, that

- if $\mathfrak{S}_1 \sim \mathfrak{S}_2$ and $\mathfrak{S}_2 \sim \mathfrak{S}_3$ then $\mathfrak{S}_1 \sim \mathfrak{S}_3$.

The physical relationship that we have denoted $\sim$ is therefore an *equivalence relation*.[8] The "diathermal wall test" has served to resolve the set of all systems

---

[8] See G. Birkhoff & S. MacLane, *Survey of Modern Algebra* (1951), page 32.

in all states into *disjoint equivalence classes*, just as "congruence" serves to resolve into equivalence classes the set of all triangles.

There is a lesson to be learned from looking more closely to the set of all triangles inscribed on the Euclidean plane. For it is geometrically evident that

- 3 numbers are required to identify an equivalence class if *congruence* is the defining relation (angle/side/angle or side/angle/side);
- only 2 numbers are required to identify an equivalence class if *similarity* is the defining relation (angle/angle);
- only one number is required to identify an equivalence class if *isometry* is the defining relation (area).

Evidently the resolution of a set into disjoint equivalence classes conveys—in and of itself—no information concerning how many numbers must be specified to *identify* an equivalence class (the "dimension" of the resolution).

The question now before us: What is the dimension of the resolution achieved by the diathermal wall test? How many numbers must be presented to identify one of the resulting equivalence classes, to distinguish it from all others?

It is a lesson of simple sense experience that systems which are equivalent in the above sense are invariably adjudged to have, in the most naive tactile sense, the same "temperature." And conversely.[9]

The important implication of the experience thus summarized is formulated in the so-called

> **Zeroth Law of Thermodynamics:** The diathermal wall test achieves a <u>one-dimensional</u> resolution of the set $\{$states of systems$\}$ into disjoint equivalence classes. Every such class (to say the same thing another way) can be distinguished from every other such class by specification of a single real number t, which we agree to call the "emperical temperature."

However natural it may be to assign larger t-values to "hotter" system-states, smaller t-values to cooler (Figure 10)... the 0th law does not by itself obligate us to do so, nor does it provide guidance as to *how* we might/should do so: it permits a natural ordering of system-states, but places no constraint on how we might elect to *graduate* that ordering.

---

[9] We agree not to belabor the fact that our powers of sensory discrimination are at best very approximate, that we only injure ourselves when we attempt to test the temperature of things that are very hot or very cold, and that it is meaningless to ask what might be the sensory perception of 10^6K! But this is physics in a nutshell. We take direct experience as our point of departure, from that experience we extract concepts/abstractions into which we breath life by embedding them within theoretical structures ... then follow where they lead. From the span of our arms we think our way to the span of the galaxies: from the pulse of music we leap to the dance of atoms, the age of the universe.
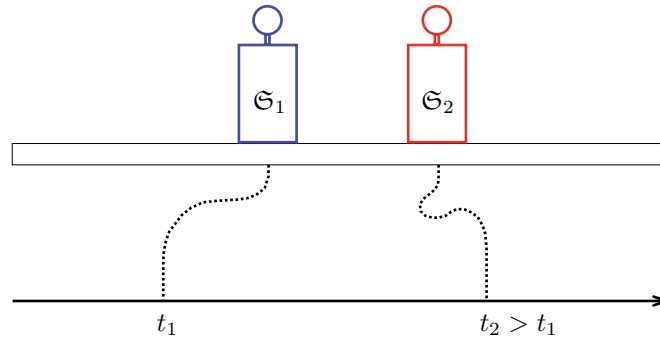
FIGURE 10: *It is natural to assign larger "emperical temperatures" to* HOT *system-states than* COOL *ones (i.e., to arrange things so that "greater than" becomes an expression of "hotter than"), but the* 0th *law—in and of itself—prescribes no particular way to do so.*

To make *practical* progress toward the development of a provisional "thermometry" we have no alternative but to proceed in immitation of the practice that leads to "chronometry." There one selects ("invents" is the better word) a dynamical system which, by agreement, will serve as a "clock"[10] and it is *relative to the dynamics of the clock* that one regulates the dynamics of other systems. Similarly, one might select some conveniently-reproducible thermal system[11] which, by agreement, will serve as a "thermometer," and use the arbitrarily graduated states of that system to *assign* emperical temperature to the states of other systems.[12]

"Arbitrary graduation" can be accomplished in infinitely many ways. If t refers to one graduation of our emperical temperature scale, and t^* to another, and if $t^*(t)$ describes the relation between them, then we have only to require that the function $t^*(t)$ be *monotonic increasing* to preserve order relationships, *i.e.*, insure that

$$t_2 > t_1 \quad \Longrightarrow \quad t_2^* > t_1^*$$

The 0th law, reduced to its starkest essentials, can be considered to assert that "**temperature exists**," which is in itself a great surprise: thermal systems

---

[10] Galileo pointed to the advantages of pendula (an idea picked up and perfected by Huygens), Newton recognized the advantages-in-principle afforded by "free particles."

[11] Perhaps a bubble of air, as proposed by Galileo, or a column of mercury, or a thermocouple.

[12] It should be borne in mind that every measurement procedure—whether intended to assign measure to time, length, mass, temperature, ...—has a *limited range of applicability*: to extend the range, to broaden the reach of the concept in question, one must stitch together an *assortment* of procedures that draw typically on distinct physical principles and assumptions.

come to us in limitless variety (as do the variables used to describe them), but each—in each of its thermalized states—can be said to possess "a temperature," however we may elect to quantify that fact.

A further surprise awaits: the 2nd law will permit us to bring into play a concept of *absolute temperature T*, and to devise a strategy for recalibrating

$$t \; \longmapsto \; T = T(t)$$

any arbitrarily-selected/graduated thermometer so that it becomes, in effect, an "absolute temperature thermometer." It emerges, moreover, that the *absolute temperature scale possess a natural zero*.[13]

6. First law of thermodynamics. Let $\boldsymbol{\xi}_1$ refer to the initial state of some system $\mathfrak{S}$, and let $\boldsymbol{\xi}_2$ refer to the final state to which $\mathfrak{S}$ is brought by the execution of some process $\mathcal{P}$. There exist, in point of emperical fact, a *multitude* of processes that achieve $\boldsymbol{\xi}_1 \longrightarrow \boldsymbol{\xi}_2$ (see the Figure 11). Let

$W[\mathcal{P}]$ = energy injected during the execution of $\mathcal{P}$ by **working on** $\mathfrak{S}$

$Q[\mathcal{P}]$ = energy injected during the execution of $\mathcal{P}$ by **heating** $\mathfrak{S}$

Though $W[\mathcal{P}]$ and $Q[\mathcal{P}]$ are process-dependent, it is an emperical fact—and the upshot of the 1st law—that their sum is process-*in*dependent:

First Law of Thermodynamics: $W[\mathcal{P}]+Q[\mathcal{P}]$ is process independent,
a function only of the endstates $\boldsymbol{\xi}_1$ and $\boldsymbol{\xi}_2$:

$$W[\mathcal{P}] + Q[\mathcal{P}] = f(\boldsymbol{\xi}_1, \boldsymbol{\xi}_2) \tag{1}$$

I give now a little argument the effect of which will be to establish what is sometimes assumed; namely, that

it is always possible to write $f(\boldsymbol{\xi}_1, \boldsymbol{\xi}_2) = U(\boldsymbol{\xi}_2) - U(\boldsymbol{\xi}_1)$

where $U(\boldsymbol{\xi})$ is a <u>function of state</u>. Consider the processes $\mathcal{P}$ that proceed from $\boldsymbol{\xi}_1$ to $\boldsymbol{\xi}_2$ *via* some designated intermediate state $\boldsymbol{\xi}_0$:

$$\boldsymbol{\xi}_1 \xrightarrow[\mathcal{P}']{} \boldsymbol{\xi}_0 \xrightarrow[\mathcal{P}'']{} \boldsymbol{\xi}_2$$

