3

Introduction to the basic elements
of

STATISTICAL MECHANICS

"A theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended its area of applicability. Therefore the deep impression that classical thermodynamics made upon me. It is the only physical theory of a universal content concerning which I am convinced that within the framework of the applicability of its basic concepts, it will never be overthrown..."

—Albert Einstein

"...what I did can be described as simply an act of desperation. By nature I am peacefully inclined, and reject all doubtful adventures. But...a theoretical interpretation [of the thermodynamically-deduced Planck distribution formula]...had to be...found at any cost, no matter how high...The two laws [of thermodynamics], it seems to me, must be upheld under all circumstances."

—Max Planck

Introduction. Classical thermodynamics—honorable discipline though it is, and as undeniably useful, self-consistent and complete as (say) classical mechanics—is nevertheless subject to some criticism. It proceeds (at least as presented here) from laws which, in their allusion to "exactness" and "integrability," have what most work-a-day physicists would consider to be an excessively formal, and intuitively uninformative, quality. Those mathematical allusions

do very efficiently deliver into our hands (among with a version of the absolute temperature concept that some might dismiss as too elegantly austere) a pair of functions of state—"internal energy" and "entropy"—and do thereby place us in position to "do function theory." But the theory does not, of itself, provide sharp insight into the physical *meaning* of those functions (especially the latter!): in classical mechanics we fancy that we can, with the mind's eye, "see" what is going on in a world behind the formalism, but thermodynamics fosters no such vision.

Deeper still is the criticism that classical thermodynamics, though preoccupied with "functions of state," accepts "states of thermal equilibrium" as the Great Given, into the meaning of which it provides no insight, which it leaves as it was found ... wrapped in mystery. That being the case, it is impossible to draw from thermodynamics itself any support for the view—so eloquently expressed by Einstein and Planck, and shared by many others—that "what thermodynamics says it says with implacable finality."

For now more than a century—owing not least to the work of Planck and Einstein themselves, but mainly to the work of Gibbs, Boltzmann and a few of their contemporaries—it has been universally accepted that the support for that view is overwhelming, but that it derives from considerations *extrinsic* to classical thermodynamics—from statistical mechanics, from the **Law of Large Numbers**. Statistical mechanics serves also to illuminate each of the issues that thermodynamics leaves in shadow: the meaning of temperature, the meaning of entropy, the meaning of "state of thermal equilibrium." And in doing so, it enables us to characterize the conditions under which the laws of thermodynamics must certainly hold, the conditions under which they may begin to lose their force.

My objective in this chapter will be to describe the essential *principles* of statistical mechanics ... with emphasis on the "statistical," and least-possible reference to the "mechanics." While the mechanical details change from system to system, the statistical digestion of those details is system-independent, and it is that fact that accounts for the compelling universality of thermodynamics. *Application* of the principles of statistical mechanics is a complex industry unto itself, and will be reserved for treatment in subsequent chapters. Nor will we be concerned here with the high-tech industry that operates just across the street, though I will take this opportunity to describe what goes on there: statistical mechanics does serve to *illuminate* the meaning of the phrase "state of thermal equilibrium," but does not tell us how physical systems manage to achieve such a state. To do so would be to trace the accepted principles of statistical mechanics to their classical/quantum mechanical underpinnings, and that is the specialized business of *ergodic theory*.

1. Model system assembled from binary sub-systems. Consider[68] the simple system $\mathfrak{S}$ illustrated in the following figure: it consists of a 2-step staircase and

[68] ... with C. Kittel & H. Kroemer, upon whose expository device (*Thermal Physics*, 2nd edition 1980) I base this discussion.

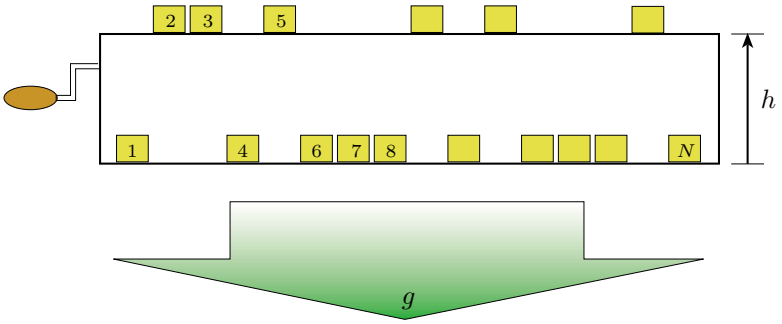

FIGURE 24: *N tokens, each of which sits either on the top step or on the bottom step. By working on the system (turning the crank) we can adjust the step-rise. The system, though deprived of all dynamical properties, does possess an elementary "energetics," and it is complex enough to provide a playground for all the most basic principles of statistical mechanics.*

a set of N tokens, and has no moving parts. We assume

- gravity to be present,
- the step-rise h to be subject to our external control,
- the tokens to be **identical** (in the sense that each has mass m) but ...
- ... to be **distinguishable** (by the numbers $1, 2, \ldots, N$ printed on them).

The i^{th} can sit (which is to say: be placed) on either step, but has no powers of spontaneous (or inertial/dynamical) motion and does not interact (dynamically or otherwise) with any of the other tokens: the tokens are, in other words, inert and independent. $\mathfrak{S}$ resembles a solid (crystal?), liquid or gas in that it has been assembled by N-fold replication of elementary sub-systems, but when one consideres the complexly interactive microdynamics going on within real solid/ liquid/gas one appreciates the profound sense in which $\mathfrak{S}$ is "mechanically rudimentary"... or (in the phrase at the top of the page) "pre-dynamical." It is *because* $\mathfrak{S}$ is so rudimentary that it yields so easily to exact detailed analysis. But—though rudimentary—the system is rich enough to exemplify all the most basic principles of statistical mechanics, and to support a thermodynamics ... as will emerge.

To describe the state of the i^{th} token we might write

$\uparrow_i$ if i^{th} token is in an **up state** (sits on the top step)

$\downarrow_i$ if i^{th} token is in an **down state** (sits on the bottom step)

and to describe the state of the N-token system we might write something like

$$\downarrow_1 \uparrow_2 \uparrow_3 \downarrow_4 \uparrow_5 \ \cdots \ \downarrow_N$$

There are clearly a total of 2^N such strings: $\mathfrak{S}$ possesses a total of 2^N distinct states, which the symbol $(\uparrow_1 + \downarrow_1)(\uparrow_2 + \downarrow_2)\cdots(\uparrow_N + \downarrow_N)$ serves formally to

generate. Thus, in the case $N = 3$, we have

$$\begin{aligned}
&(\uparrow_1 + \downarrow_1)(\uparrow_2 + \downarrow_2)(\uparrow_3 + \downarrow_3) \\
&= \quad \uparrow_1 \uparrow_2 \uparrow_3 && : \quad 3 \text{ up in } 1 \text{ ways} \\
&\quad + \downarrow_1 \uparrow_2 \uparrow_3 + \uparrow_1 \downarrow_2 \uparrow_3 + \uparrow_1 \uparrow_2 \downarrow_3 && : \quad 2 \text{ up in } 3 \text{ ways} \\
&\quad + \uparrow_1 \downarrow_2 \downarrow_3 + \downarrow_1 \uparrow_2 \downarrow_3 + \downarrow_1 \downarrow_2 \uparrow_3 && : \quad 1 \text{ up in } 3 \text{ ways} \\
&\quad + \downarrow_1 \downarrow_2 \downarrow_3 && : \quad 0 \text{ up in } 1 \text{ ways}
\end{aligned}$$

and, of course, $1 + 3 + 3 + 1 = 8 = 2^3$. We will find it convenient to speak of the "n-up configuration" (meaning simply that there are a total of n tokens on the top step), with

$$n = \underbrace{0, 1, 2, \ldots, N}_{\text{total of } N+1 \text{ distinct configurations}}$$

Having resolved the **state space** into configurations, we now resolve each configuration into distinct "complexions." We will say that

$$\text{the } n\text{-up configuration has } g(n) \text{ distinct "complexions"}$$

to indicate that g distinct states possess the property that they have n tokens up. Arguing from elementary combinatorics—or formally from

$$(\uparrow + \downarrow)^N = \sum_{n=0}^{N} \tbinom{N}{n} (\uparrow)^n (\downarrow)^{N-n}$$

—we conclude that

$$\underbrace{g(n) \equiv g(n; N)}_{\text{will be called the } \textbf{multiplicity function}} = \binom{N}{n} = \frac{(\text{total number})!}{(\text{number up})! \cdot (\text{number down})!} \tag{94}$$

and it is a familiar fact that

$$\sum_{n=0}^{N} \tbinom{N}{n} = 2^N$$

which, in language less specific to our model, says simply that

$$\sum_{\text{configurations}} g(\text{configuration}) = \text{number of states}$$

We are in position now to speak efficiently about the **energetics** of $\mathfrak{S}$. The system is "mechanically so rudimentary" that the tokens possess neither kinetic

energy nor interaction energy," but they do possess gravitational potential energy: if (for each i) $\downarrow_i$ has energy

$$E_{\text{down}} = 0 \quad \text{by agreed-upon convention}$$

then (for each i) $\uparrow_i$ has energy

$$E_{\text{up}} = \varepsilon \equiv mgh$$

and the **total energy of the N-token system** is *determined by its configuration* (that is: by the number n of "up" tokens), and is given by

$$\begin{aligned} U(\text{state of } \mathfrak{S}) &= \sum_i (\text{energy of } i^{\text{th}} \text{ token}) \\ &= (\text{number of "down" tokens}) \cdot E_{\text{down}} \\ &\qquad + (\text{number of "up" tokens}) \cdot E_{\text{up}} \\ &= n\varepsilon \end{aligned}$$

where (again) n identifies the "configuration" of the particular $\mathfrak{S}$-state in question. Though each individual token is in one or the other of only two energy states, it is evident that

- the energy of the system as a whole can assume any one of a total of $N+1$ possible values
$$E_n = n\varepsilon \quad : \quad n = 0, 1, 2, \ldots N$$
- specification of the energy serves to identify the configuration of the state
- there are $g(n)$ distinct system-states with energy E_n.

The point the preceding remarks serve to establish is that the energetics of the situation provide a language that is in some respects alternative to (and more directly "physical" than) our former (ennumerative/combinatoric) "configuration/complexion" language: we can

- use energy to classify the states of $\mathfrak{S}$, and
- say of the "energy state E_n" that it is "$g(n)$-fold degenerate."

2. Statistical properties of the model. Suppose now that we possess an **ensemble** of systems $\mathfrak{S}$; *i.e.* /, that we possess some arbitrarily large number of (real or merely mental) identical replicas of $\mathfrak{S}$

$$\mathfrak{S}_1 \quad \mathfrak{S}_2 \quad \mathfrak{S}_3 \quad \ldots \quad \mathfrak{S}_\nu \quad \ldots$$

and that each member of the ensemble is in a **randomly-determined state**.[69]

[69] The actual state-determining mechanism is of no immediate relevance or consequence: we might, for example, use N flips of a loaded coin to set the state of $\mathfrak{S}_1$, repeat the process for the other elements of $\{\mathfrak{S}\}$, then shuffle their labels.

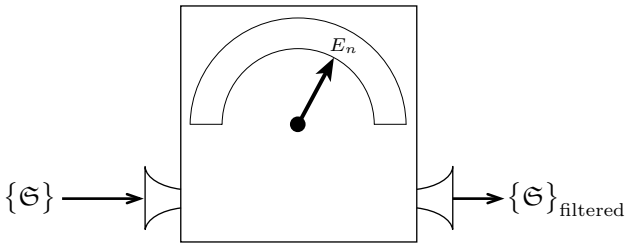

FIGURE 25: *Idealized "energy filter" that examines the elements of the ensemble* $\mathfrak{S}$ *and passes only those in states with some prescribed energy value* E_n*. Filters that select a state-property other than energy are readily imagined.*

Suppose now that the elements $\mathfrak{S}_\nu$ of $\{\mathfrak{S}\}$ are presented serially to an "energy filter," the action of which (see the figure) is to pass or reject elements of $\{\mathfrak{S}\}$ according as they are or are not in states of some specified energy E_n. The elements of $\{\mathfrak{S}\}_{\text{filtered}}$—the elements that "pass the test"—are, by construction, **equi-energetic** (all in the n-up configuration), but can be expected generally to possess a variety of complexions ... the number of possible complexions being given by $g(n)$, the **degeneracy** of E_n. Such filters supply some information—but incomplete information—about the states of the systems which they pass.

Now some language, intended to facilitate a slight shift of emphasis: we will say of the elements of $\{\mathfrak{S}\}_{\text{filtered}}$ that they have been "constrained" (by the filter) to have energy E_n. States that conform to that imposed constraint will be said to be **accessible** states.

> **REMARK:** The language just presented prepares for a move away from our model system to systems with internal *dynamics*. In such a setting it becomes natural to suppose that $\mathfrak{S}$ hops from state to state, but can never visit an "inaccessible" state—a state that would place the system in violation of energy conservation. The "constraint that energy be conserved" arises in such a setting from the laws of motion.

We can, from this point of view, look upon the multiplicity function $g(n)$ as an "accessible state counter." To express the generalized essence of that idea, we might write

$$g(\text{system}, \text{filter}) = \left\{ \begin{array}{l} \text{number of states accessible to the system that are} \\ \text{consistent with the constraint imposed by the filter} \end{array} \right.$$

Notice that the notions just put forth remain meaningful even if our "filter" looks not to the energy of a state but *to any mechanically conserved variable*. Our "energy fixation" can, I think, be attributed to the circumstance that energy conservation is the *only* conservation law for which we could mount a

claim that it is *universally* available, that it pertains to *all* of the systems to which we would apply the methods of statistical mechanics.[70]

Systems $\mathfrak{S}$ drawn from $\{\mathfrak{S}\}_{\text{filtered}}$ will (by construction) never be found to occupy inaccessible states, but with what frequencies will they be found to occupy the respective accessible states? What is the probability that an $\mathfrak{S}$ drawn randomly from $\{\mathfrak{S}\}_{\text{filtered}}$ will be found to be in some prescribed accessible state? Statistical thermodynamics proceeds from this

> **FUNDAMENTAL ASSUMPTION:** Accessible states occur with *equal* frequency in $\{\mathfrak{S}\}_{\text{filtered}}$. Since there exist g such states, the probability that an $\mathfrak{S}$ drawn randomly from $\{\mathfrak{S}\}_{\text{filtered}}$ will be found to be in any specified accessible state can be described
>
> $$P(\text{accessible state}) = \frac{1}{\text{number } g \text{ of such states}} \tag{95}$$

In the phenomenological success of thermodynamics one can read evidence that the FUNDAMENTAL ASSUMPTION is physically justified. And one can argue that the assumption *conforms most frankly to what we specifically know* about $\{\mathfrak{S}\}_{\text{filtered}}$ by virtue of its operational preparation—that any alternative assumption would be unmotivated/arbitrary/willful (and difficult to phrase in the requisite generality).[71] But it is very easy to think up "state-determining mechanisms" (in the language of page 97) that would lead to *violation* of the fundamental assumption. Evidently the fundamental assumption refers tacitly to—and draws its justification from—**Nature's state-determining mechanism** ... but what is that?

The FUNDAMENTAL ASSUMPTION **lends a specific meaning to the thermal equilibrium concept**—to the phrase "$\mathfrak{S}$ is in a state of thermal equilibrium" or "... has become thermalized"—but how does the solitary/real physical system that sits before me manage in the real world to *achieve* such a state. These questions have obviously a deeply dynamical component,[72] but it appears that dynamics-pure-and-simple is incapable-in-principle of supplying sharp and complete answers, for the questions are dynamical *but not merely* dynamical: they acquire an irreducible statistical component from the inevitably limited precision with which we can *know* the state of a many-body system. The upshot of much work by many people appears to be that *thermodynamics is consistent with and related to—but not a corollary of—mechanics*: to ask for a theory that reduces the fundamental assumption to the status of a mechanical

[70] See again the text associated with footnote 4.