as illustrated in Figure 12. By the 1st law

---

[13] Newton spoke [*Principia*, First Scholium: see page 7 in the Cajori edition (1962)] of an "absolute, true and mathematical time," and a refinement of that idea survives to this day as an entrenched convention in all of physics (though it becomes distorted in general relativity). There is no denying that its use serves to *simplify* the physics. Yet I think it cannot be argued that dynamics supplies an "absolute time," much less a time scale with a "natural zero." Cosmology might, insofar as it promotes the view that "spacetime is created 'as needed,' by the events that happen within it."
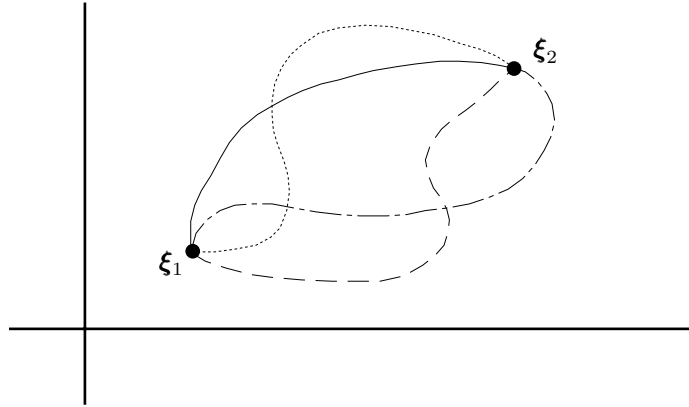
FIGURE 11: *It is only as a diagramatic convenience that the processes $\boldsymbol{\xi}_1 \rightarrow \boldsymbol{\xi}_2$ have been assumed here to be quasi-static. No such assumption enters into the statement of the 1st law. The figure is intended to dramatize the fact that distinct processes can achieve the same net effect.*
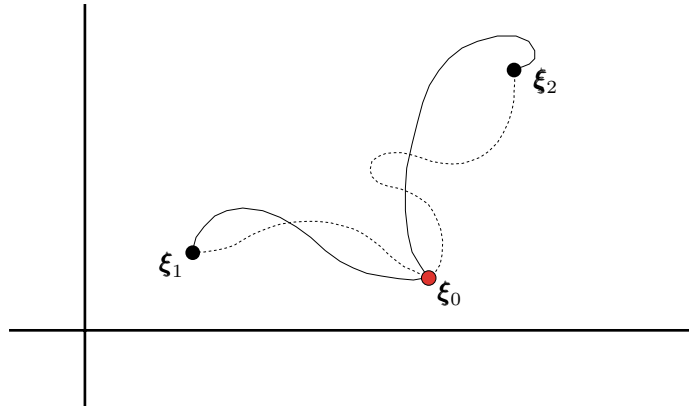
FIGURE 12: *Processes that proceed $\boldsymbol{\xi}_1 \rightarrow \boldsymbol{\xi}_2$ by way of an arbitrarily designated "fiducial state" $\boldsymbol{\xi}_0$. The "$\boldsymbol{\xi}_0$-trick" is used in the text to establish the existence of the energy function $U(\boldsymbol{\xi})$.*

$$W[\mathcal{P}] + Q[\mathcal{P}] = \left\{ W[\mathcal{P}'] + Q[\mathcal{P}'] \right\} + \left\{ W[\mathcal{P}''] + Q[\mathcal{P}''] \right\} \text{ becomes}$$

$$f(\boldsymbol{\xi}_1, \boldsymbol{\xi}_2) = f(\boldsymbol{\xi}_1, \boldsymbol{\xi}_0) + f(\boldsymbol{\xi}_0, \boldsymbol{\xi}_2) \tag{2}$$

If, in particular, $\boldsymbol{\xi}_1 = \boldsymbol{\xi}_0 = \boldsymbol{\xi}_0$ then (2) gives $f(\boldsymbol{\xi}, \boldsymbol{\xi}) = 2f(\boldsymbol{\xi}, \boldsymbol{\xi})$, from which we conclude that

$$f(\boldsymbol{\xi}, \boldsymbol{\xi}) = 0 \quad : \quad \text{all states } \boldsymbol{\xi} \tag{3}$$

If we now set $\boldsymbol{\xi}_1 = \boldsymbol{\xi}_2$ in (2) we can use (3) to obtain

$$f(\boldsymbol{\xi}_1, \boldsymbol{\xi}_2) = -f(\boldsymbol{\xi}_2, \boldsymbol{\xi}_1) \quad : \quad \text{all states } \boldsymbol{\xi}_1 \text{ and } \boldsymbol{\xi}_2$$

Returning with this information to (2), we have

$$f(\boldsymbol{\xi}_1, \boldsymbol{\xi}_2) = f(\boldsymbol{\xi}_0, \boldsymbol{\xi}_2) - f(\boldsymbol{\xi}_0, \boldsymbol{\xi}_1)$$

We conclude that there exists a function of state $U(\boldsymbol{\xi}) \equiv f(\boldsymbol{\xi}_0, \boldsymbol{\xi})$ such that (1) can be formulated

$$W[\mathcal{P}] + Q[\mathcal{P}] = U(\boldsymbol{\xi}_2) - U(\boldsymbol{\xi}_1) \tag{4}$$

The function $U(\boldsymbol{\xi})$ is *not unique*, since it depends through

$$U(\boldsymbol{\xi}_0) = 0$$

on selection of the fiducial state $\boldsymbol{\xi}_0$. From $f(\boldsymbol{\xi}_0, \boldsymbol{\xi}) = f(\boldsymbol{\xi}_0, \boldsymbol{\xi}_0) + f(\boldsymbol{\xi}_0, \boldsymbol{\xi})$ we see, however, that adjustment $\boldsymbol{\xi}_0 \to \boldsymbol{\xi}_0$ of the fiducial state serves only to shift the value of U by an additive constant:

$$U(\boldsymbol{\xi}) = U(\boldsymbol{\xi}) + \text{constant}$$
$$\text{constant} = f(\boldsymbol{\xi}_0, \boldsymbol{\xi}_0) = U(\boldsymbol{\xi}_0) = -U(\boldsymbol{\xi}_0)$$

An identical argument is used in mechanics to establish that a force field $\boldsymbol{F}(\boldsymbol{x})$ will be conservative (meaning "derivable from a potential") if and only if $\oint \boldsymbol{F} \cdot \boldsymbol{dx} = 0$.[14]

$U(\boldsymbol{\xi})$ is called the **internal energy function**. It can be construed as a description of the <u>total energy (kinetic + potential) of the microscopic elements</u> that collectively constitute $\mathfrak{S}$. From this point of view the 1st law records the surprising fact (see again page 7) that *the total energy of an equilibrated microsystem can be displayed as a function of a relatively small handful of macrovariables*—namely, the macrovariables that have roles to play on the thermodynamic stage.[15]

---

[14] See CLASSICAL MECHANICS (1983/84), page 50.

[15] Apart from that small element of surprise, the 1st law tends to strike the modern eye as an almost obvious statement of **energy conservation**. But the modern eye is in position to look through the wrong end of the historical telescope. It was the strenuous, semi-independent effort (mainly during the 1840's) of about a dozen physicists to comprehend the meaning of heat that *gave* us the concept of energy conservation. To arrive at that concept—at the "energetic view of the world" that made *possible* the formulation of the 1st law—they had first to detach themselves from the entrenched notion of a "conserved caloric." And they worked in advance of the development (therefore without the support) of an underlying micromechanics. The tale is well told in Chapters 3–10 of W. H. Cropper's *Great Physicists* (2001).

It is a particular implication of the 1$^{\text{st}}$ law (4) that

$$\left\{ U(\boldsymbol{\xi}_2) - U(\boldsymbol{\xi}_1) \right\} - W[\mathcal{P}_{\text{adiabatic}}] = 0$$

which carries the interesting implication $W[\mathcal{P}_{\text{adiabatic}}]$ is process-independent, determined entirely by the endstates. For *non*-adiabatic processes $\boldsymbol{\xi}_1 \xrightarrow[\mathcal{P}]{} \boldsymbol{\xi}_2$ one has

$$\left\{ U(\boldsymbol{\xi}_2) - U(\boldsymbol{\xi}_1) \right\} - W[\mathcal{P}] = \text{heat injected during process } \mathcal{P}$$

which is sometimes advanced as a *definition* of heat. But it works only if one has (from what source?) prior knowledge of $U(\boldsymbol{\xi})$. And since we possess means to lend direct *operational* meaning to "heat injected," I see no *need* of such a definition.

It is to recast the 1$^{\text{st}}$ law, and to prepare for a statement of the 2$^{\text{nd}}$ law, that I digress now to review some

7. Rudiments of the theory of differential forms. By an *n-dimensional linear differential form* we will understand an expression of the type

$$dF \equiv \sum_{k=1}^{n} F_k(x^1, x^2, \ldots, x^n) dx^k$$

In the standard mathematical, dynamical and thermodynamic literature[16] such constructions are commonly called "Pfaffian differential forms," while in the more general context of the exterior calculus they are known as "1-forms"—special instances of "p-forms" $(p = 0, 1, 2, \ldots, n)$.

Such a form is said to be **exact** if and only if it is the differential of a function $F(x^1, x^2, \ldots, x^n)$, and to be otherwise **inexact**. Thus

$$\sum_{k=1}^{n} \frac{\partial F(x^1, x^2, \ldots, x^n)}{\partial x^k} dx^k \quad \text{is by definition exact}$$

An obviously *necessary* condition for a given differential form $dF = F_k(\boldsymbol{x})dx^k$ ($\sum_k$ tacitly understood) to be exact is that

$$\partial F_i / \partial x^j = \partial F_j / \partial x^i \quad : \quad \left\{ i, j = 1, 2, \ldots, n \right\}$$

With weak hypotheses (which we always assume to be satisfied) the preceding conditions become also *sufficient*.

---

[16] See E. L. Ince, *Ordinary Differential Equations* (1926), page 57; E. T. Whittaker, *Analytical Dynamics* (4$^{\text{th}}$ edition 1937), page 296; H. C. Corben & P. Stehle, *Classical Mechanics* (1950), page 295; M. Born, *Natural Philosophy of Cause & Chance* (1949), pages 38 & 143.