[71] This line of argument has been developed by E. T. Jaynes in an important series of papers: "Information theory and statistical mechanics," Phys. Rev. **106**, 620 (1957) and **108**, 171 (1957).

[72] They bring us back again to the "ergodic theory" mentioned on page 94.

theorem appears to be to ask too much. The fundamental assumption has at least the merit of being simple, sharp, plausible. Our effort will be to follow where it leads.

Thermodynamics is a very soft probe: the experimental thermodynamicist measures/manipulates but a few of the collective attributes of dynamical systems known to possess very many mechanical degrees of freedom (and correspondingly many "potential attributes"). The numbers that constitute "thermodynamic data"—numbers that it is the business of thermodynamics to correlate/interpret/predict—are by nature statistical: they are **thermal averages of functions of mechanical state**, and are modeled theoretically by statements ultimately equivalent to, or deducible from . . . the following:

$$\langle F(\text{state})\rangle = \sum_{\text{accessible states}} F(\text{state})P(\text{accessible state}) \tag{96}$$

In language specific to our N-token binary model (Figure 24) the preceding statement—if we assume the "accessible states" to be (say) states of energy E_n (*i.e.*, to be "n-up states")—reads

$$\begin{aligned}\langle F(\text{state})\rangle &\equiv F(\text{state}) \text{ averaged over states of energy } E_n \\ &= \frac{1}{g(n)} \sum_{n\text{-up states}} F(n\text{-up state})\end{aligned}$$

In the particular case

$$F(\text{state}) \equiv \text{energy of that state}$$

the preceding equation reduces to a triviality, for all the accessible states have the *same* energy E_n, and there are $g(n)$ of them. That triviality is destined soon to become much more interesting.

3. Modeled effects of constraint relaxation. We will play a version of the old "Two System Game," looking to the binary model of a situation similar in many respects to that shown in Figure 14. Let

$\{\mathfrak{S}'\} \equiv \{\mathfrak{S}(n', N')\} \equiv$ thermalized ensemble of N'-token systems that have been passed through an $E_{n'}$-filter. All members of $\{\mathfrak{S}'\}$ are constrained by action of the filter to be in the n'-up configuration. They are equidistributed among a total of $g' \equiv g(n'; N')$ accessible states.

$\{\mathfrak{S}''\} \equiv \{\mathfrak{S}(n'', N'')\} \equiv$ thermalized ensemble of N''-token systems that have been passed through an $E_{n''}$-filter. Similar remarks pertain.

$\{\mathfrak{S}\} \equiv \{\mathfrak{S}'\} \oplus \{\mathfrak{S}''\} \equiv$ **non-thermalized** ensemble of $(N' + N'')$-token systems formed by **mental conjunction** of $\{\mathfrak{S}'\}$ and $\{\mathfrak{S}''\}$. All members of $\{\mathfrak{S}\}$ are in the $(n' + n'')$-up configuration, but they collectively comprise only a **sub-set** of the $(n' + n'')$-up states that are available-in-principle to an $(N' + N'')$-token system: they are equidistributed among a total of $g \equiv g' \cdot g''$ states.

The situation is illustrated below:

$$\uparrow\downarrow \qquad\qquad \downarrow\uparrow$$

States present with probability $P' = 1/g'$ *in* $\{\mathfrak{S}'\} \equiv \{\mathfrak{S}(1,2)\}$

$$\uparrow\uparrow\downarrow \qquad\qquad \uparrow\downarrow\uparrow \qquad\qquad \downarrow\uparrow\uparrow$$

States present with probability $P'' = 1/g''$ *in* $\{\mathfrak{S}''\} \equiv \{\mathfrak{S}(2,3)\}$

$$\begin{array}{ccc} \uparrow\downarrow\uparrow\uparrow\downarrow & \uparrow\downarrow\uparrow\downarrow\uparrow & \uparrow\downarrow\downarrow\uparrow\uparrow \\ \downarrow\uparrow\uparrow\uparrow\downarrow & \downarrow\uparrow\uparrow\downarrow\uparrow & \downarrow\uparrow\downarrow\uparrow\uparrow \end{array}$$

States present in $\{\mathfrak{S}\} = \{\mathfrak{S}'\} \oplus \{\mathfrak{S}''\}$*, where they occur with probability* $P = 1/g = 1/(g' \cdot g'') = \frac{1}{6} = P' \cdot P''$

We now

1) **relax the constraint**[73] that the conjunction of $\{\mathfrak{S}'\}$ and $\{\mathfrak{S}''\}$ be merely "mental;" *i.e.*, we allow the systems to interact, to trade energy;
2) **assume the subsequent interaction to be energy-conserving**;
3) allow the interaction to proceed until the composite system has **thermalized**:

$$\{\mathfrak{S}(n', N')\} \oplus \{\mathfrak{S}(n'', N'')\} \equiv \{\mathfrak{S}\}$$
$$\downarrow$$
$$\{\mathfrak{S}\}_{\text{thermalized}} \equiv \{\mathfrak{S}(n' + n'', N' + N'')\}$$

The last step is but a re-invocation of the FUNDAMENTAL ASSUMPTION, and poses all the familiar difficulties: its dynamical/statistical underpinnings are

[73] This phrase—encountered already in §4 of Chapter 1—will play a key role in our subsequent work.

semi-obscure, but to assume otherwise would be "unmotivated/willful." The deep and fundamental point of this discussion is exposed in the following adjustment of last of the the preceding figures

States present with probability $P = 1/g(3,5) = \frac{1}{10}$ *in* $\{\mathfrak{S}\}_{\text{thermalized}}$
The states below the line were made accessible by relaxation of the constraint.

and is this:

1) constraint relaxation **leaves constant or increases—never decreases—the number of accessible states**, and therefore
2) subsequent **thermalization decreases—never increases—the probability** that any given accessible state will be occupied.

What we have encountered here, as will emerge, is the simple essence of the **"law of entropy increase"**.

Analytically the situation (so far as it can be developed in the language of our model) is this: one has

$$\begin{aligned}\text{initial multiplicity} &= g(n';N')\cdot g(n'';N'')\\ \text{multiplicity after constraint relaxed} &= g(n'+n'';N'+N'')\end{aligned}$$

But

$$g(n'+n'';N'+N'') = \sum_{k=0}^{n} g(k;N')\cdot g(n-k;N'')$$

where $n \equiv n'+n''$ and the sum ranges over all k-values consistent with the conditions

$$k \leqslant N' \quad \text{and} \quad n-k \leqslant N''$$

Since the term at $k = n'$ is *by itself* precisely the initial multiplicity, we have

$$g_{\text{constrained}} \geqslant g_{\text{relaxed}}$$

with equality if and only if the $\sum$ embraces but a single term. More specifically, we have (by (94))

$$\binom{N'+N''}{n} = \sum_{k} \binom{N'}{k}\binom{N''}{n-k} \geqslant \text{any single term}$$

where the equality is known in the combinatoric literature as the "Vandermonde

convolution formula."[74] All of which works out quite nicely when applied to the tiny case used illustratively on the preceding two pages:

$$\binom{5}{3} = \binom{2}{0}\binom{3}{3} + \binom{2}{1}\binom{3}{2} + \binom{2}{2}\binom{3}{1} > \binom{2}{1}\binom{3}{2}$$

$$\Downarrow$$

$$10 = 1 \cdot 1 + 2 \cdot 3 + 1 \cdot 3 > 2 \cdot 3 = 6$$

One final aspect of this topic merits our attention, for it will serve to throw into sharp relief a striking fact that lies still just over the horizon. *Prior* to relaxation of the constraint the members $\mathfrak{S}'_\nu$ of $\{\mathfrak{S}'\}$ were in a variety of states (see again the top figure on page 101) but—by construction—all had the same energy. *After* relaxation of the constraint, and after thermalization has become complete, the systems $\mathfrak{S}'_\nu$—now components of the members of $\{\mathfrak{S}' \oplus \mathfrak{S}''\}_{\text{thermalized}}$—possess a statistically regulated variety of energies. Similar before/after remarks pertain, of course, to the members of $\{\mathfrak{S}''\}$. The

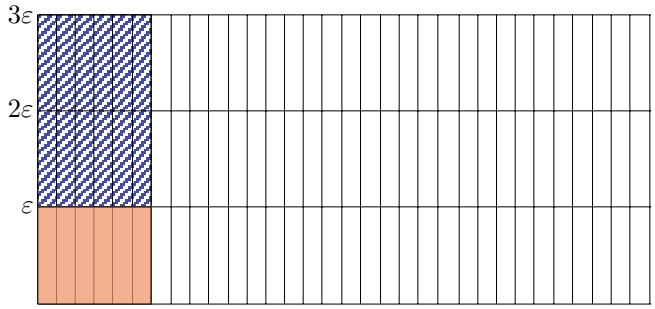

FIGURE 26: *Energy allocation within* $\{\mathfrak{S}(1,2)\} \oplus \{\mathfrak{S}(2,3)\}$. *Energy resident within* $\{\mathfrak{S}(1,2)\}$ *is* •, *that within* $\{\mathfrak{S}(2,3)\}$ *is* •.

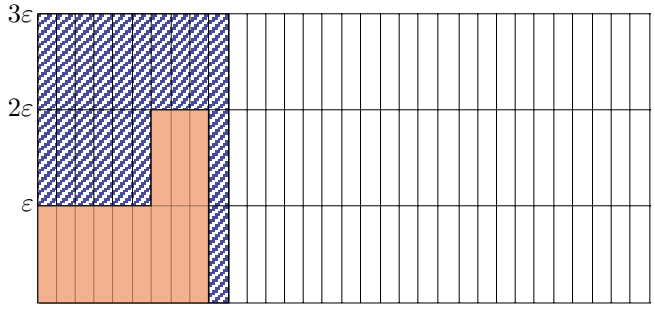

FIGURE 27: *Relaxation of the "disjointness" constraint creates four more accessible states, and energy transfer creates a more complex energy distribution pattern.*

[74] See, for example, J. Riordan, *Combinatorial Identities* (1968), page 8.

situation as it relates to our "tiny case" is illustrated in the preceding figures. The mental compose of a 2-token system with a 3-token system possesses a total of $2^2 \cdot 2^3 = 32$ states (represented by ruled columns in the figures). Of those, $2 \cdot 3 = 6$ are "accessible" if $n' = 1$ and $n'' = 2$ (see the bottom figure on page 101), and in *each* of those six cases (Figure 26)

- the energy allocated to $\mathfrak{S}'$ is ε, with certainty
- the energy allocated to $\mathfrak{S}''$ is 2ε, with certainty.

But relaxation of the "disjointness" constraint brings 4 more accessible states into play, and energy transfer $\mathfrak{S}' \rightleftarrows \mathfrak{S}''$ results in the more complex energy distribution pattern. Reading from Figure 27, we find that

$$E' = \begin{cases} 0 \text{ (and therefore } E'' = 3\varepsilon) \text{ with probability } \frac{1}{10} \\ \varepsilon \text{ (and therefore } E'' = 2\varepsilon) \text{ with probability } \frac{6}{10} \\ 2\varepsilon \text{ (and therefore } E'' = \ \varepsilon) \text{ with probability } \frac{3}{10} \end{cases}$$

on the basis of which we compute

$$\begin{aligned} \langle E' \rangle &= \ 0 \cdot \tfrac{1}{10} + \ \varepsilon \cdot \tfrac{6}{10} + 2\varepsilon \cdot \tfrac{3}{10} = 1.2\varepsilon \text{ with } \underline{\text{non-zero uncertainty}} \\ \langle E'' \rangle &= 3\varepsilon \cdot \tfrac{1}{10} + 2\varepsilon \cdot \tfrac{6}{10} + \ \varepsilon \cdot \tfrac{3}{10} = 1.8\varepsilon \text{ with } \underline{\text{non-zero uncertainty}} \end{aligned}$$

Because the energy transfer took place subject to the constraint that energy be conserved we have

$$\langle E' \rangle + \langle E'' \rangle = 3.0\varepsilon \text{ with } \underline{\text{certainty}}$$

and the post-interactive states of the component systems have become *partially correlated*.

Looking more generally to the subsystems of the thermalized composite system $\big\{\mathfrak{S}(n', N') \oplus \mathfrak{S}(n'', N'')\big\}_{\text{thermalized}}$ we have

$$\left.\begin{array}{ll} E' = k\varepsilon & \text{and therefore} \\ E'' = (n-k)\varepsilon & : \ n \equiv n' + n'' \end{array}\right\} \text{ with probability } P(k)$$

with

$$P(k) = \frac{g(k, N') \cdot g(n-k; N'')}{g(n; N)} \quad : \quad N \equiv N' + N'' \tag{97}$$

giving

$$\langle E' \rangle = n\varepsilon - \langle E'' \rangle = \frac{1}{g(n; N)} \sum_k k\varepsilon \cdot g(k; N') \cdot g(n-k; N'') \tag{98}$$

which, when n, N' and N'' are large (much less *realistically* large!), might appear to pose a formidable computational assignment. It will, however, emerge from the discussion to which we now turn that the very circumstances that make the computation seem "formidable" serve in fact to reduce it to near triviality!

4. Statement and consequences of Stirling's formula. Numbers such as those that appear in (98) can, in physically interesting cases, be described

$$\frac{\text{mass of a macroscopic hunk of stuff}}{\text{mass of constituent molecule}}$$

and lie typically within a few orders of magnitude of[75]

$$\textbf{Avogadro's number} \quad : \quad N \approx 6.0221367 \times 10^{23}$$

That is, by almost any standard, a *large* number, and the $N!$ that (98) asks us to contemplate is *really* large. Fortunately we have[76]

$$n! = \sqrt{2\pi\,n}\,n^n\,e^{\left(-n\,+\,\frac{\theta}{12n}\right)} \quad \text{with} \quad 0 < \theta < 1$$

which at $\theta = 0$ becomes **Stirling's formula**

$$\sim \sqrt{2\pi\,n}\,(n/e)^n \equiv S(n) \tag{99}$$

I will not take time to prove (99)—applications will keep us busy enough!—but some brief comments are may be in order:

1. The function $S(n)$ provides an "asymptotic" approximation to $n!$, in this characteristic sense: $n! - S(n)$ *grows without bound* but $[n! - S(n)]/n! \downarrow 0$, as the following data demonstrate:

n	$n! - S(n)$	$\dfrac{n! - S(n)}{n!}$
10	3.0104×10^4	8.2959×10^{-3}
10^2	7.7739×10^{154}	8.3298×10^{-4}
10^3	3.3531×10^{2563}	8.3329×10^{-5}
10^4	2.3719×10^{35654}	8.3333×10^{-6}

[75] HISTORICAL REMARK: The basic idea embodied in N is due (1811) to Lorenzo Romano Amedeo Carlo Avogadro (Count of Quaregna & Cerreto: 1776–1856). They were embraced and promoted by Ampère (1775–1836), but it was only in 1858 that, owing to the efforts of Stanislao Cannizzaro (1826–1910), they came to the general attention of physicists and chemists. It is perhaps not coincidental that in 1859 Maxwell, under immediate stimulation of recent papers by Clausius, turned his attention to the kinetic theory of gases.

[76] See M. Abramowitz & I. Stegun, *Handbook of Mathematical Functions* (1964), **6.1.37** page 257. Stirling's formula was first published (1730) by James Stirling (1692–1770), but was already known to Abraham DeMoive (1667–1754), who was one of the founding fathers of probability theory.

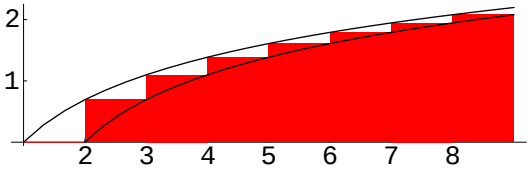

FIGURE 28: *The shaded area bounded by the "logarithmic staircase" provides a representation of*

$$\log n! = \log 2 + \log 3 + \ldots + \log n$$

The upper curve is a graph of $log\,(x)$*, the lower curve a graph of* $\log(x-1)$.

2. Useful insight into the design of Stirling's formula can be obtained very simply from the preceding figure: immediately

$$\int_1^{n+1} \log(x)\,dx > \log 1 + \log 2 + \cdots + \log n > \int_2^{n+1} \log(x-1)\,dx$$

which gives

$$(n+1)\log(n+1) - n > \log n! > n\log n - n + 1$$

while in Stirling approximation

$$\log n! \sim n\log n - n + \log\sqrt{2\pi n}$$

3. From the definition (due to Euler) of the **gamma function**

$$\Gamma(z+1) \equiv \int_0^\infty e^{-t}\,t^z\,dt$$

it follows easily that

$$\Gamma(1) = 1 \quad \text{and} \quad z\Gamma(z) = \Gamma(z+1)$$

and therefore that

$$\Gamma(n+1) = n! \quad : \quad n = 0, 1, 2, \ldots$$

The gamma function assigns a natural meaning to "non-integer factorial," (we find, for example, that $\Gamma(\frac{3}{2}) = \frac{1}{2}! = \frac{1}{2}\sqrt{\pi}$, $\Gamma(\pi+1) = \pi! = 7.18808$) and—more to the point—permits one to bring the methods of classical *analysis* to the study of $n!$: it is, in fact, by using standard methods to study the *asymptotics of the gamma function* that Stirling's formula and

its refinements—such as the following

$$\Gamma(z) \sim \sqrt{2\pi}\, e^{-z} z^{z-\frac{1}{2}} \left[1 + \tfrac{1}{12z} + \tfrac{1}{288z^2} - \tfrac{139}{51840z^3} - \tfrac{571}{2488320z^4} + \cdots\right]$$

—are most readily obtained.[77]

Turning now to asymptotic evaluation of $g(n;N) = \binom{N}{n}$, we have

$$\log g(n;N) = \log N! - \log n! - \log(N-n)!$$

which in Stirling approximation becomes

$$\sim \log S(N) - \log S(n) - \log S(N-n) \equiv B(n,N)$$

It is a familiar fact—illustrated in the following figure, that Pascal's pile of

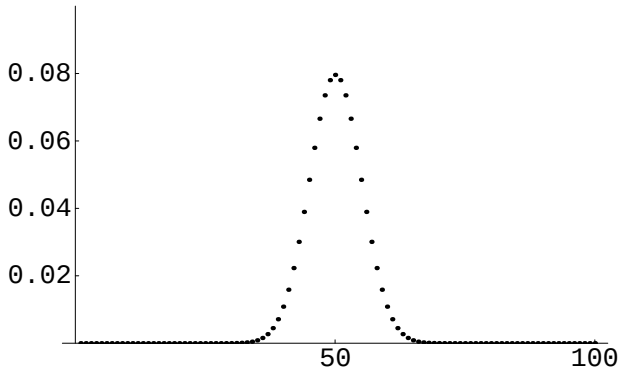

FIGURE 29: *Normalized binomial coefficients* $\binom{N}{n}/2^N$ *in the case* $N = 50$. *The "Pascal pile" peaks at its central value* $\frac{1}{2}N$.

binomial coefficients peaks at its central value. We write $n = \frac{1}{2}N + s$ where s is an "excursion variable" (indicates the placement of n *relative* to $\frac{1}{2}N$) and, entrusting the labor to *Mathematica*, find

$$\begin{aligned} B(\tfrac{1}{2}N + s, N) &= \log \frac{2^N}{\sqrt{\frac{1}{2}N\pi}} - \frac{2(N-1)}{N^2}s^2 - \frac{4(N-3)}{3N^4}s^4 + \cdots \\ &= \log \frac{2^N}{\sqrt{\frac{1}{2}N\pi}} - \frac{1}{\frac{1}{2}N}s^2 + \cdots \end{aligned}$$

where the abandoned terms are or order N^{-2} and become relatively insignificant

[77] I note, however, that Stirling's formula was known and used long before Euler (1707–1783) presented the "theory of Euler integrals" (∼1770).

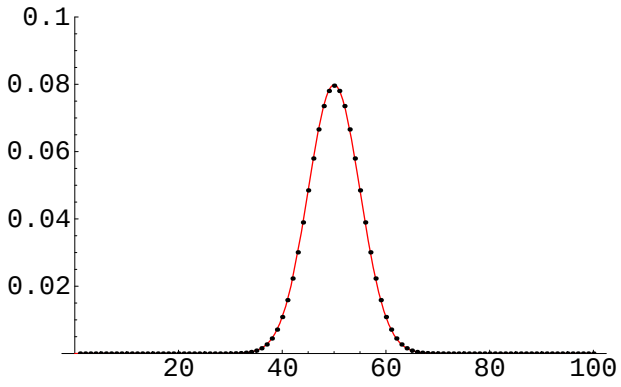

FIGURE 30: *Graph of* $G\Big(n - \frac{1}{2}100; \sqrt{\frac{1}{4}100}\Big)$ *superimposed on the binomial data displayed in Figure 29.*

as N becomes large. What we have thus established is that

$$g(n;N) \equiv \binom{N}{n} \approx 2^N \cdot \frac{1}{\sqrt{\frac{1}{2}N\pi}} \exp\left\{-\frac{1}{\frac{1}{2}N}\big[n - \tfrac{1}{2}N\big]^2\right\} \tag{100}$$

in the approximation that N is large and $\big|s/N\big| \equiv \big|\big[n - \frac{1}{2}N\big]/N\big| \ll 1$.

Recall now that the Gaussian (or "normal") distribution function

$$G(x-m;\sigma) \equiv \tfrac{1}{\sigma\sqrt{2\pi}} \exp\left\{-\tfrac{1}{2}\big[\tfrac{x-m}{\sigma}\big]^2\right\} \tag{101}$$

is "bell-shaped" when plotted, symmetrically deployed about a central maximum at $x = m$, and has these important properties:

$$\int_{-\infty}^{+\infty} G(x-m;\sigma)\,dx = 1 \quad : \text{ all } m \text{ and all } \sigma \tag{101.1}$$

$$\langle x\rangle \equiv \int_{-\infty}^{+\infty} G(x-m;\sigma)\,x\,dx = m \quad : \text{ all } \sigma \tag{101.2}$$

$$\big\langle (x-m)^2\big\rangle \equiv \int_{-\infty}^{+\infty} G(x-m;\sigma)\,(x-m)^2\,dx = \sigma^2 \quad : \text{ all } m \tag{101.3}$$

In this notation (100) becomes

$$\frac{g(n;N)}{2^N} \approx G\Big(n - \tfrac{1}{2}N; \sqrt{\tfrac{1}{4}N}\Big) \tag{102}$$

How good is the approximation? On evidence of Figure 30 it is wonderfully good, even on the tails of the distribution where $\big[n - \frac{1}{2}N\big]/N \approx \pm\frac{1}{2}$.[78]

[78] Is it remarkable that Stirling's formula—which was seen on page 105 to be in some respects so crude—has led to a result of such precision?

That the binomial distribution

$$\frac{1}{2^N}\binom{N}{n} \text{ becomes normal as } N \text{ becomes large} \tag{103}$$

is a fact familiar to every statistician, but the statement fails to capture one important aspect of the situation. If the distributions are scaled so that each stands on the same base; *i.e.*, if we take the independent variable to be not n (which ranges on $\{0, 1, 2, \ldots, N\}$) but $\nu \equiv n/N$ (which for all N ranges on $\{0, \ldots, 1\}$) then the *shape* of the distribution is seen to change as N increases. The effect is most easily demonstrated in Gaussian approximation, where in the natural variable n we have

$$G\Big(n - \tfrac{1}{2}N; \tfrac{1}{2}\sqrt{N}\Big) \quad : \quad \text{variance increases as } N^{+\frac{1}{2}}$$

but in terms of the relative variable ν that same information is described by

$$G\Big(\nu - \tfrac{1}{2}; \tfrac{1}{2\sqrt{N}}\Big) \quad : \quad \text{relative variance decreases as } N^{-\frac{1}{2}} \tag{104}$$

The effect of decreasing relative variance is shown in the following figure

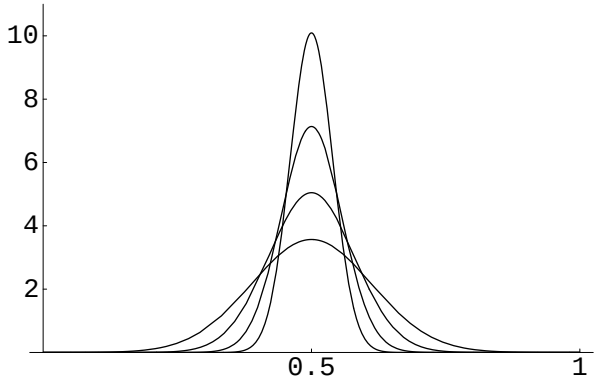

FIGURE 31: *Binomial distribution plotted as a function of* $\nu \equiv n/N$. *The central peaks become narrower/taller as* N *increases. The figure was drawn in Gaussian approximation* (104)*, with* N *set equal successively to* $20, 40, 80, 160$.

and for physically realistic numbers becomes quite dramatic:

$$\frac{1}{\sqrt{4 \cdot (\text{Avogadro's number})}} = 6.44 \times 10^{-13}$$

On the scale of the figure the central peak is much too narrow to draw (about $1/10000^{\text{th}}$ of an atomic diameter!).

A result of which we will soon have practical need is brought to light by carrying this train of thought forward just a little bit: let $f(x)$ be a function defined on the unit interval $0 \leqslant x \leqslant 1$, and let that function generate number strings $\{f_0, f_1, f_2, \ldots, f_N\}$ by the rule $f_n \equiv f(\frac{n}{N})$. Taking the "binomial mean" of those numbers to be given by

$$\langle f \rangle \equiv \sum_{n=0}^{N} f_n \, \frac{1}{2^N} \binom{N}{n} \tag{105.1}$$

we have

$$\approx \sum_{n=0}^{N} f_n \, G\Big(n - \tfrac{1}{2}N; \tfrac{1}{2}\sqrt{N}\Big) \tag{105.2}$$

$$\approx \int_0^N f(\tfrac{n}{N}) \, G\Big(n - \tfrac{1}{2}N; \tfrac{1}{2}\sqrt{N}\Big) \, dn \tag{105.3}$$

$$= \int_0^1 f(\nu) \, G\Big((\nu - \tfrac{1}{2})N; \tfrac{1}{2}\sqrt{N}\Big) \, N d\nu \tag{105.4}$$

$$= \int_0^1 f(\nu) \, G\Big(\nu - \tfrac{1}{2}, \tfrac{1}{2\sqrt{N}}\Big) \, d\nu \tag{105.5}$$

But $G(x - m; \sigma)$ provides a familiar representation of the Dirac delta function $\delta(x - m)$ as $\sigma \downarrow 0$, so we have

$$\begin{array}{l} \downarrow \\ = \displaystyle\int_0^1 f(\nu) \, \delta(\nu - \tfrac{1}{2}) \, d\nu \quad \text{as} \quad N \uparrow \infty \\ = f(\tfrac{1}{2}) \end{array} \tag{105.6}$$

Notice that we started at (105.1) with a statement posed in the language of discrete analysis; that it was Stirling's formula that at (105.2) converted this into a statement posed in the language of continuous analysis; that at (105.3) we took advantage of that conversion to approximate a $\sum$ by an $\int$; that the step (105.3) $\rightarrow$ (105.4) involves simple adjustment of the variable of integration; that (105.4) $\rightarrow$ (105.5) exploits an elementary property of the Gaussian $G(x - m; \sigma)$. The point thus demonstrated is that—while generally

$$\langle f(x) \rangle \equiv \int f(x) P(x) \, dx \neq f(\langle x \rangle)$$

—if the distribution function is sharply localized $P(x) = \delta(x - \langle x \rangle)$ then

$$\begin{array}{l} \downarrow \\ = f(\langle x \rangle) \end{array} \tag{106}$$

5. Gaussian product of two Gaussians. In §3 we looked to processes of the form

$$\begin{array}{l}\big\{\mathfrak{S}(n',N')\big\}\oplus\big\{\mathfrak{S}(n'',N'')\big\}\equiv\big\{\mathfrak{S}\big\}\\ \qquad\qquad\qquad\qquad\qquad\Big\downarrow\ \text{constraint relaxation}\\ \qquad\qquad\qquad\qquad\qquad\big\{\mathfrak{S}\big\}_{\text{thermalized}}\equiv\big\{\mathfrak{S}(n'+n'',N'+N'')\big\}\end{array}$$

and in response to the question *How much of the total system energy resides finally in either component*? were led at (98) to a conclusion that we now recognize can be expressed

$$\begin{aligned}\langle E'\,\rangle &= E-\langle E''\rangle\\ &= \frac{1}{G\Big(n-\frac{1}{2}N;\frac{1}{2}\sqrt{N}\Big)}\\ &\qquad\cdot\sum_k k\varepsilon\cdot G\Big(k-\tfrac{1}{2}N';\tfrac{1}{2}\sqrt{N'}\Big)\cdot G\Big(n-k-\tfrac{1}{2}N'';\tfrac{1}{2}\sqrt{N''}\Big)\end{aligned}\tag{107}$$

in excellent (!) approximation.[79] It is the form of that result—specifically, the fact that it involves a *product of Gaussians* that motivates the following discussion.

It is an elementary fact that

$$\prod_\alpha e^{\text{polynomial } p_\alpha(x) \text{ of order } n}=e^{\text{polynomial } P(x) \text{ of order } n}$$

which in the case $n=2$ gives rise to the conclusion[80] that

$$\prod_\alpha(\text{Gaussian})_\alpha=\text{Gaussian}$$

More specifically, one has, in the notation introduced at (101),

$$\begin{aligned}&G\big(x-m';\sigma'\big)\cdot G\big(x-m'';\sigma''\big)\\ &\qquad=G\big(m'-m'';\sqrt{\sigma'^2+\sigma''^2}\,\big)\cdot G\big(x-m;\sigma\big)\end{aligned}\tag{108}$$

with

$$\left.\begin{aligned}m&\equiv\frac{m'\sigma''^2+m''\sigma'^2}{\sigma'^2+\sigma''^2}\\ \sigma&\equiv\sqrt{\frac{\sigma'^2\sigma''^2}{\sigma'^2+\sigma''^2}}\end{aligned}\right\}\tag{109}$$

—this by an argument that involves nothing more complicated than completion

[79] Note that use has been made here of $2^{N'}2^{N''}/2^N=1$.

[80] For an important application to a different subject area see QUANTUM MECHANICS (1967), Chapter 1, pages 25 *et seq*.

of a square and some adroit rearrangement/simplification. Evidently

$$\frac{1}{\sigma^2} = \frac{1}{\sigma'^2} + \frac{1}{\sigma''^2} \tag{110.1}$$

which is reminiscent of the formula that describes resistors in parallel, and establishes that

$$\sigma < \text{lesser of } \sigma' \text{ and } \sigma''$$

It is evident also that

$$m = (\sigma/\sigma')^2\, m' + (\sigma/\sigma'')^2\, m'' \tag{110.2}$$

NOTE: $(\sigma/\sigma')^2$ and $(\sigma/\sigma'')^2$ are positive numbers that add to unity.

which by a little "center of mass" argument entails that

$$m \text{ lies intermediate between } m' \text{ and } m''$$

and stands *closer to the sharper* of the initial distributions. The x-independent factor $G\big(m'-m''; \sqrt{\sigma'^2+\sigma''^2}\,\big)$ that appears on the right side of (108) serves to *scale* the second (x-dependent) factor. The situation as it has developed is illustrated on the next page.