I adopt the "dbar" notation dF to describe differential forms-in-general so as to be in position to write dF *only when exactness has been explicitly assumed or established*. This is a convention fairly standard to the thermodynamic literature, but not commonly encountered in other disciplines.

An inexact differential form dF is said to be **integrable** if and only if there exists a function $\chi(x^1, x^2, \ldots, x^n)$ such that $\chi \cdot dF$ is exact, and to be otherwise **non-integrable**. The function χ—if it exists—is said to comprise an **integrating factor** of the differential form dF.

We are interested in this subject because (as will emerge) the 1$^{\text{st}}$ law can usefully be formulated as an exactness postulate, and the 2$^{\text{nd}}$ law as an integrability postulate. It is to gain a more detailed sense of the "strength" of those postulates that we inquire now more closely into the subject, looking especially to the **integrability conditions**—the conditions necessary and sufficient to insure the *existence* of an integrating factor.

Trivially, if $n = 1$ then *every* differential is *exact*:

$$F(x)\, dx = d\left\{ \int^x F(\xi)\, d\xi \right\}$$

If $n = 2$ then—not at all trivially—*every* differential is *integrable*. The point is established by construction—by describing a procedure by means of which one can-in-principle *exhibit* the integrating factor. Here I am content to sketch the procedure as it pertains to the illustrative case[17]

$$dF \equiv X\, dx + Y\, dy = y\, dx - dy$$

Note first that dF is transparently inexact ($\frac{\partial}{\partial y}[y] \neq \frac{\partial}{\partial x}[-1]$). Note also that "Pfaff's differential equation" $dF = 0$ can be written

$$\frac{dy}{dx} + \frac{X}{Y} = \frac{dy}{dx} - y = 0$$

The solutions

$$y(x) = e^{x+a}$$

inscribe an a-parameterized population of curves on the (x, y)-plane, curves of which

$$f(x, y) = \text{constant, with } f(x, y) \equiv \log y - x \tag{5}$$

provides an "implicit" description. Differentiation with respect to x now gives

$$f_x + f_y \frac{dy}{dx} = f_x - f_y \frac{X}{Y} = \frac{\partial}{\partial x}(\text{constant}) = 0$$

---

[17] For an account of the general argument see (for example) MATHEMATICAL THERMODYNAMICS (1967), page 25. The argument trips on the circumstance that in general one can talk about but not explicitly display the function $f(x, y)$ contemplated below at (5).

so we have

$$Yf_x = Xf_y \equiv \chi \cdot XY \quad : \quad \text{serves to } define \ \chi \tag{6}$$

giving $f_x = \chi X$ and $f_y = \chi Y$. We find ourselves in position now to write

$$df = f_x dx + f_y dy = \chi \cdot (Xdx + Ydy) = \chi \cdot dF \tag{7}$$

In our example, (6) reads

$$[-1][-1] = [y][y^{\text{-}1}] \equiv \chi \cdot [y][-1] \quad : \quad \text{supplies} \quad \chi(x,y) = -y^{\text{-}1}$$

while (7) becomes $df = -dx + y^{\text{-}1}dy = -y^{\text{-}1}(ydx - dy) = \chi \cdot dF$ and it is now obvious that $\chi \cdot dF$ does pass the exactness test.

If $n \geqslant 3$ then integrating factors only *sometimes* exist, and *finding* them becomes a highly non-trivial exercise. On page 27 of the notes just cited I discuss a celebrated counterexample[18]

$$dF = -y \, dx + x \, dy + k \, dz$$

where the assumption that an integrating factor exists can be shown to lead to a contradiction. It can be shown (see Ince,[16] §2.8)—was, in fact, known already to Euler—that if

$$dF = F_1 dx + F_2 dy + F_3 dz$$

and if we allow ourselves to write

$$\boldsymbol{F} = \begin{pmatrix} F_1 \\ F_2 \\ F_3 \end{pmatrix}$$

then the integrability condition

$$\boldsymbol{F} \cdot (\boldsymbol{\nabla} \times \boldsymbol{F}) = 0 \tag{8.3}$$

is both necessary and sufficient.[19]   For $n > 3$ the conditions become more numerous: one has

$$W_{ijk} = 0 \quad : \quad i,j,k = 1,2,\dots,n \geqslant 3 \tag{8.n}$$

---

[18] ...borrowed from S. Chandrasekhar [*Introduction to the Study of Stellar Structure* (1939), page 20: Chandrasekhar's Chapter 1 provides, by the way, an unsurpassed account of the "Laws of Thermodynamics"], who borrowed it from Born, who borrowed it from C. Carathéodory (1909). It was Carathéodory—a differential geometer based in Göttingen—who, working at Born's instigation, was responsible for the introduction of Pfaffian forms into the literature of thermodynamics. The work of J. F. Pfaff was then already ancient: it dates from the second decade of the 19th Century.

[19] The non-integrability of the counterexample can in this light be considered to follow from $\boldsymbol{F} \cdot (\boldsymbol{\nabla} \times \boldsymbol{F}) = 2$.

with

$$W_{ijk} \equiv F_i \left\{ \frac{\partial F_j}{\partial x^k} - \frac{\partial F_k}{\partial x^j} \right\} + F_j \left\{ \frac{\partial F_k}{\partial x^i} - \frac{\partial F_i}{\partial x^k} \right\} + F_k \left\{ \frac{\partial F_i}{\partial x^j} - \frac{\partial F_j}{\partial x^i} \right\}$$

The integrability conditions (8.n) are $\frac{1}{6}n(n-1)(n-2)$ in number, of which $\frac{1}{2}(n-1)(n-2)$ are independent. We conclude that integrability is a highly non-trivial state of affairs if (and only if) $n \geqslant 3$.

8. Differential thermodynamic processes. To describe the differential energy injected into $\mathfrak{S}$ when we do a little work on the system we write

$$\dW = W_1(\boldsymbol{\xi})d\xi_1 + W_2(\boldsymbol{\xi})d\xi_2 + \cdots + W_n(\boldsymbol{\xi})d\xi_n = \sum_i W_i(\boldsymbol{\xi})d\xi_i$$

while to describe a differential injection of heat we write

$$\dQ = Q_1(\boldsymbol{\xi})d\xi_1 + Q_2(\boldsymbol{\xi})d\xi_2 + \cdots + Q_n(\boldsymbol{\xi})d\xi_n = \sum_i Q_i(\boldsymbol{\xi})d\xi_i$$

Here the coefficient functions $W_i(\boldsymbol{\xi})$ and $Q_i(\boldsymbol{\xi})$ record the kind of data that might show up in our lab books after an arduous series of mechanical and calorimetric measurements. The presumed *inexactness* of the differentials (as reflected in our $\dbar$-notation) provides differential expression of the fact (see again page 15) that $W[\mathcal{P}]$ and $Q[\mathcal{P}]$ are, in general, process-dependent. If we restrict our attention to <u>quasi-static</u> processes we can write

$$W[\mathcal{P}] = \int_{\mathcal{P}} \dW \quad \text{and} \quad Q[\mathcal{P}] = \int_{\mathcal{P}} \dQ$$

and if $\mathcal{P}$ refers (see the following figure) to a <u>quasi-static loop</u> traced in state space we can write

$$\oint \dW \neq 0 \quad \text{and} \quad \oint \dQ \neq 0$$

to provide elegant allusion to the process-dependence of $W[\mathcal{P}]$ and $Q[\mathcal{P}]$. To say the same thing yet another way: we expect it to follow from the data in our lab books that

$$\frac{\partial W_i}{\partial \xi_j} - \frac{\partial W_j}{\partial \xi_i} \neq 0 \quad \text{and} \quad \frac{\partial Q_i}{\partial \xi_j} - \frac{\partial Q_j}{\partial \xi_i} \neq 0$$

Which brings us back again to the surprising upshot of the

First Law of Thermodynamics (differential formulation): The *sum* of $\dW$ and $\dQ$ is *exact*. Which is to say: there exists a function of state $U(\boldsymbol{\xi})$ such that

$$\dW + \dQ = dU \tag{9}$$

From (9) it follows that if $\boldsymbol{\xi}_1 \xrightarrow[\mathcal{P}]{} \boldsymbol{\xi}_2$ is quasi-static then

$$\int_{\mathcal{P}} \dW + \int_{\mathcal{P}} \dQ = U(\boldsymbol{\xi}_2) - U(\boldsymbol{\xi}_1) \tag{10}$$
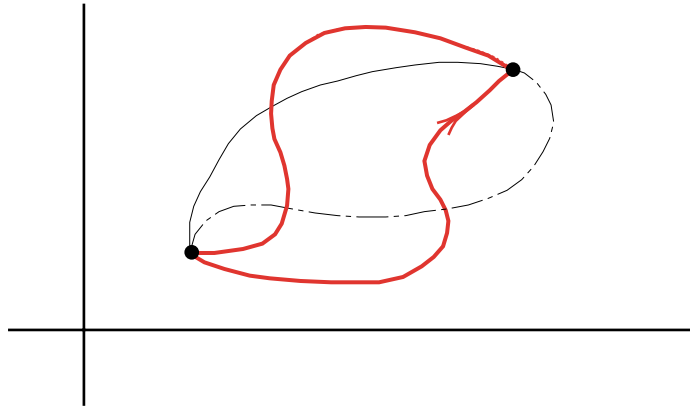
FIGURE 13: *The processes shown schematically in Figure 11 now __are__ assumed to be quasi-static, representable by "paths" inscribed on thermal state space. Two paths* ● ⟶ ● *have been joined head-to-tail to create a closed loop, a* **cycle**.

and that for quasi-static cycles

$$\oint dW + \oint dQ = 0 \tag{11}$$

The integrated statement (10) can be phrased

$$\begin{aligned} \text{work done on } \mathfrak{S} \; + \; \text{heat injected into } \mathfrak{S} \\ = \text{change in internal energy of } \mathfrak{S} \end{aligned} \tag{12}$$

but that frequently-repeated characterization of the 1st law somewhat misses the point ... which is that the 1st law delivers into our hands a __function of state__: the internal energy function $U(\boldsymbol{\xi})$.