Returning now to the problem that motivated this discussion (see again (107)), we use an elementary property $G(x-m;\sigma) = G(m-x;\sigma)$ of the Gaussian to write

$$\begin{aligned} &G\Big(k-\tfrac{1}{2}N'; \tfrac{1}{2}\sqrt{N'}\,\Big)\cdot G\Big(n-k-\tfrac{1}{2}N''; \tfrac{1}{2}\sqrt{N''}\,\Big) \\ &\qquad = G\Big(k-\tfrac{1}{2}N'; \tfrac{1}{2}\sqrt{N'}\,\Big)\cdot G\Big(k-n+\tfrac{1}{2}N''; \tfrac{1}{2}\sqrt{N''}\,\Big) \end{aligned}$$

which by (108) becomes

$$= G\Big(n-\tfrac{1}{2}N; \tfrac{1}{2}\sqrt{N}\,\Big)\cdot G\Big(k-m;\sigma\Big) \tag{111}$$

where $N \equiv N' + N''$ and, by (109),

$$\begin{aligned} \frac{1}{\sigma^2} &= \frac{4}{N'} + \frac{4}{N''} \\ &\Downarrow \\ \sigma &= \tfrac{1}{2}\sqrt{\tfrac{N'N''}{N'+N''}} \end{aligned} \tag{112.1}$$

$$\begin{aligned} m &= \tfrac{1}{2}N'\Big(\frac{N'N''}{4N}\Big/\frac{N'}{4}\Big) + \big(n-\tfrac{1}{2}N''\big)\Big(\frac{N'N''}{4N}\Big/\frac{N''}{4}\Big) \\ &\Downarrow \\ m &= \tfrac{N'}{N'+N''}n \end{aligned} \tag{112.2}$$

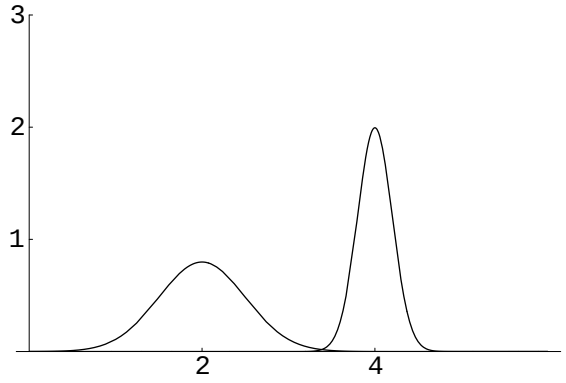

FIGURE 32: *Superimposed graphs of* $G(x-2;0.5)$ *and* $G(x-4;0.2)$. *Adding the two functions would give nearly the same result because there is so little overlap. But it is precisely that overlap that contributes to their product.*

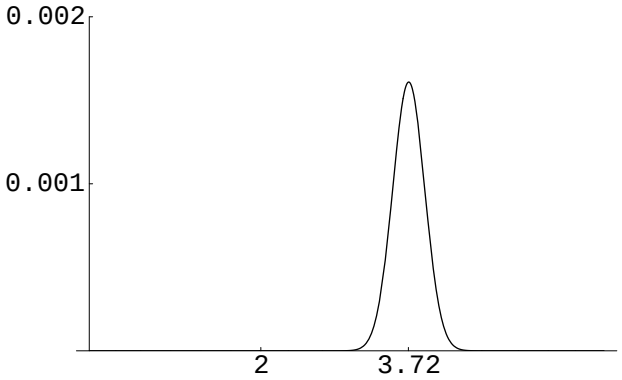

FIGURE 33: *Superimposed graphs of* $G(x-2;0.5)\cdot G(x-4;0.2)$ *and of* $G(4-2;0.538516)\cdot G(x-3.72414;0.185695)$ *where*

$$0.538516 = \sqrt{(0.5)^2 + (0.2)^2}$$

and where $m = 3.72414$ *and* $\sigma = 0.185695$ *were computed from* (109). *That the fit is so perfect is evidence that* (108) *is correct. Note the greatly reduced scale, and also that* $2 < 3.72 < 4$ *but lies closer to 4, which marks the location of the sharper Gaussian.*

Returning now with (111) to (107), we have (after a pretty cancellation)

$$\langle E' \rangle = E - \langle E'' \rangle = \sum_k k\varepsilon \cdot G\big(k - m; \sigma\big)$$
$$= \sum_k k\varepsilon \cdot G\Big(k - \tfrac{N'}{N'+N''}\, n\,;\, \tfrac{1}{2}\sqrt{\tfrac{N'N''}{N'+N''}}\Big) \qquad (113)$$

The striking simplicity of this result is, as will soon emerge, the least of its charms!

6. Enter...the Law of Large Numbers. Recall the physical situation: we initially had n' tokens up in $\mathfrak{S}'$, $n'' = n - n'$ tokens up in $\mathfrak{S}''$. We then allowed the two systems to interact ... ultimately to thermalize ... subject, however, to the constraint that the *total* number up remain constantly equal to n. The number up within $\mathfrak{S}'$ became at this point a random variable (called k). What we learn from (113) is that k is normally distributed ... but normally distributed in a very distinctive way.

Notice first that, according to (113), the expected number of up tokens in $\mathfrak{S}'$ is given finally by

$$n'_{\text{final}} = \langle k \rangle = \tfrac{N'}{N'+N''}\, n \qquad (114)$$

... which is to say: we can expect $\mathfrak{S}'$ to end up with its *fair share* of the n available up-tokens. Those $\langle k \rangle$ can be distributed among N' sites in

$$\binom{N'}{\langle k \rangle}$$

distinct ways, to each of which—by fundamental assumption—we assign equal likelihood.

Which brings us to the key question: *How confident can we be in our expectation* (114) *that we will find* $\langle k \rangle$ *tokens up in* $\mathfrak{S}'$? The probability that we will find *precisely* $\langle k \rangle$ up is given, according to (113), by

$$P_{\max} \equiv G\Big(0\,;\, \tfrac{1}{2}\sqrt{\tfrac{N'N''}{N'+N''}}\Big) = \tfrac{2}{\sqrt{2\pi}}\sqrt{\tfrac{N'+N''}{N'N''}} \qquad (115.0)$$

while[81] the probability that we will find some other/arbitrary number k is given by

$$P(k) = G\Big(k - \langle k \rangle\,;\, \tfrac{1}{2}\sqrt{\tfrac{N'N''}{N'+N''}}\Big) = P_{\max} \cdot \exp\left\{ -\tfrac{1}{2}\left[\frac{k - \langle k \rangle}{\tfrac{1}{2}\sqrt{\tfrac{N'N''}{N'+N''}}} \right]^2 \right\}$$

[81] Recall from (101) the definition of $G(x - m; \sigma)$.

Having in mind questions like *What is the probability that k is (say) 1% bigger than* $\langle k\rangle$? we use the preceding result to write

$$P\big((1+\epsilon)\langle k\rangle\big) \equiv P_\epsilon = P_{\max}\cdot\exp\left\{-\tfrac{1}{2}\left[\frac{\epsilon\frac{N'}{N'+N''}\,n}{\frac{1}{2}\sqrt{\frac{N'N''}{N'+N''}}}\right]^2\right\}$$
$$= P_{\max}\cdot\exp\left\{-\tfrac{N'}{N''}\tfrac{2}{N'+N''}\,n^2\epsilon^2\right\} \qquad (115.1)$$

EXAMPLE: Let systems $\mathfrak{S}'$ and $\mathfrak{S}''$ each contain 10^{-20} moles of tokens; *i.e.*, let $N' = N'' = 6000$, which makes $\mathfrak{S}'$ and $\mathfrak{S}''$ quite small as thermodynamic systems go. Assume also that $n = 5000$. Then (115.1) reads

$$P_\epsilon = P_{\max}\cdot\exp\Big\{-\frac{2}{12000}5000^2\,\epsilon^2\Big\} = P_{\max}\cdot\exp\Big\{-4166\,\epsilon^2\Big\}$$

If we set $\epsilon = \pm\frac{1}{100}$ else $\epsilon = \pm\frac{1}{20}$ else $\epsilon = \pm\frac{1}{10}$ (corresponding to 1% else 5% else 10% *deviations from the expected state of affairs*) we find

$$\text{probability of } \ 1\% \text{ deviation} = e^{-\frac{4166}{10000}}P_{\max} = 6.593\times10^{-1}\ P_{\max}$$
$$\text{probability of } \ 5\% \text{ deviation} = e^{-\frac{4166}{400}}\ P_{\max} = 2.998\times10^{-5}\ P_{\max}$$
$$\text{probability of } 10\% \text{ deviation} = e^{-\frac{4166}{100}}\ P_{\max} = 8.078\times10^{-19}P_{\max}$$

Evidently a 1% "deviation from expectation" are, for such a small system, commonplace, but deviations of more than about 5% are very rare.

EXAMPLE: Suppose, more realistically, that systems $\mathfrak{S}'$ and $\mathfrak{S}''$ each contain 10^{22} tokens (about $1/60^{\text{th}}$ of a mole). Equation (115.1) then becomes

$$P_\epsilon = P_{\max}\cdot\exp\Big\{-10^{-22}\,\epsilon^2 n^2\Big\}$$

Looking for the likelihood of one part per million we set $\epsilon = 10^{-6}$ and obtain

$$= P_{\max}\cdot\exp\Big\{-10^{-34}\,n^2\Big\}$$

Evidently one-part-per-million deviations will be commonplace if $n \preccurlyeq 10^{17}$, but for larger n-values become rare: if, for example, $n = 10^{19}$ we have

$$= P_{\max}\cdot\exp\Big\{-10^4\Big\} = 1.135\times10^{-4343}P_{\max}!$$

REMARK: Arguably more sensible than the question posed at the top of the page is the question *What is the probability that k differs from* $\langle k\rangle$ *by 1% or more*? What, in other words, is the value of

$$\left\{\int_{-\infty}^{(1-\epsilon)\langle k\rangle} + \int_{(1+\epsilon)\langle k\rangle}^{\infty}\right\}P(k)\,dk = 1 - 2\int_{\langle k\rangle}^{(1+\epsilon)\langle k\rangle} P(k)\,dk$$

From information supplied in the caption of the following figure we conclude

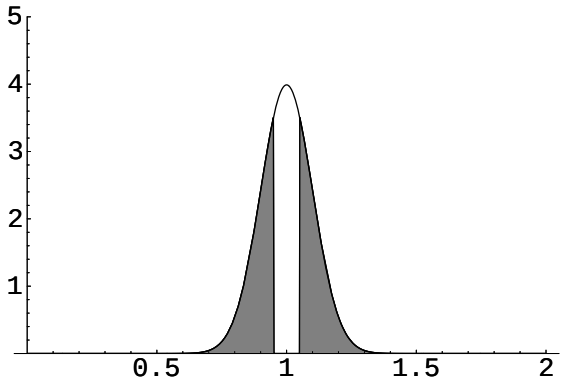

FIGURE 34: *Graph of* $G(x-m;\sigma)$ *in the case* $m=1$, $\sigma=\frac{1}{10}$. *The shaded region has area*

$$1-2\int_m^{m+\epsilon m} G(x-m;\sigma)\,dx = 1-\text{erf}\Big(\frac{\epsilon m}{\sqrt{2}\,\sigma}\Big) \quad : \quad \epsilon = 0.05$$

where $\text{erf}(z)$ *refers (see Abramowitz & Stegun,*[76] *Chapter 7) to the "error function." For* $y \equiv \epsilon m/\sqrt{2}\sigma \gg 1$ *Mathematica supplies the asymptotic expansion*

$$\sim \tfrac{1}{\sqrt{\pi}} e^{-y^2}\Big\{\frac{1}{y} - \frac{1}{2y^3} + \frac{3}{4y^5} - \cdots\Big\}$$

that if $1 \ll y \equiv \frac{1}{\sqrt{2}}\epsilon\langle k\rangle/\sigma$ (which is to say: if $\sigma \ll \frac{1}{\sqrt{2}}\epsilon\langle k\rangle$) then

$$\big\{\text{probability that } |k-\langle k\rangle| > \epsilon\cdot\langle k\rangle\big\} \sim \tfrac{1}{\sqrt{\pi}} y^{-1} e^{-y^2}$$

But the conclusion is the same as that reached by our former line of argument: taking numbers from the first of the examples considered on the preceding page, we have

$$\big\{\text{probability}\ldots\big\} = \frac{1}{\sqrt{\pi}4166\epsilon^2} e^{-4166\epsilon^2} = \begin{cases} 8.9285\times 10^{-1} & : \quad \epsilon = \frac{1}{100} \\ 1.6240\times 10^{-6} & : \quad \epsilon = \frac{1}{20} \\ 1.0939\times 10^{-20} & : \quad \epsilon = \frac{1}{10} \end{cases}$$

Suppose that in (115.1) the numbers $\big\{N', N'', n\big\}$ were scaled in such a way as to preserve all ratios:

$$\left.\begin{array}{rcl} N' & \longrightarrow & \lambda N' \\ N'' & \longrightarrow & \lambda N'' \\ n & \longrightarrow & \lambda\, n \end{array}\right\} \tag{116}$$

Then, for every fixed value of ϵ,

$$P_{\max} \cdot \exp\left\{-\tfrac{N'}{N''}\tfrac{2}{N'+N''}\,n^2\epsilon^2\right\} \longrightarrow P_{\max} \cdot \exp\left\{-\lambda\tfrac{N'}{N''}\tfrac{2}{N'+N''}\,n^2\epsilon^2\right\}$$

$$\Big\downarrow \text{ limit as } \lambda \uparrow \infty$$

$$0 \quad \text{unless } \epsilon = 0$$

which is to say:

> Deviation from expectation becomes progressively less likely as system-size increases, and becomes impossible in the limit.

This is the **Law of Large Numbers**—familiar to experimentalists as the reason that expanded data sets provide better estimates of true value, familiar to coin-flippers as the reason that

$$\frac{\text{heads}}{\text{tails}} \longrightarrow 1 \text{ with certainty}$$

as the number of flips becomes very large.

7. Abstracted essentials of the model. Our "binary token model" (Figure 24) admits of a great variety of interpretations: it might, for example, be considered (with merely verbal changes) to refer

- to the pennies present/absent in the pockets of a population of citizens[82]
- to the results of an ensemble of coin-toissing experiments
- to the physics of binary alloys, of binary spin systems, of binary magnetic domains.[83] Etc.

And the model admits of "soft generalization" in several directions: it might, for example, be generalized to include

- multi-level staircases
- multi-level staircases with irregular steps
- installation of springs that are stretched when adjacent tokens sit on different steps ...

It was recommended to our attention, however, not by the rich variety of its direct applications but by the circumstance that it gives rise to a *very simple state-ennumeration problem*.[84]

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[82] Many persons have been struck/influenced by the formal relevance of thermodynamic concepts and lines of argument to economic problems: see, for example, N. Georgescu-Roegen, *The Entropy Law & the Economic Program* (1971) and any number of passages/footnotes in P. A. Samuelson, *Foundations of Economic Analysis* (1947, reprinted 1965).

[83] See Kittel & Kroemer,[68] page 16.

[84] Generalizations tend to complicate the analysis and to degrade the utility of the model.

Models are invariably specific: their role is to facilitate discovery, but at best they serve only to illustrate—not to "establish"—points of general principle. Here we take the first tentative steps in a program intended to isolate and to build upon the generalizable features of the binary token model.

At (113) we found—in answer to a question posed at the beginning of §5—that the energy expected to reside in the component $\{\mathfrak{S}'\}$ of $\{\mathfrak{S}\}_{\text{thermalized}}$ can be described

$$\begin{aligned}\langle E'\rangle &= \varepsilon\cdot\sum_k kG\Big(k-\tfrac{N'}{N'+N''}n;\tfrac{1}{2}\sqrt{\tfrac{N'N''}{N'+N''}}\Big)\\ &= \varepsilon\cdot\langle k\rangle\end{aligned}$$

Evidently $\langle E'\rangle$ and $\langle k\rangle$ measure essentially the same thing. But, while

$$\langle k\rangle = \left\{\begin{array}{l}\text{expected number of up-tokens in the}\\ \{\mathfrak{S}'\}\text{-component of } \{\mathfrak{S}\}_{\text{thermalized}}\end{array}\right.$$

is conceptually specific to the model, the construction

$$\langle E'\rangle = \left\{\begin{array}{l}\textbf{expected energy} \text{ resident in the}\\ \{\mathfrak{S}'\}\text{-component of } \{\mathfrak{S}\}_{\text{thermalized}}\end{array}\right.$$

possesses a **model-independent / generalizable conceptual significance**. We note also that

$$\varepsilon \equiv mgh = (\text{token weight})\cdot h$$

is—*via* h—**subject to our explicit external control** (though conceptually specific to the model). The implication is that we stand to lend our results the *appearance of generality* if we systematically transfer independent variable status from n', n'', $n\equiv n'+n''$, k, ... to the corresponding energies. In that same spirit we will allow ourselves to speak henceforth of "particles" rather than of "tokens" (though "particle" will be susceptible to a variety of specific interpretations).