9. Second law of thermodynamics. The 2nd law—and arguably thermodynamics itself—can be traced to the publication of *Reflexions sur la Puissance Motrice de Feu* ("Reflections on the Motive Power of Fire," 1824), which recorded the effort of Sadi Carnot, a young French engineer, to construct a general theory of heat engines ... just as his father before him had attempted (with less success) to construct a general theory of mechanical devices. It is remarkable that Carnot theoretical success as he did, for he labored still under the conception that heat ("fire") is a weightless, immutable *substance*. But he enjoyed no popular success at all: his work lay neglected for twenty years, until taken up and applied to more general objectives by Rudolph Claussius (1822–1888: his "Über die Bewegende Kraft der Wärme" was published in 1850) and Lord Kelvin (William Thomson: 1824–1907).

That the 2nd law came struggling into the world is reflected in the fact that historically it has been—and is still to this day—formulated in a confusing variety of ways . . . of which I reproduce an abbreviatred sampling:[20]

> **Second Law of Thermodynamics** [Kelvin, 1851]: "No cyclic process exists which produces no other effect than the extraction of heat from a body and its conversion into an equivalent amount of mechanical work."

> **Second Law of Thermodynamics** [Causius, 1854/1865]: "No cyclic process exists which has as its sole effect the transference of heat from a colder body to a hotter body."

> **Second Law of Thermodynamics** [Carathéodory, 1909]: "There exist in the infinitesimal neighborhood of every state $\boldsymbol{\xi}$ states $\boldsymbol{\xi}^*$ that are adiabatically inaccessible from $\boldsymbol{\xi}$."

For the purposes at hand I prefer, however, to work from this variant of Carathéodory's postulate:

> **Second Law of Thermodynamics**: The inexact differential $\dslash Q$ is in every case *integrable*. Which is to say: there invariably exist functions of state $\chi(\boldsymbol{\xi})$ and $\sigma(\boldsymbol{\xi})$ such that $\chi \cdot \dslash Q = d\sigma$.

In practice, we will find it most convenient to write

$$\dslash Q = \tau \cdot d\sigma \tag{13}$$

with $\tau(\boldsymbol{\xi}) \equiv 1/\chi(\boldsymbol{\xi})$.

We are about to enter into a lovely argument which, *modulo* certain natural conventions, will bring (13) to the form

$$\dslash Q = T \, dS$$

where T refers to the "absolute temperature" and S to the "entropy"[21] of $\mathfrak{S}$. In U, T and S we possess the basic stuff of thermodynamics: a universal state variable and two universally-available system-characterizing functions of state, one supplied to us by the 1st law, the other by the 2nd law. Because U(state) and S(state) are *functions* of state *we can bring function theory to bear upon them*, and it is from that exercise that thermodynamics acquires its distinctive form.

---

[20] For longer lists and commentary, see A. H. Wilson, *Thermodynamics & Statistical Physics* (1960) page 18; MATHEMATICAL THERMODYNAMICS (1967) pages 36–40.

[21] The term was first employed (1865) by Clausius, who derived it from the Greek *en* (meaning "in") and *tropos* (meaning "transformation").

10. Kelvin's theorem: first step toward the invention of "absolute temperature."
What follows is my own rendition of Wilson's account of Carathéodory's elegant
re-creation of an idea pioneered by Kelvin over a several-year period during the
early 1850's. It leads to what might more properly be called "Carathéodory's
theorem," but what I will here call

> **Kelvin's theorem**: The integrating factor τ possesses always
> the factored design
> $$\tau = \big\{\text{universal function of emperical temperature}\big\}$$
> $$\cdot\big\{\text{ system-specific function of state}\big\}$$

from which the "absolute temperature" concept will be shown to follow directly
as a natural consequence.

Let $\mathfrak{S}$ be a composite system, assembled from subsystems $\mathfrak{S}'$ and $\mathfrak{S}''$ that
we take to be in diathermal contact (see Figure 14). From (13) we have

$$\begin{aligned}
đQ' &= \tau'(\boldsymbol{\xi}')\,d\sigma'(\boldsymbol{\xi}') \\
đQ'' &= \tau''(\boldsymbol{\xi}'')\,d\sigma''(\boldsymbol{\xi}'') \\
đQ &= \tau(\boldsymbol{\xi}',\boldsymbol{\xi}'')\,d\sigma(\boldsymbol{\xi}',\boldsymbol{\xi}'')
\end{aligned}$$

Evidently

$$đQ = đQ' + đQ''$$

which by (13) becomes

$$\tau(\boldsymbol{\xi}',\boldsymbol{\xi}'')\,d\sigma(\boldsymbol{\xi}',\boldsymbol{\xi}'') = \tau'(\boldsymbol{\xi}')\,d\sigma'(\boldsymbol{\xi}') + \tau''(\boldsymbol{\xi}'')\,d\sigma''(\boldsymbol{\xi}'') \qquad (14)$$

Now a trick. We promote $t\ (=\ t'\ =\ t'')$, σ' and σ'' to the status of state
variables, which is to say: we take not $\xi_1', \xi_2', \ldots, \xi_m'$ but (say)

$$x_1' \equiv \xi_1', x_2' \equiv \xi_2', \ldots, x_{m-2}' \equiv \xi_{m-2}', \sigma' \text{ and } t$$

to be the state descriptors of $\mathfrak{S}'$, and we take

$$x_1'' \equiv \xi_1'', x_2'' \equiv \xi_2'', \ldots, x_{n-2}'' \equiv \xi_{n-2}'', \sigma'' \text{ and } t$$

to be the state descriptors of $\mathfrak{S}''$. Equation (14) then becomes

$$\tau(\boldsymbol{x}',\boldsymbol{x}'',\sigma',\sigma'',t)\,d\sigma(\boldsymbol{x}',\boldsymbol{x}'',\sigma',\sigma'',t) = \tau'(\boldsymbol{x}',\sigma',t)\,d\sigma' + \tau''(\boldsymbol{x}'',\sigma'',t)\,d\sigma''$$

or (divide by τ and develop $d\sigma$)

$$\underbrace{\sum_{i=1}^{m-2}\frac{\partial\sigma}{\partial x_i'}dx_i' + \sum_{j=1}^{n-2}\frac{\partial\sigma}{\partial x_i''}dx_i'' + \frac{\partial\sigma}{\partial\sigma'}d\sigma' + \frac{\partial\sigma}{\partial\sigma''}d\sigma'' + \frac{\partial\sigma}{\partial t}dt}_{d\sigma} = \frac{\tau'}{\tau}d\sigma' + \frac{\tau''}{\tau}d\sigma''$$

This statement carries the immediate implication that σ must in fact be
independent of all the x''s, all the x'''s and t:

$$\sigma(\cancel{\boldsymbol{x}'},\cancel{\boldsymbol{x}''},\sigma',\sigma'',\cancel{t}) \equiv \sigma(\sigma',\sigma'')$$
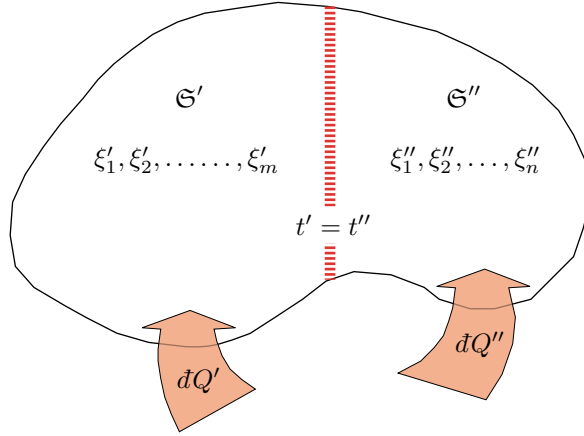
FIGURE 14: *Composite system $\mathfrak{S} = \mathfrak{S}' \oplus \mathfrak{S}''$. The subsystems are in diathermal contact, so have identical emperical temperatures. The argument hinges on the requirement that the theory of $\mathfrak{S}$ and the theory of $\mathfrak{S}' \oplus \mathfrak{S}''$ must lead to identical conclusions.*