Thus motivated, we write

$$g'(U',N',h') \equiv \left\{\begin{array}{l}\text{number of } U'\text{-energy states accessible}\\ \text{to the } N'\text{-particle elements of } \{\mathfrak{S}'\}\end{array}\right.$$

h': typical external **control parameter**

and adopt the convention that we may casually surpress those arguments that are not of immediate interest.

If (by virtue of the action of appropriate energy-filters: Figure 25) it is known that

- the N'-particle elements of $\{\mathfrak{S}'\}$ all have energy U'
- the N''-particle elements of $\{\mathfrak{S}''\}$ all have energy U''

then the $N\equiv N'+N''$-particle elements of $\{\mathfrak{S}\}\equiv\{\mathfrak{S}'\}\oplus\{\mathfrak{S}''\}$ all have energy

$U \equiv U' + U''$, and occur with a multiplicity that can in our adjusted notation be described

$$g'(U', N') \cdot g''(U'', N'') \tag{117}$$

↑ ——— ↑ now *not* necessarily the same functions

Energy-conserving interaction/thermalization $\{\mathfrak{S}\} \longrightarrow \{\mathfrak{S}\}_{\text{thermalized}}$ yields an ensemble the elements of which are equidistributed among states which are (compare page 102)

$$g(U, N) = \int g'(u, N') \cdot g''(U - u, N'')\, du \geqslant g'(U', N') \cdot g''(U'', N'') \tag{118}$$

in number. The probability that a system drawn from $\{\mathfrak{S}\}_{\text{thermalized}}$ will be found to possess a $\{\mathfrak{S}'\}$-component with energy u can be described[85]

$$P(u) = \frac{g'(u, N') \cdot g''(U - u, N'')}{g(U, N)} \tag{119}$$

In the many-particle "**thermodynamic limit**" we expect[86] to have, by force of the Law of Large Numbers,

$$\begin{array}{l} \downarrow \\ = \delta(u - \hat{U}') \end{array} \tag{120}$$

where

$$\hat{U}' \quad \text{maximizes} \quad \frac{g'(U') \cdot g''(U'' = U - U')}{g(U)}$$

To *compute* $\hat{U}'$ we write

$$\frac{\partial}{\partial U'}\Big[\frac{g' \cdot g''}{g}\Big] = \frac{1}{g}\Big[\frac{\partial g'}{\partial U'} \cdot g'' + g' \cdot \frac{\partial g''}{\partial U''} \cdot \underbrace{\frac{\partial U''}{\partial U'}}_{= -1 \text{ by } U\text{-conservation}}\Big] = 0$$

and (dividing by $g' \cdot g''$) obtain

$$\frac{1}{g'}\frac{\partial g'}{\partial U'} = \frac{1}{g''}\frac{\partial g''}{\partial U''} \tag{121.1}$$

Therefore

$$\frac{\partial \log g'}{\partial U'} = \frac{\partial \log g''}{\partial U''} \tag{121.2}$$

---

[85] Compare (97).

[86] See again (105.5) and §6.

which reads

$$\frac{\partial \sigma'}{\partial U'} = \frac{\partial \sigma''}{\partial U''} \tag{121.3}$$

if—yielding to a natural formal impulse—we **define**[87]

$$\sigma(U, N, \ldots) \equiv \log g(U, N, \ldots) \tag{122}$$

$$= \left\{ \begin{array}{l} \underline{\text{logarithm of the multiplicity}} \text{ of} \\ \text{the } U\text{-energy states within the} \\ N\text{-particle system } \mathfrak{S} \end{array} \right.$$

Equation (121) assert that energy transfer $\mathfrak{S}' \leftrightarrows \mathfrak{S}''$ proceeds until

$$\left. \begin{array}{l} \text{expression on the left (which} \\ \text{is determined entirely by the} \\ \text{the structure of } \mathfrak{S}') \end{array} \right\} = \left\{ \begin{array}{l} \text{expression on the left (which} \\ \text{is determined entirely by the} \\ \text{the structure of } \mathfrak{S}'') \end{array} \right.$$

It is impossible to resist the inference that in (121) we have been brought back—this time by statistical reasoning, rather than by thermodynamic axiomatics—to the upshot of the 0^{th} Law:[88] **Energy transfer continues until $\mathfrak{S}'$ and $\mathfrak{S}''$ have come to the same emperical temperature**. We infer, more precisely, that[89]

$$\frac{\partial}{\partial U} \log g(U, N, \ldots) = \left\{ \begin{array}{l} \text{universal (in the sense system-independent)} \\ \text{function of emperical temperature} \end{array} \right. \tag{123}$$

and this—in anticipation of the demonstration that we are thus led back into precise agreement with established convention—we sharpen still further: we take

$$S = k \cdot \log g(U, N, \ldots) \tag{124}$$

to comprise the **statistical definition of absolute entropy**, and[90]

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{N, \ldots} \tag{125}$$

to comprise the **statistical definition of absolute temperature**.

In CLASSICAL ELECTRODYNAMICS (2001) I was content (Chapter 1, §2) to produce Maxwell's equations "by bootstrap" (specifically: by an argument that uses mainly Coulomb's law + some transformation theory), since the test of the physical accuracy of those equations resides not in the imagined security of their derivation but in their diverse applications. So it is here: we have produced

[87] Here "…" refers tacitly to such variables/parameters as may additionally be present: h is the example at hand, but each physical system $\mathfrak{S}'$, $\mathfrak{S}''$, $\mathfrak{S}'''$, … gives rise to its own characteristic list.

[88] See again Chapter 1, §5.

[89] Compare Chapter 1, page 26.

[90] See again equation (27.1) in Chapter 2.

(124) and (125) by tentative abstraction from a primitive model + an appeal to some rudimentary classical thermodynamics. One could expend a good deal of effort in an attempt to "secure the foundations" of (124) and (125). I proceed, however, in the conviction that it is on the success of its applications that the credentials of the theory ultimately hinge . . . and that only after we have gained familiarity with typical applications will we be in position to estimate where the most critical foundational problems actually lie.

8. The Boltzmann factor. Let us agree now to focus our attention upon some designated one of the "particles" that collectively comprise $\mathfrak{S}$, consigning its (very numerous) mates to the role of "reservoir." Writing

$$\text{isolated total system} = \text{particle} + \text{reservoir}$$

we

- write U to denote the *conserved energy of the total system* and
- write $\varepsilon_0, \varepsilon_1, \varepsilon_2, \ldots \ll U$ to denote the *allowed energy states of the particle.*[91]

We ask: *What is the probability* $\mathcal{P}(\varepsilon_m)$ *that the designated particle will, upon inspection, be found to have energy* ε_m? This—necessarily—is the probability that the reservoir will be found to have energy $U - \varepsilon_m$, so by fundamental assumption (page 99) we have

$$\mathcal{P}(\varepsilon_m) = \frac{\text{number of reservoir states of energy } U - \varepsilon_m}{\text{total number of reservoir states}} \tag{126}$$

$$= \frac{g(U - \varepsilon_m)}{\sum_{\varepsilon} g(U - \varepsilon)}$$

It follows in particular that ε_m-occupancy and ε_n-occupancy have *relative* probability given by

$$\frac{\mathcal{P}(\varepsilon_m)}{\mathcal{P}(\varepsilon_n)} = \frac{g(U - \varepsilon_m)}{g(U - \varepsilon_n)}$$

Drawing upon (124) we have

$$= e^{[S(U - \varepsilon_m) - S(U - \varepsilon_n)]/k}$$

But $S(U - \varepsilon) = S(U) - \dfrac{\partial S(U)}{\partial U}\varepsilon + \frac{1}{2}\dfrac{\partial^2 S(U)}{\partial U^2}\varepsilon^2 - \cdots$ so (in an approximation

[91] It is merely for expository convenience that I have assumed the "allowed energy states of the particle" to be discrete. Boltzmann himself is reported to have favored this assumption on quirky philosophical grounds . . . with the result that his papers were seen in retrospect to have an eerily "quantum mechanical look" about them.

that gets better and better as the size N of the reservoir increases) we have

$$\frac{\mathcal{P}(\varepsilon_m)}{\mathcal{P}(\varepsilon_n)} = e^{-[\varepsilon_m - \varepsilon_n]\frac{\partial S(U)}{\partial U}/k}$$

Only apparently does the expression on the right depend (*via* the $\frac{\partial S(U)}{\partial U}$-factor) on the specific thermodynamic structure of the reservoir, for it is asserted at (125) that $\frac{\partial S(U)}{\partial U} = \frac{1}{T}$ holds *universally*. We therefore have

$$\begin{aligned} &= e^{-[\varepsilon_m - \varepsilon_n]/kT} \\ &= \frac{e^{-\varepsilon_m/kT}}{e^{-\varepsilon_n/kT}} \end{aligned} \tag{127}$$

independently of the design of the reservoir. Expressions of the type $e^{-\mathcal{E}/kT}$ are ubiquitous in thermal physics, and are called **Boltzmann factors**.

PRINCIPLES OF ROUGH & READY APPLICATION: If $\mathcal{E}$ is the energy associated with some elementary process which occurs within a thermalized system then we expect detailed calculation bearing on that process to yield expressions of the type

$$(\text{stuff}) \cdot e^{-\mathcal{E}/kT}$$

and on this basis we expect such a process to occur with significant frequency if and only if $\mathcal{E}/kT \preccurlyeq 1$, where (see again page 34)

$$\begin{aligned} 1/k &= 7.24312 \times 10^{15} \text{ K/erg} \\ &= 1.16049 \times 10^{4} \text{ K/eV} \end{aligned}$$

As a memorable rule of thumb one has

$$T_{\text{characteristic}} \approx 10^4 \cdot (\text{characteristic energy in eV}) \text{ Kelvin} \tag{128}$$

Example: At what temperature can one expect the atoms in a sample of hydrogen gas to begin spontaneously to ionize? One has $\mathcal{E}_{\text{ionization}} = 13.6$ eV so $T \approx 136,000$ K.

Example: At what temperature does blackbody radiation begin to give rise spontaneously to electron/positron pairs: $\gamma \longrightarrow e^+ + e^-$? From $m_{\text{electron}}c^2 \approx \frac{1}{2}$ MeV we obtain $T \approx 10^{10}$ K.

Example: How much energy must be invested to rupture one of the bonds which in ice bind the water molecules to each other? Ice melts at 0°C, so evidently

$$\mathcal{E} \approx 273 \times 10^{-4} \text{ eV} = 1.04 \times 10^{-21} \text{ calories}$$

Multiplication by Avogadro's number suggests that we should expect to invest about 626 calories per mole or $626/18 = 35$ calories per gram to melt ice. Actually, ice has a *latent heat of fusion* of about 79.7 calories/gram.

The list of such examples could be extended to very great lengths.

In response to the question posed at the beginning of this discussion we now have

$$\mathcal{P}(\varepsilon_m) = \frac{1}{\mathcal{Z}} e^{-\varepsilon_m/kT} \tag{129.1}$$

where $\mathcal{Z}$ is a normalization factor: to achieve $\sum_m \mathcal{P}(\varepsilon_m) = 1$ we set

$$\mathcal{Z} = \sum_m e^{-\varepsilon_m/kT} \tag{129.2}$$

It is, however, important to notice that at (126) we tacitly assumed the particulate ε_m-state to be non-degenerate. If, on the other hand, that state is $g(\varepsilon_m)$-fold degenerate then the probability that the particle will be found to be *in one or another* of those states is increased by that factor:

$$\mathcal{P}(\varepsilon_m) = \frac{1}{\mathcal{Z}} g(\varepsilon_m)\, e^{-\varepsilon_m/kT} \tag{130}$$

$$\mathcal{Z} = \sum_m g(\varepsilon_m)\, e^{-\varepsilon_m/kT} \tag{131.1}$$

$$= \sum_{\text{states}} e^{-\frac{1}{kT}\varepsilon(\text{state})} \tag{131.2}$$

At (131.2) we see why $\mathcal{Z}$ is called the "sum-over-states" (or "**Zustandsumme**") and not the "sum-over-energies" (which would amount to the same thing if and only if all ε-states were non-degenerate: $g(\varepsilon) = 1$ for all ε). To clarify the latter point (and at risk of belaboring the obvious) I write

$$\begin{aligned}
\mathcal{Z} &= \sum_{\text{states}} e^{-\frac{1}{kT}\varepsilon(\text{state})} \\
&= \sum_{\varepsilon} \sum_{\text{states of energy } \varepsilon} e^{-\varepsilon/kT} \\
&= \int g(\varepsilon)\, e^{-\varepsilon/kT}\, d\varepsilon
\end{aligned}$$

NOTE: $g(\varepsilon)$ is frequently called the **density of states**. If the spectrum is discrete then $g(\varepsilon)$ becomes a weighted sum of δ-functions, and the integral becomes a sum. The integration ranges upward from $\varepsilon_{\text{ground state}}$.

$$= \textbf{Laplace transform} \text{ of } g(\varepsilon) \tag{132}$$

It is from a close relative of $\mathcal{Z}$ that we will soon extract the thermodynamics of the system. But (132) provides a kind of "2-way window," for suppose $\mathcal{Z}$ were (by thermodynamic measurement?) known: we could then—by inverse Laplace transformation—recover $g(\varepsilon)$, which conveys sharp microdynamical information.

Illustrative application to the 2-state token model: Pretend[92] that the token model (Figure 24) has come into thermal equilibrium with a reservoir at temperature T. Then

$$\left.\begin{aligned} \mathcal{P}(\downarrow) &= \left\{\begin{array}{l}\text{probability that a selected token}\\ \text{will be found in the } \downarrow \text{ state}\end{array}\right.\\ &= \frac{1}{1+e^{-mgh/kT}} \\ \\ \mathcal{P}(\uparrow) &= \left\{\begin{array}{l}\text{probability that a selected token}\\ \text{will be found in the } \uparrow \text{ state}\end{array}\right.\\ &= \frac{e^{-mgh/kT}}{1+e^{-mgh/kT}} \\ &= 1-\mathcal{P}(\downarrow) \end{aligned}\right\} \tag{133}$$

We notice that

- the $\uparrow$ state is unpopulated at $T=0$
- $\mathcal{P}(\downarrow) > \mathcal{P}(\uparrow) > 0$ for $0 < T < \infty$
- we achieve a uniform population $\mathcal{P}(\downarrow) = \mathcal{P}(\uparrow) = \frac{1}{2}$ as $T \to \infty$.

Those points are illustrated below:

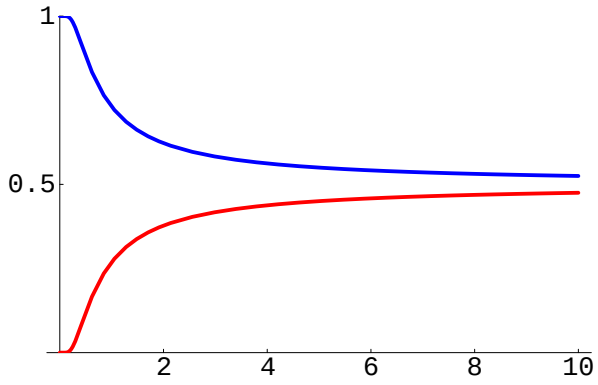

FIGURE 35: *Graphs of $\mathcal{P}(\downarrow)$ and of $\mathcal{P}(\uparrow)$, computed on the basis of* (133) *and shown* **blue**/**red** *respectively. The value of kT/mgh ranges in the figure from 0 to 10.*

9. Construction and thermodynamics of a macrocanonical ensemble. We do thermodynamics on many-body *systems*, not on their individual elements, and it is in view of that fact that we undertake now an important "conceptual shift," a fundamental reinterpretation of some of the results already in hand.