We now have

$$
\left.
\begin{array}{l}
\dfrac{\tau'(\boldsymbol{x}', \sigma', t)}{\tau(\boldsymbol{x}', \boldsymbol{x}'', \sigma', \sigma'', t)} = \dfrac{\partial \sigma(\sigma', \sigma'')}{\partial \sigma'} \\[4mm]
\dfrac{\tau''(\boldsymbol{x}'', \sigma'', t)}{\tau(\boldsymbol{x}', \boldsymbol{x}'', \sigma', \sigma'', t)} = \dfrac{\partial \sigma(\sigma', \sigma'')}{\partial \sigma''}
\end{array}
\right\} \quad : \text{ functions only of } \sigma' \text{ and } \sigma''
$$

The dominoes are now set up; watch them all fall down: By the first equation τ must be independent of $\boldsymbol{x}''$, as by the second equation it must be independent also of $\boldsymbol{x}'$. Therefore, by the first equation, τ' must be independent of $\boldsymbol{x}'$, as by the second equation τ'' must be independent of $\boldsymbol{x}''$. The net implication of this pretty argument is that

$$
\tau'(\cancel{\boldsymbol{x}'}, \sigma', t) \equiv \tau'(\sigma', t)
$$

$$
\tau''(\cancel{\boldsymbol{x}''}, \sigma'', t) \equiv \tau''(\sigma'', t)
$$

$$
\tau(\cancel{\boldsymbol{x}'}, \cancel{\boldsymbol{x}''}, \sigma', \sigma'', t) \equiv \tau(\sigma', \sigma'', t)
$$

and, moreover, that the ratios

$$
\frac{\tau'(\sigma', t)}{\tau(\sigma', \sigma'', t)} \text{ and } \frac{\tau''(\sigma'', t)}{\tau(\sigma', \sigma'', t)} \text{ must be } t\text{-independent:}
$$

$$
\frac{\partial}{\partial t}\left(\frac{\tau'}{\tau}\right) = \frac{\tau'}{\tau}\left\{\frac{1}{\tau'}\frac{\partial \tau'}{\partial t} - \frac{1}{\tau}\frac{\partial \tau}{\partial t}\right\} = 0
$$

$$
\frac{\partial}{\partial t}\left(\frac{\tau''}{\tau}\right) = \frac{\tau''}{\tau}\left\{\frac{1}{\tau''}\frac{\partial \tau''}{\partial t} - \frac{1}{\tau}\frac{\partial \tau}{\partial t}\right\} = 0
$$

But this information can be expressed

$$\frac{1}{\tau'(\sigma',t)}\frac{\partial\tau'(\sigma',t)}{\partial t} = \frac{1}{\tau''(\sigma'',t)}\frac{\partial\tau''(\sigma'',t)}{\partial t} = \frac{1}{\tau'(\sigma',\sigma'',t)}\frac{\partial\tau'(\sigma',\sigma'',t)}{\partial t}$$

and it is clear (dominoes again!) that those equations can be simultaneously and universally valid only if

$$\frac{1}{\tau'}\frac{\partial\tau'}{\partial t} = \frac{1}{\tau''}\frac{\partial\tau''}{\partial t} = \frac{1}{\tau}\frac{\partial\tau}{\partial t} = g(t)$$

where $g(t)$ is some <u>universal (in the sense "system-independent") function of the emperical temperature t</u>.

The preceding equations can be written

$$\tfrac{\partial}{\partial t}\log\tau'(\sigma',t) = \tfrac{\partial}{\partial t}\log\tau''(\sigma'',t) = \tfrac{\partial}{\partial t}\log\tau(\sigma',\sigma'',t) = g(t)$$

and give

$$\log\tau'(\sigma',t) = \int^t g(\vartheta)\,d\vartheta + \log\Sigma'(\sigma')$$

$$\log\tau''(\sigma'',t) = \int^t g(\vartheta)\,d\vartheta + \log\Sigma''(\sigma'')$$

$$\log\tau(\sigma',\sigma'',t) = \int^t g(\vartheta)\,d\vartheta + \log\Sigma(\sigma',\sigma'')$$

where $\log\Sigma'(\sigma')$, $\log\Sigma''(\sigma'')$ and $\log\Sigma(\sigma',\sigma'')$ are simply the names we have given to what are, in effect, "constants of partial integration." Exponentiation leads finally to

$$\tau'(\sigma',t) = \Sigma'(\sigma')\cdot e^{\left\{\int^t g(\vartheta)\,d\vartheta\right\}}$$

$$\tau''(\sigma'',t) = \Sigma''(\sigma'')\cdot e^{\left\{\int^t g(\vartheta)\,d\vartheta\right\}}$$

$$\tau(\sigma',\sigma'',t) = \Sigma(\sigma',\sigma'')\cdot e^{\left\{\int^t g(\vartheta)\,d\vartheta\right\}}$$

and to the conclusion that in all cases τ possesses the factored form

$$\tau = \left\{\begin{array}{c}t\text{-independent function of state which is}\\ \text{specific to the system in question}\end{array}\right\}\cdot\left\{\begin{array}{c}\text{universal (i.e., system-independent)}\\ \text{function of }t\end{array}\right\}$$

Thus "Kelvin's theorem," by an argument that I consider to be a work of art.

11. Emergence of the "absolute temperature" concept. Introduce the definition

$$T = T(t) \equiv C\cdot\exp\left\{\int^t g(\vartheta)\,d\vartheta\right\} \geqslant 0 \tag{15}$$

where C is a positive constant of adjustable physical dimension and value. We turn immediately to a remarkable stability property of the function $T(t)$.

Let

$$t \ \longrightarrow \ t^* = t^*(t) \quad : \quad t^*(\bullet) \text{ monotonic increasing}$$

describe a *regraduation of the emperical temperature scale*. Such a regraduation (by $\frac{\partial}{\partial t^*} \log \tau = \frac{dt}{dt^*} \cdot \frac{\partial}{\partial t} \log \tau$) induces

$$g(t) \ \longrightarrow \ g^*(t^*) = \tfrac{dt}{dt^*} g(t)$$

from which it follows that

$$
\begin{aligned}
T(t) \ \longrightarrow \ T^*(t^*) &= C \cdot \exp\left\{ \int^{t^*} g^*(\vartheta^*) \, d\vartheta^* \right\} \\
&= C \cdot \exp\left\{ \int^{t^*} g(\vartheta) \tfrac{d\vartheta}{d\vartheta^*} \, d\vartheta^* \right\} \\
&= C \cdot \exp\left\{ \int^{t} g(\vartheta) \, d\vartheta \right\} \\
&= T(t)
\end{aligned}
$$

Remarkably, the T-scale is *stable with respect to arbitrary regraduations of the emperical temperature scale*: it is <u>independent of and insensitive to the particular emperical scale on which it is, in any given instance, based</u>. To say the same thing another way: The T-scale is independent of what system we have elected to serve as our "emperical thermometer."

Thus does one support the claim that the T scale provides an "absolute" quantification of the temperature concept.

We recognize that "construction of the T-scale" remains at this point a *program . . . that has yet to be carried to completion*. For we have yet to consider—in general or in particular—how one discovers the $g(t)$ appropriate to the system that serves as our designated emperical thermometer. We recognize also that the "absolutism" claimed of T attaches also to each of the scales

$$\mathcal{T} = f(T) \quad : \quad f(\bullet) \text{ monotonic increasing}$$

and that we have yet to argue that the T-scale is more "natural" (in the sense "useful") than any of those alternatives.

12. Absolute entropy. Where on page 24 we wrote $đQ' = \tau' d\sigma'$ and $đQ'' = \tau'' d\sigma''$ we are in position now to write

$$
\begin{aligned}
đQ' &= T \cdot C^{-1} \Sigma'(\sigma') d\sigma' \\
&\equiv T \cdot dS' \\
đQ'' &= T \cdot C^{-1} \Sigma''(\sigma'') d\sigma'' \\
&\equiv T \cdot dS''
\end{aligned}
$$

where S' describes the "absolute entropy" of $\mathfrak{S}'$. It is a function $S'(\boldsymbol{\xi}')$ of the state of $\mathfrak{S}'$, defined as follows: construct

$$s'(\sigma') \equiv C^{-1}\int^{\sigma'} \Sigma'(\eta)\,d\eta = C^{-1}\cdot\big\{\text{antiderivative of }\Sigma'(\sigma')\big\}$$

(which is defined only to within an arbitrary additive constant S_0') and then write $S'(\boldsymbol{\xi}') \equiv s'(\sigma'(\boldsymbol{\xi}'))$. $S''(\boldsymbol{\xi}'')$ is constructed similarly, and describes the absolute entropy of $\mathfrak{S}''$. But . . .