[92] Pretense is required, for the model is, in point of fact, *mechanically too impoverished to respond* to contact with a reservoir.

When, at the beginning of §8, I referred to "particles"—"molecules" would have served as well—I had in mind the literal "parts of a many-body system," the molecules of the chemist's imagination, and it was with contrived artificiality that I portrayed the N-particle-system-minus-one-of-its-parts as a "reservoir." But we are free if we wish

1. to consider the N-particle system to be itself a kind of "molecule"—a macromolecule, with allowed energies $E_0, E_1, E_2, \ldots$ and multiplicity structure $g(E)$ quite different from those of its isolated constituent parts
2. to consider the "reservoir" to be literally that—a "heat bath," a very large system of known temperature T and of arbitrary/irrelevant/unknown detailed construction
3. to contemplate the **statistical properties of the ensemble** (or "mental gas") that comes into being when many replicas of the N-particle system are placed in diathermal contact with the reservoir:

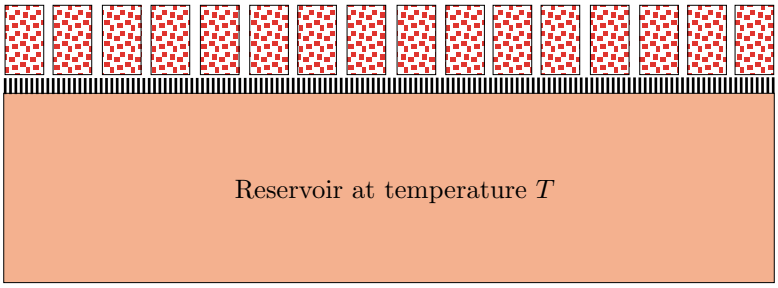

FIGURE 36: *We have measured the temperature T of the many-body system $\mathfrak{S}$ that sits before us on the lab bench. To develop the statistical properties—and ultimately the thermodynamics—of $\mathfrak{S}$ we imagine it to have been drawn from a* **macrocanonical ensemble** *of such systems, a mental population $\{\mathfrak{S}\}$ of identical copies of $\mathfrak{S}$, each of which has been placed in diathermal contact with a reservoir at temperature T.*

The physical/practical implications of the preceding reinterpretive remarks are momentous, but the reinterpretation affects not at all the pattern/validity of the argument that gave rise to (130/131/132). We conclude that the **probability that a thermalized many-body system will, upon inspection, be found to be in a designated state** can be described

$$P(\text{state}) = \frac{1}{Z}\, e^{-E(\text{state})/kT} \tag{134}$$

where

$$Z \equiv \sum_{\text{states}} e^{-E(\text{state})/kT} = \int g(E)\, e^{-E/kT}\, dE \tag{135}$$

follows from the requirement that

$$\sum_{\text{states}} P(\text{state}) = 1$$

Equation (134) defines the so-called **macrocanonical distribution function** and is—particularly since it entails the definition (135) of the "Zustandsumme" or "**partition function**"—fundamental to all practical applications of statistical mechanics. We note that according to (134)—which, of course, pertains only to *thermalized* systems—

- states of the *same* energy are *equi*populated
- the population density is, at fixed T, an *exponentially decreasing* function of $E(\text{state})$
- it is the role of T (actually of $1/T$) to quantify the *rate* of decrease.

I turn now to discussion of how one proceeds from (134) to a description of the **thermodynamic properties** of the many-body system $\mathfrak{S}$. What we need to do is to describe U and S as functions of thermodynamic state variables—as functions, that is to say, of T, N, and those few mechanical parameters $\boldsymbol{\alpha}$ which (like h in the token model) are subject to our operational control. Now it is entirely natural to associate U with the expected value $\langle E \rangle$ of the system energy; *i.e.*, to write

$$U = \langle E \rangle \tag{136}$$

Several trains of thought—none of which have we yet had opportunity to pursue—make it almost equally natural to write

$$S = -k\langle \log P \rangle \tag{137}$$

which we are content to do ... but tentatively: to see where it leads.

Looking first to the implications of (136) we have

$$\begin{aligned}
U &= \sum_{\text{states}} E(\text{state})P(\text{state}) \\
&= \frac{1}{Z}\sum_{\text{states}} E(\text{state})\, e^{-\beta E(\text{state})} \\
&\qquad\qquad \beta \equiv \tfrac{1}{kT} \;:\; \text{a frequently handy abbreviation} \\
&= -\frac{1}{Z}\frac{\partial}{\partial\beta}\sum_{\text{states}} e^{-\beta E(\text{state})} \\
&= -\frac{1}{Z}\frac{\partial}{\partial\beta}Z \\
&= -\frac{\partial}{\partial\beta}\log Z
\end{aligned}$$

But $\dfrac{\partial}{\partial\beta} = \dfrac{dT}{d\beta}\dfrac{\partial}{\partial T} = -kT^2\dfrac{\partial}{\partial T}$ so we arrive finally at the statement

$$U = kT^2 \frac{\partial}{\partial T} \log Z \tag{138}$$

in which connection we note that the partition function Z is a function of precisely the variables of thermodynamic interest: all thermodynamically extraneous variables get "summed away" in the Z-construction process.

Equation (137) poses analytical problems which are similar but—since most of the work has already been done—simpler: we have

$$\begin{aligned} S &= -k \sum_{\text{states}} P(\text{state}) \underbrace{\log P(\text{state})}_{= -\log Z - \beta E(\text{state})} \\ &= k \log Z + k\beta U \\ &= k\Big(1 - \beta \frac{\partial}{\partial \beta}\Big) \log Z \end{aligned} \tag{139}$$

giving

$$S = k\Big(1 + T \frac{\partial}{\partial T}\Big) \log Z \tag{140}$$

> **REMARK:** Looking to the right sides of (138) and (140) we understand why it is that statistical mechanics spend most of their time computing partition functions: *to know Z is to know "everything"*!

From (138) it follows that

$$\log Z = -\frac{U - TS}{kT}$$

But[93] $U - TS = F$ so

$$\log Z = -\frac{F}{kT} \quad \text{equivalently} \quad Z = e^{-F/kT} \tag{141.1}$$

One sees here why statistical physicists tend to consider the F-representation to be the "representation of choice"—this though it is in the U-representation that basic implications of the *laws* of thermodynamics are most conveniently developed: $\frac{\partial}{\partial T}$ appears on the right side of (138), but is absent from (141.1). Notice that if we were to take (141)—written

$$F = -kT \log Z \tag{141.2}$$

as our starting point, then the thermodynamic relationships[93]

$$S = -\Big(\frac{\partial F}{\partial T}\Big)_{N,\boldsymbol{\alpha}} \quad \text{and} \quad U = F + TS$$

[93] See again the review of the properties of the "free energy" F that appears on pages 58 & 59.

promptly give back (140) and (138). Notice also that

$$U = \begin{cases} kT^2 \dfrac{\partial}{\partial T}\Big[-\dfrac{F}{kT}\Big] & : \text{ thermodynamic } \textbf{Gibbs-Helmholtz relation} \\ kT^2 \dfrac{\partial}{\partial T} \log Z & : \text{ unproblematic equation (138)} \end{cases}$$

and that if we considered ourselves free to make *conjoint* use of those statements[94] we would have

$$\log Z = -\frac{F}{kT} + \big\{T\text{-independent function of thermodynamic state}\big\}$$

But $\big\{\text{etc.}\big\}$ *vanishes* according to (141): that it does so must be a consequence of (140), and ultimately of the "problematic" thermodynamic $\leftrightarrow$ statistical bridge erected at (137). If we could establish $\big\{\text{etc.}\big\} = 0$ on independent grounds then we would have reduced (137) to the status of a *theorem*. There are, however, better ways to proceed:

The mechanical states available to a many-body system are set—*via* the laws of mechanics—by the control parameters $\boldsymbol{\alpha} \equiv \big\{\alpha_1, \alpha_2, \ldots, \alpha_r\big\}$, and so in particular are the numbers $E(\text{state})$: to emphasize the latter fact we write

$$E(\text{state}) \equiv E_{\text{state}}(\boldsymbol{\alpha})$$

In this more precise notation (134) reads

$$P(\text{state}; T, \boldsymbol{\alpha}) = \frac{1}{Z(T, \boldsymbol{\alpha})}\, e^{-\beta E_{\text{state}}(\boldsymbol{\alpha})}$$

which by (141) becomes

$$= e^{-\beta[F(T,\boldsymbol{\alpha}) - E_{\text{state}}(\boldsymbol{\alpha})]} \tag{142}$$

We proceed from the elementary observation that the normalization condition

$$\sum_{\text{states}} P(\text{state}; T, \boldsymbol{\alpha}) = 1$$

is necessarily invariant under $(T, \boldsymbol{\alpha}) \to (T + dT, \boldsymbol{\alpha} + d\boldsymbol{\alpha})$:

$$\sum_{\text{states}} \Big\{ \frac{\partial P}{\partial T} dT + \sum_j \frac{\partial P}{\partial \alpha_j} d\alpha_j \Big\} \Big\Downarrow = 0$$

[94] The Gibbs-Helmholtz relation follows directly from the relations[93] just quoted:

$$U = F + TS = F - T\Big(\frac{\partial F}{\partial T}\Big)_{N,V} = -T^2\Big(\frac{\partial}{\partial T}\frac{F}{T}\Big)_{N,V}$$

Working from (142) we have

$$\sum_{\text{states}} \Big\{ \big[F-E\big]d\beta + \beta dF - \beta \sum_j \frac{\partial E}{\partial \alpha_j} d\alpha_j \Big\} P = 0$$

$$\Downarrow$$

$$\beta \Big\{ \underbrace{\big[F-U\big] \cdot \frac{d\beta}{\beta}}_{= -TS \cdot \left(-\frac{dT}{T} \right)} + d\big[U - TS\big] - \sum_j \Big\langle \frac{\partial E}{\partial \alpha_j} \Big\rangle d\alpha_j \Big\} = 0$$

$$\Downarrow$$

$$\beta \Big\{ \cancel{SdT} + dU - TdS - \cancel{SdT} - \sum_j \Big\langle \frac{\partial E}{\partial \alpha_j} \Big\rangle d\alpha_j \Big\} = 0$$

But $\sum_j \Big\langle \frac{\partial E}{\partial \alpha_j} \Big\rangle d\alpha_j$ provides a sharply detailed description of what we <u>mean</u> by the "differential work $đW$ performed on a thermalized many-body system," so (unless $\beta = 0$; *i.e.*, unless $T = \infty$) we have

$$dU = TdS + đW$$

We embraced (137) "tentatively . . . to see where it leads." Remarkably

- our FUNDAMENTAL ASSUMPTION (page 99)
- the Law of Large Numbers
- the thermo $\leftrightarrow$ statistical bridges erected at (136) and (137)

have led us back to precisely to Clausius' differential formulation (25) of the combined 1st and 2nd laws of thermodynamics!

> *". . . although, as a matter of history, statistical mechanics owes its origin to investigations in thermodynamics, it seems eminently worthy of independent development, both on account of the elegance and simplicity of its principles, and because it yields new results and places old truths in a new light* [*even in subject areas*] *quite outside of thermodynamics. . . The laws of thermodynamics may easily be obtained from the principles of statistical mechanics, of which they are the incomplete expression.*"
>
> —Josiah Willard Gibbs

We might fairly look upon our successful reproduction of (25) as evidence in support of *each* of our assumptions. If Gibbs' position seems a bit subdued, it might be because he had independent reasons to credit each of those assumptions. Thermodynamic virtuoso though he was, it was his intention in 1902 to promote a statistical mechanical view of the many-body world: he tended—in this statement and others—to dismiss thermodynamics as merely the best we can do with our imperfect knowledge of what is *really* going on (microscopically) within many-body systems.

From Bohr we learned that

- classical mechanics is logically complete but physically incomplete
- quantum mechanics is logically incomplete—that an "autonomous quantum mechanics" stripped of all reference to classical concepts is unthinkable.

I claim the relationship between thermodynamics and statistical mechanics to be precisely analogous . . . but in this regard my views may be somewhat eccentric. Gibbs in particular chose never to emphasize (so far as I am aware) that *it is by thermodynamic observation that we know what we know about the statistical mechanical world*.

I have remarked (page 127) that "statistical mechanics spend most of their time computing partition functions." What does such activity feel like?

10. Thermodynamics of the 2-state N-token model. The toy system familiar from Figure 24 can (if the tokens are distinguishable) exist in a total of 2^N distinct states: there exist $g(n) = \binom{N}{n}$ distinct variants of the "n-up state," and each has energy $E_n = nmgh$. The partition function is given therefore by

$$Z = \sum_{n=0}^{N} \binom{N}{n} e^{-nmgh/kT}$$

which (we happen to notice) can be written

$$= \underbrace{\left[1 + e^{-mgh/kT}\right]^N}_{\text{familiar from (133) as } \mathcal{Z}_{\text{token}}} \tag{143}$$

giving

$$\begin{aligned} \log Z(T,h,N) &= N \log\left[1 + e^{-mgh/kT}\right] \\ &= -\frac{1}{kT} F(T,h,N) \end{aligned} \tag{144}$$

Working now from (138) we have

$$\begin{aligned} U(T,h,N) &= kT^2 \frac{\partial}{\partial T} \log Z \\ &= Nmgh \frac{e^{-mgh/kT}}{1 + e^{-mgh/kT}} \\ &= N\Big\{\varepsilon(\downarrow)\mathcal{P}(\downarrow) + \varepsilon(\uparrow)\mathcal{P}(\uparrow)\Big\} \quad \text{by (133)} \\ &\equiv N \cdot u(T,h) \end{aligned} \tag{145}$$

$$\begin{aligned} u(T,h) &\equiv \text{expected energy per token} \\ &= \text{"specific internal energy"} \end{aligned}$$

while (139) gives

$$\begin{aligned} S(T,h,N) &= k\log Z + \frac{1}{T}U \\ &= kN\log\left[1+e^{-mgh/kT}\right] + \frac{1}{T}Nmgh\frac{e^{-mgh/kT}}{1+e^{-mgh/kT}} \\ &\equiv Ns(T,h) \end{aligned} \tag{146}$$

$$s(T,h) \equiv \text{entropy per token}$$

The function-theoretic complexity of $U(T,h,N)$ and $S(T,h,N)$ comes to us as no surprise—we have encountered indication already[95] that such complexity may be typical even of the simplest systems—but it does (preliminarily to any attempted "thermodynamic analysis") place upon us an obligation to do what we can to *simplify/understand* the functions in question. To that end we note first that (145) can be written

$$U = mgh\langle n\rangle \tag{147}$$

with

$$\begin{aligned} \langle n\rangle &= N\frac{1}{1+e^{+mgh/kT}} \\ &= \text{expected number of tokens in the up-state} \end{aligned} \tag{148}$$

Evidently

$$\left.\begin{aligned} e^{-mgh/kT} &= \frac{\langle n\rangle}{N-\langle n\rangle} \\ &\Updownarrow \\ \frac{1}{kT} &= \frac{1}{mgh}\log\frac{N-\langle n\rangle}{\langle n\rangle} \end{aligned}\right\} \tag{149}$$

Returning with this information to (146) we obtain

$$\begin{aligned} S &= kN\log\left[1+\frac{\langle n\rangle}{N-\langle n\rangle}\right] + mgh\langle n\rangle\cdot\frac{k}{mgh}\log\frac{N-\langle n\rangle}{\langle n\rangle} \\ &= k\left\{N\log\frac{N}{N-\langle n\rangle} + \langle n\rangle\log\frac{N-\langle n\rangle}{\langle n\rangle}\right\} \\ &= k\Big\{\big[N\log N - N\big] - \big[\langle n\rangle\log\langle n\rangle - \langle n\rangle\big] \\ &\qquad - \big[(N-\langle n\rangle)\log(N-\langle n\rangle) - (N-\langle n\rangle)\big]\Big\} \end{aligned} \tag{150}$$

which in Stirling approximation[96] becomes

[95] See again the ideal gas functions described on page 63.