What can one say about the composite system $\mathfrak{S} = \mathfrak{S}' \oplus \mathfrak{S}''$? We expect to be able to write

$$dQ = T\cdot dS \tag{16}$$

but what do we know about the entropy S of the composite system? The question is usually passed over in silence (else its answer is assumed to be obvious), but it deserves and rewards attention. From $dQ = dQ' + dQ''$ it follows, by results already in hand, that

$$\Sigma(\sigma',\sigma'')\,d\sigma(\sigma',\sigma'') = \Sigma\frac{\partial\sigma}{\partial\sigma'}d\sigma' + \Sigma\frac{\partial\sigma}{\partial\sigma''}d\sigma'' = \Sigma'(\sigma')\,d\sigma' + \Sigma''(\sigma'')\,d\sigma''$$

and therefore that

$$\Sigma\frac{\partial\sigma}{\partial\sigma'} = \Sigma'(\sigma')$$

$$\Sigma\frac{\partial\sigma}{\partial\sigma''} = \Sigma''(\sigma'')$$

By differentiation

$$\frac{\partial}{\partial\sigma''}\Sigma'(\sigma') = 0 = \frac{\partial\Sigma}{\partial\sigma''}\frac{\partial\sigma}{\partial\sigma'} + \Sigma\frac{\partial^2\sigma}{\partial\sigma''\partial\sigma'}$$

$$\frac{\partial}{\partial\sigma'}\Sigma''(\sigma'') = 0 = \frac{\partial\Sigma}{\partial\sigma'}\frac{\partial\sigma}{\partial\sigma''} + \Sigma\frac{\partial^2\sigma}{\partial\sigma'\partial\sigma''}$$

from which we obtain

$$\frac{\partial\Sigma}{\partial\sigma'}\frac{\partial\sigma}{\partial\sigma''} - \frac{\partial\Sigma}{\partial\sigma''}\frac{\partial\sigma}{\partial\sigma'} = \det\begin{pmatrix}\dfrac{\partial\Sigma}{\partial\sigma'} & \dfrac{\partial\Sigma}{\partial\sigma''}\\[2mm] \dfrac{\partial\sigma}{\partial\sigma'} & \dfrac{\partial\sigma}{\partial\sigma''}\end{pmatrix} \equiv \frac{\partial(\Sigma,\sigma\ )}{\partial(\sigma',\sigma'')} = 0$$

What this tells us is that $\Sigma(\sigma',\sigma'')$ and $\sigma(\sigma',\sigma'')$ are *not independent* functions of their arguments; to know one is, in principle, to know the other. In short:

$$\Sigma = \Sigma(\sigma)$$

and $\Sigma(\sigma',\sigma'') = \Sigma(\sigma(\sigma',\sigma''))$. It is for *this* reason that

$$\begin{aligned}dQ &= T\cdot C^{-1}\Sigma(\sigma',\sigma'')\,d\sigma(\sigma',\sigma'') \quad\text{can be written}\\ &= T\cdot C^{-1}\Sigma(\sigma)\,d\sigma\\ &= T\cdot dS\end{aligned}$$

where $S(\boldsymbol{\xi}',\boldsymbol{\xi}'')$ is got by dropping the primes from the procedure described at the top of the page.

We are now secure in the knowledge that $đQ = đQ' + đQ''$ can be expressed $T\,dS = T\,dS' + T\,dS''$ or again $dS = dS' + dS''$. And this—on the assumption only that the additive constants S_0, S_0' and S_0'' have been properly coordinated —emerges as a statement of the **diathermal additivity of entropy**:

$$S = S' + S'' \tag{17}$$

To summarize:
- the construction of the absolute temperature scale,
- the fundamental statement $đQ = T\,dS$, and
- the additivity of entropy

have *all* emerged as by-products of the integrability assumption (13). There is—contrary to the impression conveyed by some authors—no need to bring such tools into play by separate/explicit postulate.

In view of the conceptual weight borne by the integrability hypothesis, it becomes pertinent to observe that it speaks many dialects. Which is to say: one has

$$đQ = \tau\,d\sigma = \tau^*\,d\sigma^*$$

provided τ^* and σ^* are produced out of τ and σ by what I call a **thermodynamic gauge transformation**

$$\sigma \longrightarrow \sigma^* = f(\sigma)$$
$$\tau \longrightarrow \tau^* = (df/d\sigma)^{-1}\tau$$

But notice:

$$\frac{1}{\tau^*}\frac{\partial \tau^*}{\partial t} = \frac{1}{\tau}\frac{df}{d\sigma}\cdot\frac{\partial}{\partial t}\left(\frac{df}{d\sigma}\right)^{-1}\tau = \frac{1}{\tau}\frac{\partial \tau}{\partial t} = g(t)$$

so the equation (15) that serves to define the conversion $t \to T(t)$ from emperical to absolute temperature is *gauge invariant*. And so also, therefore,[22] is the definition of the absolute entropy.

It is by virtue of such formal "stability properties" as were developed above and on page 27 that the absolute temperature and absolute entropy concepts secure—within thermodynamics—their claim to our attention. The statistical approach to thermal physics will lend independent support to those claims.

13. Pressing ideal gases into service as absolute thermometers. In principle, *any* system can be made to serve as an "absolute thermometer" or—to say the same thing another way—to serve *as its own* absolute thermometer.[23] My objective here is to illustrate *how* this is done.

Inevitably, some systems lend themselves to the procedures in question more simply/usefully than others. We will take "ideal gas" to be our working substance for reasons that merit passing comment:

---

[22] Write $đQ = T \cdot dS = T^* \cdot dS^*$ and use $T = T^*$, which is an expression of the fact just established.

[23] In extreme cryogenic situations, where one is working beyond the limits of established thermometric technique, there is, in fact, no other way to proceed.

Classical mechanics (also quantum mechanics) proceeds—as announced by Newton's 1st Law—in reference to the postulated mechanics of *free particles*,[24] which acquire therefore the status of "simplest possible" mechanical systems. Gases—which microphysics teaches us to regard as *nearly-free particle systems* (populations of particles that move freely except for weak particle-particle and particle-wall interactions that are, however, strong enough to achieve thermal equilibrization)—occupy a similar position thermal physics, and it was the study of gases (especially air and steam) that—more than any other experimental activity—served historically to motivate and guide the development of thermodynamics. It is a lucky fact that most "real gases" behave nicely/simply under the conditions that were available in 17th & 18th Century laboratories, for under more extreme conditions they behave more awkwardly (for example, they condense: Faraday achieved the liquification of clorine in 1823). "Ideal gases" are abstractions from which those awkward properties have been discarded. They are well approximated in the laboratory by real gases of low density; *i.e.*, by gas samples that are "rare," yet not so rare as to have become perfect vacuums.[25]   So when we contemplate the construction of an "ideal gas thermometer" we contemplate a procedure that could, in fact, be approximated in the laboratory (as Galileo was the first to remark)...but I will not belabor that part of the story.

Later we will have occasion to examine the thermal physics of gases in fine detail. Here we assemble only such basic information as is essential to our immediate needs—the lesson being that *some* such information is *always* essential if we are going to turn the system that sits before us on the lab bench into an absolute thermometer.

$\boxed{\text{Observational fact \#1}}$ is that to describe the thermodynamic state of any given sample of real/ideal gas we must specify **2 state variables**, which we will here take to be pressure p and volume V.[26]

$\boxed{\text{Observational facts \#2 \& 3}}$ are that the product pV depends only upon the emperical temperature t

$$pV = \mathcal{F}(t) \tag{18.1}$$

and that so also does the internal energy:

$$U = \mathcal{U}(t) \tag{18.2}$$

---

[24] The primacy of free particles is enshrined in the Feynman diagrams of quantum field theory, where the vertices refer (figuratively) to the birth/death, and the connecting lines to the motion...of *free* particles.

[25] It is a curious fact—well appreciated by theoretical astrophysicists—that *all* many-body systems behave like ideal gases at sufficiently high temperature, just as all particles move like free particles (indeed: like *massless* free particles) at sufficiently high energy.

[26] To these must be added a third variable (mass M, or mole number N, though the latter presumes a more detailed command of the physics of gases than we presently require: my effort will be to use the least possible amount of imported physical knowledge).

Notice that we have, as yet, made no assumption concerning how the functions $\mathcal{F}(t)$ and $\mathcal{U}(t)$ may be related, and that their specific designs hinge on how we have elected to set up the emperical t-scale.

By the 1$^{\text{st}}$ law we now have

$$
\begin{aligned}
\dh Q = dU - \dh W &= dU + p\,dV \\
&= \frac{d\mathcal{U}}{dt}dt + \frac{\mathcal{F}}{V}dV \\
&= \mathcal{F}\left\{ \frac{1}{\mathcal{F}}\frac{d\mathcal{U}}{dt}dt + d\log\frac{V}{V_0} \right\} \\
&= \mathcal{F}\left\{ d\log\psi(t) + d\log\frac{V}{V_0} \right\} \\
&\qquad \log\psi(t) \equiv \text{antiderivative of } \frac{1}{\mathcal{F}(t)}\frac{d\mathcal{U}(t)}{dt} \\
&= \mathcal{F}(t)\cdot d\log\left\{ \psi\frac{V}{V_0} \right\}
\end{aligned}
\tag{19}
$$

> **REMARK**: Both $\mathcal{F}(t)$ and $\mathcal{U}(t)$ have the dimensions of energy, so $\psi(t)$ is dimensionless. The V_0 has been introduced as a dimensional necessity, but makes no contribution to the differential.

A more detailed description of $\psi(t)$ will have to await the receipt of further information concerning the structure of the functions $\mathcal{F}(t)$ and $\mathcal{U}(t)$. But for the moment it is sufficient to notice that in (19) we have an equation of the form

$$
\dh Q = \tau\,d\sigma \quad \text{with} \quad \tau \equiv \mathcal{F}(t) \quad \text{and} \quad \sigma \equiv \log\left\{ \psi\frac{V}{V_0} \right\}
$$

The universal function $g(t)$ (see again page 26) has therefore the form

$$
g(t) \equiv \tfrac{\partial}{\partial t}\log\left[\tau/\tau_0\right] = \tfrac{d}{dt}\log\left[\mathcal{F}(t)/\mathcal{F}_0\right]
$$

(Note in this connection that when we wrote $\tau = \mathcal{F}(t)$ the integrating factor τ acquired physical dimension, and it became improper to write $\log\tau$. Whence the fiducial denominators ...which are, however, invisible to the calculus.) Returning with this information to (15) we obtain

$$
\begin{aligned}
T = T(t) &\equiv C\cdot\exp\left\{ \int^t g(\vartheta)\,d\vartheta \right\} \\
&= C\cdot\exp\left\{ \int^t \tfrac{d}{d\vartheta}\log\left[\mathcal{F}(\vartheta)/\mathcal{F}_0\right]\,d\vartheta \right\} \\
&= C\cdot\exp\left\{ \log\left[\mathcal{F}(t)/\mathcal{F}_0\right] \right\} \\
&= \left[C/\mathcal{F}_0\right]\cdot\mathcal{F}(t) \\
&= \text{constant with dimensions } \frac{\text{temperature}}{\text{energy}}\cdot pV
\end{aligned}
\tag{20}
$$

What this, in conjunction with (18.1) says is that

> For ideal gases, pV provides a direct
> measure of the absolute temperature T.

In practice, we would only have to obtain measured values p_0 and V_0 of the pressure and volume of our sample at some agreed-upon "standard" absolute temperature T_0, use this information to fix the value of $C = T_0/p_0V_0$, then take

$$T = (pV/p_0V_0)T_0$$

to be the equation that *defines the operation* of our "absolute gas thermometer." In *actual* practice one proceeds a bit differently: one digs deep enough into the physics of gases to obtain

Observational fact #4 : The emperical temperature scales defined

$$\mathcal{T} = \left[R \cdot \frac{\text{number } N \text{ of molecules}}{\text{Avogadro's number } N_0}\right]^{-1} \cdot pV \equiv (nR)^{-1} \cdot pV$$

are *coincident* for *all ideal gas samples of all sizes*. This is true whatever the value assigned to the constant R, but by established convention (having to do with the temperature that will be assigned to the freezing point of water) one sets

$$R \equiv \text{gas constant (per mole)} = 0.082 \, \frac{\text{atmosphere-liters}}{\text{mole-degrees}}$$

$$= 8.31451 \, \frac{\text{Joule}}{\text{mole-degrees}}$$

These developments (which involve bringing molecules into the story) place us in position to state that if, in (15), we set $C = (nR)^{-1}$ and interpret "degrees" —which prior to Kelvin's discovery had to mean "gas degrees"—now to mean "degrees Kelvin,"[27] then

$$T = \text{emperical ideal gas temperature } \mathcal{T}$$

And it is with that identification *taken for granted* that in the theory of ideal gases we allow ourselves to write

$$pV = nRT \tag{21}$$

What can we now say about the entropy of an ideal gas? Borrowing

$$\tau(\sigma, t) = \Sigma(\sigma) \cdot e^{\left\{\int^t g(\vartheta)\, d\vartheta\right\}}$$

from page 26, we observe that in the present setting $e^{\left\{\int^t g(\vartheta)\, d\vartheta\right\}} = \mathcal{F} = \tau$

---

[27] The phrase "degrees Kelvin" is, by universal convention, considered to be improper: one says simply "Kelvin." And, while one writes $°F$ and $°C$, one writes not $°K$ but simply K.

supplies $\Sigma(\sigma) = 1$. So (see again the top of page 28)

$$s(\sigma) \equiv C^{-1} \int^{\sigma} \Sigma(\eta)\, d\eta = C^{-1}\sigma + \text{constant}$$

which, when we take the value of σ from (19), becomes

$$s(\sigma) = C^{-1} \log \psi(t) \frac{V}{V_0} + \text{constant}$$

Two pages ago we encountered a description of $\log \psi$ that works with *any* measure of temperature. If we elect to work with absolute temperature, then adjustments $\mathcal{F}(t) \to nRT$, $\mathcal{U}(t) \to U(T)$ are called into play, and we have

$$\log \psi = \text{antiderivative of } \frac{1}{nRT} \frac{dU(T)}{dT}$$

but can proceed no further until we know something about the functional structure of $U(T)$. We are rescued by

$\boxed{\text{Observational fact \#4}}$: For ideal gases the internal energy depends *linearly* on T (and also on the size of the sample):

$$U(T) = nC_V T \tag{22}$$

where C_V, the "molar specific heat at constant volume," is a constant. From this information it follows that

$$\log \psi = \text{antiderivative of } \frac{1}{nRT} \frac{d(nC_V T)}{dT}$$
$$= (C_V/R) \log \frac{T}{T_0}$$

so we have, finally,

$$S(T, V, n) = nR\left\{ (C_V/R) \log \frac{T}{T_0} + \log \frac{V}{V_0} \right\}$$
$$= nC_V \log \frac{T}{T_0} + nR \log \frac{V}{V_0} \tag{23}$$

This—since it says an important thing about an important class of (idealized) systems—is an important result that will haunt us as we enter ever deeper into thermal physics, and about which I will have many things to say. For the moment I want to remark only

- that in the conversion of an ideal gas sample into an absolute thermometer we had (with the aid of some arbitrarily-selected emperical thermometer and other instruments) to discover certain "observational facts" about ideal gases. Comparable steps must be taken *whatever* the system we have elected to employ as an absolute thermometer ... and usually they are not so easy;

- that (23) describes a *function of state*, one which we have managed to extract directly from the laws of thermodynamics and the barest rudiments of gas physics;

- that the functional structure of $S(T, V, n)$ does, at this early point in our thermodynamic experience, seem implausible, for in mechanics we have learned not expect logarithms to pop up in the middle of simple problems, to intrude into discussions of "simple systems." It becomes plausible to speculate that $\exp\{S/k\}$ might be of more fundamental importance than entropy itself ... as, indeed, when we dig into the statistical underpinnings of thermodynamics, it turns out to be! The factor k arose here, by the way, from writing $nR = (N/N_0)R \equiv Nk$: it is

Boltzmann's constant $k = R/N_0 =$ gas constant *per molecule*

$$= 1.38066 \times 10^{-23} \text{ Joule/Kelvin}$$

$$= 1.38066 \times 10^{-16} \text{ erg/Kelvin}$$

$$= 8.61739 \times 10^{-5} \text{ eV/Kelvin}$$

and occurs in the exponent from dimensional necessity. In this notation (23) becomes

$$S = Nk \log \frac{V\,T^\nu}{V_0 T_0^\nu} \quad \text{with} \quad \nu \equiv C_V/R$$

and gives

$$e^{S/k} = \left[\frac{V\,T^\nu}{V_0 T_0^\nu}\right]^N \tag{24}$$

We are, however, still a long way from being able to argue that

$$\nu = \tfrac{1}{2}(\text{number of mechanical degrees of freedom, per molecule})$$

$$= \tfrac{3}{2} \text{ for monatomic molecules}$$

We are a long way too from being able to argue that the expression $\left[VT^{\frac{3}{2}}/V_0 T_0^{\frac{3}{2}}\right]^N$ on the right side of (24) can be read as the embodiment of an elegant *statistical* principle of unrestricted generality and transparently deep significance. I allude here to the equation

$$S = k \log W$$

that has been described[28] as Ludwig Boltzmann's "greatest scientific achievement" and is inscribed on the monument that marks his grave.

14. Non-negativity of absolute temperature. That $T \geqslant 0$ was remarked already at the point (15) of definition, where it was seen to follow from a mathematical triviality:

$$(\text{positive real}) \cdot e^{(\text{real exponent})} \geqslant 0$$

In point of historical fact it was the non-negativity of "ideal gas temperature"— actually, a collateral idea: the existence of a "least possible" gas temperature $\mathcal{T} = 0$—that was first remarked. Only after it had been established that $\mathcal{T} = T$ did $\mathcal{T} \geqslant 0$ become a statement about a property of absolute temperature.