[96] See page 106. The red terms were introduced to facilitate this step, but add to zero.

$$S = k \log g\big(\langle n\rangle; N\big) \tag{151}$$
$$g\big(\langle n\rangle; N\big) = \binom{N}{\langle n\rangle} = \text{multiplicity of the } \langle n\rangle\text{-up state}$$

We have at this point revealed (146) to be the opaque, system-specific expression of a striking general proposition:

$$\begin{aligned} S &= k \log \left\{ \begin{array}{l} \text{number of distinct ways the} \\ \text{expected state can be achieved} \end{array} \right\} \\ &= k \log \big\{ \text{“expected complexion”} \big\} \end{aligned} \tag{152}$$

REMARK: Remove the words “expected” and we have come here upon the “elegant statistical principle” which, as was remarked on page 34, is inscribed on Boltzmann’s tombstone. We have come, that is to say, upon *a conception of entropy that pertains even to unexpected states*. But of all states, by force of the Law of Large Numbers, the expected states are overwhelmingly the most likely. By fundamental assumption (95) the preceding statement can be expressed

$$S = -k \log \left\{ \begin{array}{l} \text{probability that any particular} \\ \text{expected state will be selected} \\ \text{from the population of such states} \end{array} \right\}$$

And, because the Law of Large Numbers forces distributions to become sharply localized at their means, we have

$$\log(\text{expected probability}) = \big\langle \log(\text{probability}) \big\rangle$$

. . . which brings us back again to (137), our point of departure.

While statistical calculation has, in this instance, yielded sharp descriptions of $U(U,h,N)$ and $S(T,h,N)$, the canonical “1-function formulation of classical thermodynamics” (page 40) presumes that we possess either $U(S,h,N)$ or $S(U,h,N)$. Insertion of $\langle n\rangle = U/mgh$ into (150) does indeed yield $S(U,h,N)$, so we could, if we wished, step directly into the “S-representation” (page 41) . . . though if we did so we would find ourselves in a relatively unfamiliar place. It is, on the other hand, clear from the designs of (145) and (146) that

$$\begin{array}{c} S = S(T,h,N) \\ \downarrow \\ T = T(S,h,N) \\ \downarrow \\ U(T,h,N) = U(S,h,N) \end{array} \qquad \text{and} \qquad \begin{array}{c} S = S(U,h,N) \\ \downarrow \\ U = U(S,h,N) \end{array}$$

are both analytically unfeasible: we <u>cannot write down</u> the function $U(S,h,N)$!

How, under such a circumstance, are we to undertake to say things about (for example)

$$W \equiv \Big(\frac{\partial U}{\partial h}\Big)_{S,N} \equiv \text{thermodynamic force conjugate to } h$$

—which, by the way, is in this case *literally* a "force": $[W] = \frac{\text{energy}}{\text{length}}$. By some entirely typical "feinting & dodging" (which is why I bring the matter up): by, in this case, passing to the F-representation, where T—not S—is the "natural" variable. We have

$$\begin{aligned} F(T,h,N) = U - TS &= -kT\log Z \\ &= kTN\log\frac{N-\langle n\rangle}{N} \quad : \quad \text{use (144) and (149)} \end{aligned}$$

Therefore $W = \Big(\frac{\partial F}{\partial h}\Big)_{T,N}$—the analog of $p = -\Big(\frac{\partial F}{\partial V}\Big)_{T,N}$—becomes

$$W = -kTN\frac{N}{N-\langle n\rangle}\frac{1}{N}\Big(\frac{\partial\langle n\rangle}{\partial h}\Big)_{T,N}$$

But from (148/149) it follows that

$$\begin{aligned} \Big(\frac{\partial\langle n\rangle}{\partial h}\Big)_{T,N} &= -N\frac{1}{\Big[1+e^{mgh/kT}\Big]^2}\frac{mg}{kT}\,e^{mgh/kT} \\ &= -\frac{1}{N}\langle n\rangle^2\,\frac{mg}{kT}\,\frac{N-\langle n\rangle}{\langle n\rangle} \end{aligned}$$

so after much cancellation we arrive at the gratifyingly simple statement

$$W = mg\langle n\rangle = \left\{\begin{array}{l}\textbf{weight} \text{ of tokens that have been} \\ \text{bumped thermally to the top step}\end{array}\right. \tag{153}$$

Evidently

$$W = Nmg\frac{1}{1+e^{mgh/kT}} \tag{154}$$

constitutes the **equation of state** of the N-token system, with respect to which it plays the same role that $p = NkT/V$ plays in ideal gas theory. Returning with this information to (147) we have

$$U = Wh$$

We find ourselves in position at last to write

$$dU = TdS + Wdh \quad : \quad \text{compare} \quad dU = TdS - pdV$$

and to get down to thermodynamic business: to compute $C_h \equiv (\partial U/\partial T)_h$ and other "observables," *etc*.

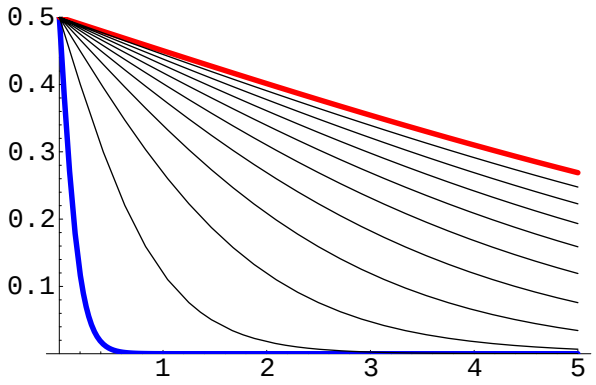

FIGURE 37: **Isotherms** *of the N-token system*: *graphs, that is to say, of* $w \equiv W/Nmg$ *vs.* h, *for various values of* $\theta \equiv kT/mg$. *In this notation the equation of state* (154) *reads* $w = \left[1 + e^{h/\theta}\right]^{-1}$. *The* θ*-values range from* **coldest** $\theta = 0.1$ *through 0.5, 1.0, . . . , 4.0, 4.5 to* **hotest** $\theta = 5.0$. *At infinite temperature half the tokens are up, half down—irrespective of the value of the step height* h. *At finite temperatures, decreasing the value of* h *never tickles more than half of the tokens onto the upper step.*

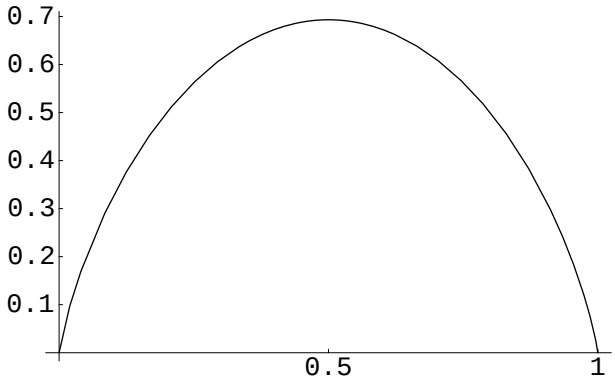

FIGURE 38: *Graph of* $s \equiv S/Nk$ *vs.* $x \equiv \langle n \rangle / N = U/Nmgh$, *in which notation* (150) *reads*

$$s = \log \frac{1}{1-x} + x \log \frac{1-x}{x}$$

The entropy increases until $x = \frac{1}{2}$, *then decreases again until, at* $x = 1$, *all the tokens are up (which can happen in only one way).*

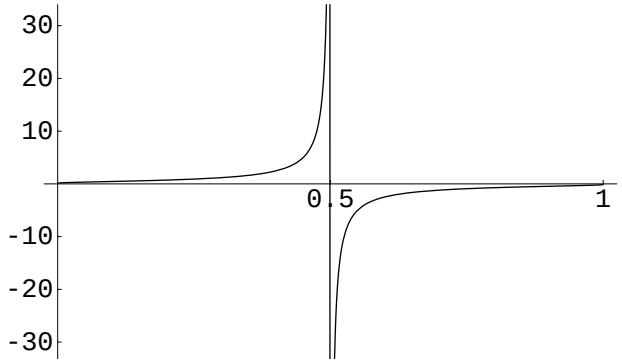

FIGURE 39: *Graph of* $[\frac{ds}{dx}]^{-1}$*, which by*

$$\frac{\partial S}{\partial U} = \frac{1}{T}$$

is proportional to temperature. As $x \uparrow \frac{1}{2}$ *(half the tokens up) the temperature becomes infinite, but if still more tokens are pumped up the slope of the tangent (preceding figure) becomes negative, which is to say*: the temperature becomes negative! *This is a ramification of the fact that the tokens have not only ground states but also "top states." Though most physical systems do not have this property, some—for example, lasers—do. We will return later to a more careful account of the* **negative temperature** *concept.*

The preceding figures illustrate some aspects of the thermodynamics of our 2-state token model. I seems to me fairly amazing that a system so rudimentary as that illustrated in Figure 24 can give rise to such an intricate set of theoretical relationships as has emerged in the last six pages. But that is scarcely the half of it . . . for consider the inverse problem: Suppose that our equations and and figures had been abstracted from work in the thermodynamic laboratory. *How would one deduce—after the fact—that the underlying microsystem is the one pictured in Figure 24*? It was a problem of that order that confronted Planck.

10. Thermodynamics of a system of distinguishable quantum oscillators. Let $\mathfrak{S}$ consist of N identical but distinguishable 1-dimensional quantum oscillators, the whole being (by action of a heat bath) at temperature T. To describe the state of such an oscillator it is (according to the mechanics of such systems) sufficient to specify the energy

$$\varepsilon_s = (s + \tfrac{1}{2})\hbar\omega \quad : \quad s = 0, 1, 2, \ldots$$

To describe the state of the N-oscillator *system* we write

$$\boldsymbol{s} \equiv \{s_1, s_2, \ldots, s_j, \ldots, s_N\}$$
$$\uparrow\text{—identifies state of } j^{\text{th}} \text{ oscillator}$$

The energy of an oscillator system in state $\boldsymbol{s}$ is given by

$$E(\boldsymbol{s}) \equiv E_n = (n + \tfrac{1}{2}N)\hbar\omega \quad : \quad n = s_1 + s_2 + \cdots + s_N$$

—the presumption here being that the oscillators are non-interactive.

The ε_s-state of an individual oscillator is (by quantum *mechanical* calculation) non-degenerate,[97] but the E_n-state of $\mathfrak{S}$ has multiplicity

$$g(n;N) = \text{number of ways } n \text{ can be developed } s_1 + s_2 + \cdots + s_N$$

To indicate that (for example) $s_1 = 2$, $s_2 = 4$, $s_3 = s_4 = 0$, $s_5 = 1$, …, $s_{N-1} = 3$, $s_N = 1$ we could write

$$\bullet\bullet\,|\,\bullet\bullet\bullet\bullet|||\,\bullet\,|\cdots|\,\bullet\bullet\bullet\,|\bullet$$

Clearly

$$\begin{aligned} g(n;N) &= \text{number of such strings } (n\ \bullet\text{'s and } N-1 \text{ fences } |) \\ &= \frac{(N+n-1)!}{n!(N-1)!} \end{aligned}$$

It is computationally useful to note (and becomes clear upon a moment's reflection) that

$$\sum_{n=0}^{\infty} g(n;N)\lambda^n = \Big[\sum_{s=0}^{\infty} \lambda^s\Big]^N = \Big[\frac{1}{1-\lambda}\Big]^N \tag{155}$$

i.e., that $\big[1/(1-\lambda)\big]^N$ gives rise as a **generating function** to the numbers $g(n;N) : n = 1, 2, 3, \ldots$

Turning our attention now to the construction of the partition function, we have

$$\begin{aligned} Z &= \sum_{\boldsymbol{s}} e^{-E(\boldsymbol{s})/kT} \\ &= \sum_{n=0}^{\infty} g(n;N)\, e^{-E_n/kT} \\ &= e^{-\frac{1}{2}N\hbar\omega/kT} \underbrace{\sum_{n=0}^{\infty} g(n;N)\, e^{-n\hbar\omega/kT}}_{= \left[\frac{1}{1-e^{-\hbar\omega/kT}}\right]^N \quad \text{by (155)}} \end{aligned}$$

[97] This statement would require adjustment if the oscillator were 2- or 3-dimensional.

We digress to observe that for each *individual* oscillator

$$\mathcal{Z} = \sum_{s=0}^{\infty} e^{-(s+\frac{1}{2})\hbar\omega/kT} = e^{-\frac{1}{2}\hbar\omega/kT} \cdot \frac{1}{1-e^{-\hbar\omega/kT}}$$

so that we can, if we wish, write (compare (143))

$$Z = \big[\mathcal{Z}\big]^N \tag{156}$$

—this in consequence ultimately of our assumption that the oscillators are *non-interactive*: in the contrary case we expect to have something like

$$Z = \big[\mathcal{Z}\big]^N \cdot \Big\{1 + \lambda \cdot (\text{correction term})\Big\}$$

where λ quantifies the *strength of the interaction*.

In any event, we now have

$$Z = \left[\frac{e^{-\frac{1}{2}\hbar\omega/kT}}{1-e^{-\hbar\omega/kT}}\right]^N = \left[\frac{1}{2\sinh(\hbar\omega/2kT)}\right]^N \tag{157}$$

The F-potential can therefore be described (see again (141.2))

$$F(T,\omega,N) = NkT\log 2\sinh\frac{\hbar\omega}{2kT} \tag{158}$$

while (138/139) provide

$$U(T,\omega,N) = \tfrac{1}{2}N\hbar\omega\coth\frac{\hbar\omega}{2kT} \tag{159}$$

$$S(T,\omega,N) = -Nk\log 2\sinh\frac{\hbar\omega}{2kT} + \frac{1}{T}\cdot\tfrac{1}{2}N\hbar\omega\coth\frac{\hbar\omega}{2kT} \tag{160}$$

Once again it proves feasible to write $S(U,\omega,N)$ but—for the reason stated at the bottom of page 49—not feasible to write $U(S,\omega,N)$: we therefore expect to have to do some "feinting & dodging"—to employ "work-arounds"—to reach thermodynamnic objectives.