---

[28] E. Broda, *Ludwig Boltzmann: Man/Physicist/Philosopher* (1983), page 33.

The point to which I draw attention is that the historic (and still frequently repeated) claim that

$$\text{thermodynamics of ideal gases} \implies T \geqslant 0$$

does—by itself—not quite work, that the purported conclusion follows only when ideas technically extraneous to the "thermodynamics of ideal gases" are brought into play.

According to Kurt Mendelssohn[29] it was Guillaume Amontons[30] who first drew from the observation that

$$\Delta p \sim \Delta(\text{temperature}) \quad : \quad \text{any isovolumetric gas sample}$$

the conclusion that—<u>since the pressure of a gas cannot be negative</u>—there must exist a "coldest possible" temperature (estimated by him to be $-240°C$) at which $p = 0$.[31] But plenty of systems *are* capable of exhibiting negative pressures, are (like springs) as able to suck as to push on the walls that enclose them. On what grounds does Amontons assert that

$$\text{gas pressure } p \geqslant 0$$

To phrase the question in more modern terms: it is obvious that

$$pV = nRT \text{ and } p \geqslant 0 \text{ } jointly \implies T \geqslant 0$$

but from where do we obtain the inequality included among our hypotheses?

---

[29] *The Quest for Absolute Zero* (2nd edition 1977), page 10.

[30] Amontons (1663–1705) was a (deaf) French physicist who busied himself mainly with the invention of scientific instruments and diverse "useful devices" (perpetual motion machines, an "optical telegraph" that involved a network of telescopes stationed on hilltops, many others). The interest in thermometry that he developed near the end of his short life led him to independent rediscovery of many of the properties of gases that had been discovered by Robert Boyle (1627–1691) and Edme Mariotte ($\sim$1620–1684) several decades earlier, and to the publication of (among other memoirs) "Le thermomètre réduit à une mesure fixé" (1703). There he drew attention to the fact that water ceases getting hotter at boiling, and that the boiling point might therefore serve usefully as a fixed point in the design of temperature scales. It was there also that he mentioned the point of interest to us here.

[31] The author of the Amontons entry in *Cambridge Biographical Dictionary of Scientists* claims that the conclusion here attributed to Amontons is "barely implied" in the memoir mentioned above,[30] but that it was cited and developed in a posthumous publication (1779) by the prolific/influential Johann Lambert (1728–1777). Mendelssohn points out that Amontons' work anticipates the more accurate work published by Jacques Charles (1746–1823) and Joseph Gay-Lussac (1778–1850) a full century later (1802). Gay-Lussac's improved experimental technique placed the "coldest possible temperature" at $-273°C$ and was responsible for general acceptance of the notion of an "absolute zero" of temperature.

Amontons, it develops, had embraced—as had Boyle before him,[32] and as do we—a "corpuscular" view of the constitution of gases—a view that carries with it a kinetic interpretation of the *meaning* of pressure, and from that interpretation $p \geqslant 0$ follows automatically. Amontons went on to conclude that at $p = 0$ (which is to say: *at the coldest possible temperature*) *all corpuscular motion ceases*.

The upshot of the preceding discussion:

- if we take $T \geqslant 0$ to be a thermodynamic given, implicit in (15), then the proposition that—for gases—$p \geqslant 0$ acquires the status of a *thermodynamic* statement, a corollary of $pV = nRT$, but

- if $T \geqslant 0$ is our objective, and is to be extracted from the theory of gases, then $p \geqslant 0$ must be obtained from some extra-thermodynamic source; namely, from "what it means to be a gas," from kinetic theory.

Amontons had, in his time, no alternative but to follow the latter course, but it is remarkable that he had the sagacity to do so, for he worked 36 years before Daniel Bernoulli's first tentative sketch of a "kinetic theory of gases" (1738),[33] and 150 years before Maxwell established that such a theory deserves to be taken seriously.

Given the theoretical existence of states with $T = 0$, it becomes natural to contemplate going into the laboratory and *preparing* such a state, so that it might be studied experimentally. The 3$^{\text{rd}}$ Law of Thermodynamics speaks, however, to the **unattainability of absolute zero**, the precise claim being (no surprise to the turn-of-the-century founding fathers of cryogenics!) that $T = 0$ cannot be achieved by any finite sequence of refrigeration cycles. The 3$^{\text{rd}}$ law came into the world as "Nernst's heat theorem" (1906), which was intended to resolve a class of problems encountered in physical chemistry.[34] It can be phrased in many superficially-dissimilar ways—none of which are we yet in position to discuss—but can be traced to a low-temperature *property shared by all physically-possible entropy functions*...and beyond that, to an elegant statistical circumstance.

It will emerge, finally, that within the context provided by physical systems of a certain specialized type (lasers provide the most conspicuous examples) it

---

[32] Boyle, though he began his work the better part of a generation before Newton, was a systematic proponent of what he called the "corpuscular philosophy." In particular, he held "heat" to be a manifestation of corpuscular motion—this nearly 200 years before that concept finally managed to prevail over what during the interval had become the "caloric" orthodoxy.

[33] Bernoulli cited as evidence in support of his theory the fact that it conformed to Amontons' observations.

[34] See Cropper,[15] Chapter 10 or Mendelssohn,[29] Chapter 5 for sketches of the historical details (which physicists are likely to find a bit tedious). Physical chemistry was, in 1900, a relatively new field in which Walter Nernst (1864–1941) was a leading figure: it was (and is still today) concerned largely with the application of thermodynamic principles to chemical processes.

does make useful good sense—statistically, but also by natural extension of some standard thermodynamic formalism—to assign **negative absolute temperatures** to a certain class of contrived states. Those, however, are not states of thermal equilibrium (they are achieved by external stimulation), and $T < 0$ is found to lie "on the far side of $T = \infty$."

15. Concluding remarks. The 0th, 1st and 2nd laws have been presented in forms intended to *lay bare the essential architecture of classical thermodynamics*, and in language borrowed not from engineering or from chemistry but from ordinary work-a-day mathematical physics. But in my effort to avoid language that physicists tend to find alien, and bizarrely intrusive into a subject that purports to be timelessly fundamental, I have been forced to adopt a language that the authors of textbooks tend almost universally to dismiss as "too obscure." And indeed: I may in fact have obscured the simple practical essence of what we have accomplished ... so let me spell that out, in simplest possible terms:

- The 0th and 2nd laws served conjointly to supply a variable T that can be assigned unambiguously to *every thermalized state of every system*, however many and physically diverse may be the additional variables needed to describe such states. The temperature variable T is, by the way, <u>dimensionally autonomous</u>: in thermodynamics

$$\theta \equiv \text{physical dimension of temperature}$$

  joins the M, L, T and Q that symbolize the physical dimensions of mass, length, time and electrical charge.

- The 1st law assures us that with every system $\mathfrak{S}$ we can associate a <u>function of state</u> $U(\text{state})$ that refers physically to the *energetics* of the system

$$[U(\text{state})] = \text{energy}$$

  and permits us to write $đQ + đW = dU$.

- The 2nd law assures us that with every system $\mathfrak{S}$ we can associate a second <u>function of state</u> $S(\text{state})$ that—whatever it refers to—cannot refer to an "energy:" this much is clear on dimensional grounds

$$[S(\text{state})] = \text{entropy} = \frac{\text{energy}}{\text{temperature}}$$

  What S—and, in a separate way, also T—does refer to (in a way that thermodynamics by itself will never put us in a position to discuss) is the *statistical deployment* of the energy. But within thermodynamics S acquires its importance from the fact that it permits us to write $đQ = T dS$.

  With *functions* U and S in hand we find ourselves in position to "do function theory," to *develop elaborately patterned relationships that describe the thermodynamic properties of systems-in-general*.

From where do we obtain the $\underline{U \text{ and } S \text{ specific to } \mathfrak{S}}$ that will enable us to *particularize* those patterned relationships, to describe the thermodynamic properties of $\mathfrak{S}$-in-particular? One procedure might be diagramed

$$\text{observational data} \xrightarrow[\text{selected relationships}]{} U(\text{state}) \ \& \ S(\text{state})$$

Another—which embraces much of the practical utility of statistical mechanics —proceeds

$$\begin{bmatrix} \text{statistical mechanical} \\ \text{analysis of a postulated} \\ \text{microdynamical model} \end{bmatrix} \xrightarrow[\text{selected relationships}]{} U(\text{state}) \ \& \ S(\text{state})$$

In situations of the latter sort one then proceeds

$$\text{discovered } U \ \& \ S \xrightarrow[\text{selected relationships}]{} \text{predicted data}$$

$$\updownarrow \text{compare}$$

$$\text{observed data}$$

and, on the basis of the final comparison, forms an opinion about the accuracy of the model.

Each of the programs sketched above presumes fairly detailed familiarity with the "network of patterned relationships" that are latent in the laws of thermodynamics. And the second program presumes familiarity also with the computational methods of statistical mechanics. That, in a nutshell, is a description of the work that lies before us: it is in quest of familiarity with those subjects that we now roll up our sleeves . . .