From (159) it follows that

$$\lim_{T\downarrow 0} U(T,\omega,N) = N\cdot\tfrac{1}{2}\hbar\omega = \text{net "zero point energy"} \tag{161}$$

and that (see Figure 40)

$$\begin{aligned} C \equiv \Big(\frac{\partial U}{\partial T}\Big)_{\omega,\,N} &\equiv \text{heat capacity} \\ &= Nk\cdot\underbrace{\Big[\frac{\hbar\omega}{2kT}\operatorname{csch}\frac{\hbar\omega}{2kT}\Big]^2}_{\text{approaches unity for } T\gg \frac{1}{2}kT/\hbar\omega} \end{aligned} \tag{162}$$

Functional inversion of (159) gives

$$\frac{\hbar\omega}{2kT} = \coth^{-1}\frac{2U}{N\hbar\omega}$$

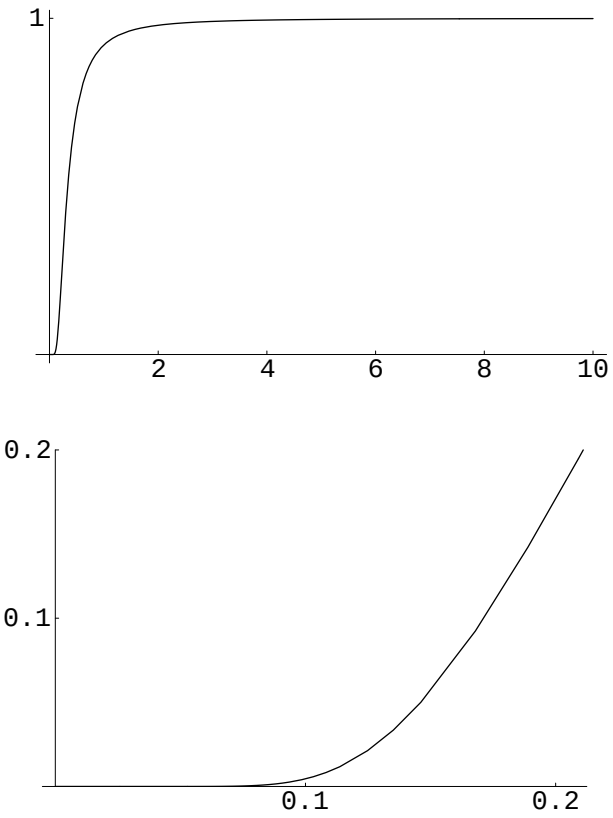

FIGURE 40: *Above: the* **heat capacity of a system of oscillators**, *as described at* (162). *The independent variable is* $2kT/\hbar\omega$, *the dependent variable is* C/Nk. *Below: a magnified display of the low-temperature region.*

which when introduced into (160) gives

$$S = Nk\Big\{ -\log 2\sinh\Big[\coth^{-1}\frac{2U}{N\hbar\omega}\Big] + \frac{2U}{N\hbar\omega}\coth^{-1}\frac{2U}{N\hbar\omega}\Big\}$$

When expressed in terms of $s \equiv S/Nk$ and $u \equiv 2U/N\hbar\omega$ which acquires the somewhat less intimidating design

$$s = u\coth^{-1}u - \log 2\sinh\big[\coth^{-1}u\big] \quad : \quad u \geqslant 1 \tag{163}$$

which is plotted in Figure 41.

One can readily imagine oscillator systems for which ω enjoys the status of a "control parameter."[98] The "force" conjugate to ω (analog of the negpressure

[98] Recall that for a simple pendulum $\omega = \sqrt{g/\ell}$: both g and ℓ are subject to control.

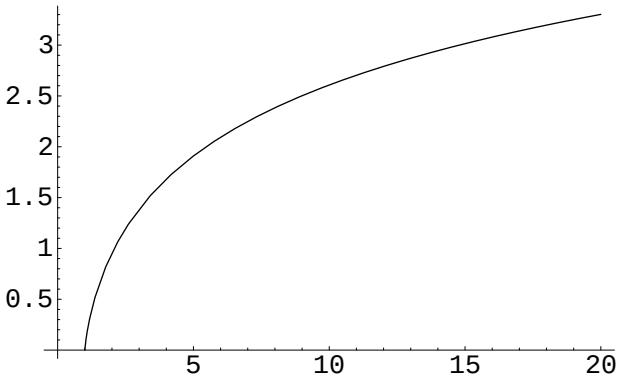

FIGURE 41: *Graph of $S(U)$ for a system of oscillators, based upon* (163). *The slope of the tangent is proportional to $1/T$, so decreasing slope reflects increasing temperature. The curve is entirely typical in that it is* **downward convex but never has negative slope**. *That the "negative temperature" issue does not arise can be traced to the fact the oscillator energy spectrum is unbounded above. Here s runs $\uparrow$, u runs $\rightarrow$.*

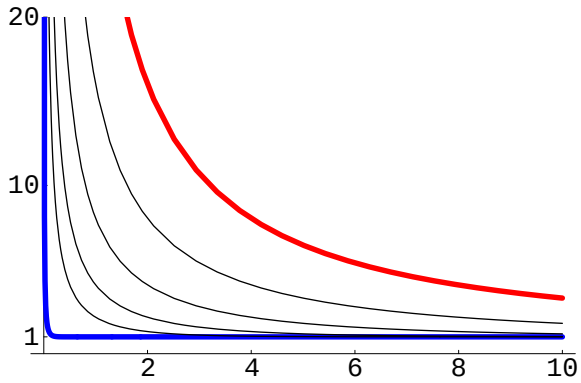

FIGURE 42: **Isotherms** *of a system of oscillators, as they are described at* (165). *The θ-values range from* **coldest** $\theta = 0.1$ *through 2, 4, 8, 16 to* **hotest** $\theta = 32$. *Here a runs $\uparrow$, ω runs $\rightarrow$.*

conjugate to volume) can be described

$$A \equiv \left(\frac{\partial F}{\partial \omega}\right)_{T,\,N} = \tfrac{1}{2} N\hbar \coth \frac{\hbar\omega}{2kT} \quad : \quad \text{dimensionality of "action"}$$
$$= U/\omega \tag{164}$$

Evidently we have now in hand the **equation of state** of the oscillator system,

which in terms of $a \equiv 2A/N\hbar$ and $\theta \equiv 2kT/\hbar$ can be described

$$a = \coth(\omega/\theta) \tag{165}$$

The resulting isotherms are shown in Figure 42.

I am again amazed that a system that is mechanically so simple can give rise to thermal physics that appears—at least superficially—to be so complicated. And again: the **inverse problem**—proceeding backwards from our accumulated results to the statistical model from which they sprang—would appear to require a whole new set of analytical techniques.

11. Thermodynamics of a system of quantum mechanical boxed particles. Let $\mathfrak{S}$ consist of N identical/distinguishable/non-interactive mass points m, each of which is confined quantum mechanically to the interior of a 1-dimensional potential well of width ℓ, the whole being (by action of a heat bath) at temperature T. From mechanics we know that to describe the state of a particle in a square well it is sufficient to specify the energy

$$\begin{aligned} \varepsilon_n \;&=\; \varepsilon_0 \cdot n^2 \quad : \quad n = 1, 2, 3, \ldots \\ \varepsilon_0 &\equiv h^2/8m\ell^2 \end{aligned}$$

The partition function of the N-particle system can be described[99]

$$Z = \Big[\sum_{n=1}^{\infty} e^{-\alpha n^2} \Big]^N \quad \text{with} \quad \alpha \equiv \frac{\varepsilon_0}{kT} = \frac{h^2}{8kTm\ell^2} \tag{167}$$

In the approximation that $\alpha \ll 1$ (requires that $\hbar$ be "small," else that m and/or ℓ and/or T be large) one has

$$\sum_{n=1}^{\infty} e^{-\alpha n^2} \approx \int_0^{\infty} e^{-\alpha n^2}\, dn = \sqrt{\frac{\pi}{4\alpha}} = \sqrt{2\pi m\ell^2 kT/h^2}$$

giving

$$Z \approx \big[2\pi m\ell^2 kT/h^2\big]^{\frac{N}{2}} \tag{168}$$

Arguing now in the usual way from (138) and (139) we have

$$U(T, \ell, N) = N \cdot \tfrac{1}{2}kT \tag{169}$$

$$\begin{aligned} S\,(T, \ell, N) &= N \cdot \tfrac{1}{2}k\Big\{ \log\big[2\pi m\ell^2 kT/h^2\big] + 1 \Big\} \qquad (170) \\ &= N \cdot s(T, \ell) \\ s(T, \ell) &\equiv \tfrac{1}{2}k \log T + k \log \ell + s_0 \qquad (171) \end{aligned}$$

[99] Compare (143) and (156). Operative here once again is our assumption that the constituent elements of $\mathfrak{S}$ are *non-interactive*.

with $s_0 \equiv \frac{1}{2}k\big\{\log\big[2\pi mk/h^2\big]+1\big\}$, while (141) supplies

$$F(T,\ell,N) = -kT\log Z = -N\cdot\tfrac{1}{2}k\log\big[2\pi m\ell^2 kT/h^2\big]$$

The "negforce" conjugate to ℓ (analog of the pressure conjugate to volume, which in this instance is literally a force: $[\wp] = \frac{\text{energy}}{\text{length}}$) is given by

$$\wp \equiv -\Big(\frac{\partial F}{\partial \ell}\Big)_{T,\,N} = \frac{NkT}{\ell}$$

so we have the equation of state

$$\wp\ell = NkT \tag{172}$$

The heat capacity at constant box-length is in this case constant

$$C_\ell = \Big(\frac{\partial U}{\partial T}\Big)_{\ell,\,N} = N\cdot\tfrac{1}{2}k \tag{173}$$

Equations (169) and (170) jointly supply

$$S(U,\ell,N) = \tfrac{1}{2}Nk\Big\{\log\frac{4\pi m\ell^2 U}{Nh^2}+1\Big\} \tag{174}$$

which—somewhat exceptionally, on the evidence of our recent experience—is readily inverted to provide an explicit description of $U(S,\ell,N)$.

We are not surprised by the "ideal gas-like" appearance of our results—they refer, after all, to what we might think of as a "1-dimensional quantum gas"—but the following serves to remind us that they pertain only in the approximation that the dimensionless parameter

$$\alpha \equiv \frac{1}{8kT}\frac{h^2}{m\ell^2} \ll 1 \;:\; \text{requires } \begin{cases}\text{the temperature not to be too low,}\\ \text{the box not to be too small}\end{cases}$$

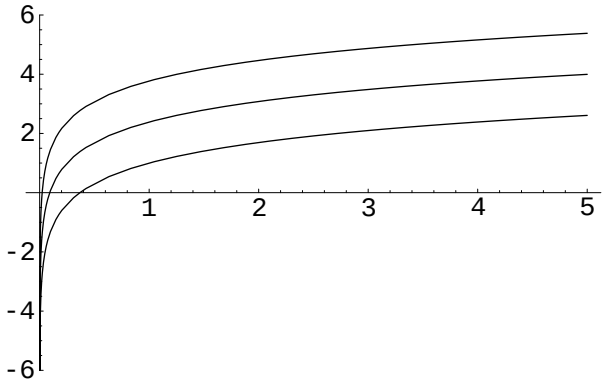

FIGURE 43: *Graph of* (174)*, written* $s(u,\ell) = \log(u\ell^2)+1$ *with* $s \equiv 2S/Nk$ *and* $u \equiv 4\pi mU/Nh^2$*. The* ℓ*-values used were* $\ell = 1$ *(bottom curve),* $\ell = 2$ *and* $\ell = 4$ *(top curve). Negative* S*-values are—whether one argues from* (137) *or from* (152)*—absurd. Their occurance is evidence of the failure of an approximation. Here* s *runs* $\uparrow$*,* u *runs* $\rightarrow$*.*

The low temperature/small box regime Jacobi's theory of **theta functions**[100] supplies the remarkable identity

$$\sum_{n=0}^{\infty} e^{-\alpha n^2} = \sqrt{\frac{\pi}{4\alpha}} \cdot \sum_{m=-\infty}^{\infty} e^{-\pi^2 m^2/\alpha^2} \tag{175}$$

The expression on the right converges very rapidly when $\alpha \ll 1$, and gives back our $\sqrt{\pi/4\alpha}$ in leading approximation. On the other hand, the expression on the left converges rapidly when $\alpha \gg 1$, and supplies

$$\approx 1 + e^{-\alpha} \quad \text{in leading approximation}$$

In that approximation we have

$$Z(\alpha) = \left[1 + e^{-\alpha}\right]^N \quad : \quad \alpha \equiv \frac{1}{8kT}\frac{h^2}{m\ell^2} \gg 1 \tag{176}$$

giving

$$\begin{aligned} U &= kT^2 \frac{d\log Z(\alpha)}{d\alpha}\frac{\partial\alpha}{\partial T} \\ &= N\frac{h^2}{8m\ell^2}\left[1 + e^{\alpha}\right]^{-1} \approx N\frac{h^2}{8m\ell^2}e^{-\alpha} \\ &\qquad\qquad = NkT\,\alpha\, e^{-\alpha} \\ S &= Nk\log\left[1 + e^{-\alpha}\right] + \frac{U}{T} \end{aligned} \tag{177}$$

Expanding the logarithm we get

$$= Nk\Big\{\left[1 - \tfrac{1}{2}e^{-\alpha} + \cdots\right]e^{-\alpha} + \alpha\, e^{-\alpha}\Big\} \approx Nk\,\alpha\, e^{-\alpha}$$

But (177) supplies $\alpha = \log\left[Nh^2/8Um\ell^2\right]$ so we come finally to the conclusion that at low temperatures the entropy of a "1-dimensional quantum gas" can be described

$$S(U,\ell,N) \approx \underbrace{Nk\,\frac{8Um\ell^2}{Nh^2}}_{\text{note the disappearance of } N}\log\frac{Nh^2}{8Um\ell^2} \tag{178}$$

Figures 44 & 45 provide indication of the significance of this result.

[100] For an excellent account of this beautiful subject see R. Bellman, *A Brief Introduction to Theta Functions* (1961). For reference to the elementary proof of (175), which hinges on the "Poisson summation formula," see page 7 in "Applied theta functions of one or several variables" (1997). Theta functions (which come in four flavors) are known to *Mathematica* as `EllipticTheta[a,u,q]` with $a = 1, 2, 3, 4$. We have interest mainly in $\vartheta_3(u, q)$.

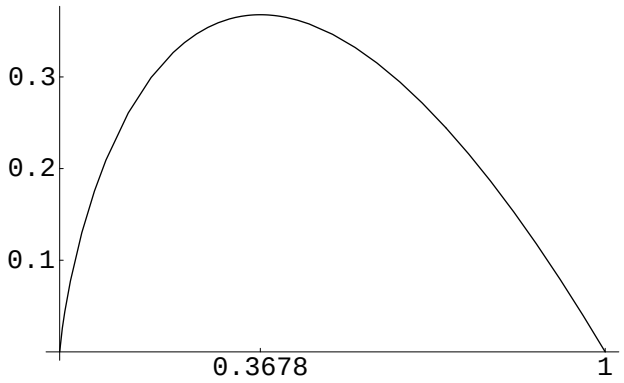

FIGURE 44: *Low-temperature U-dependence of entropy according to* (178)*, which has been written* $s = -u \log u$ *with* $s \equiv S/Nk$ *and* $u \equiv 8Um\ell^2/Nh^2$*. We have* $S \downarrow 0$ *in the limit* $U \downarrow 0$ *as indication that the* **groundstate of the system is non-degenerate***. The nose-over at* $u = 0.3678$ *announces the acute failure of the approximation upon which* (178) *is based. Here* s *runs* $\uparrow$*,* u *runs* $\rightarrow$*.*

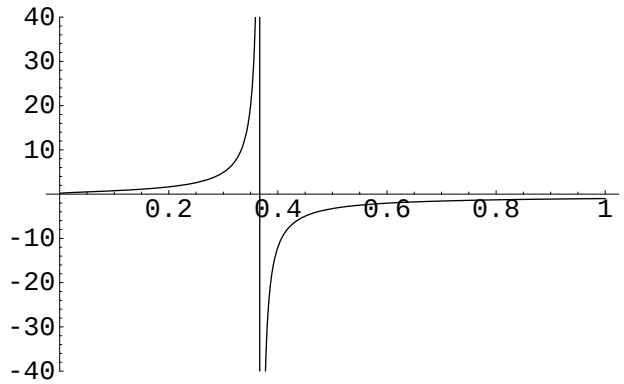

FIGURE 45: *Graph of* $\left[ds/du\right]^{-1} \sim T$*. The region of seeming "negative temperature" is an artifact of the approximation, which on evidence of the figures is reliable only for* $u \ll 0.3678$*.*

From $\wp \equiv -\partial F/\partial \ell$ and $F = -NkT \log\left[1 + e^{-\alpha}\right]$ we are led by quick calculation to a low-temperature equation of state

$$\wp \ell = N \frac{h^2}{m\ell^2}\, e^{-\alpha(T,\ell)} \tag{179}$$

that certainly does not look very gas-like, and in which $h^2/m\ell^2$ appears to have taken over the role of k. Equally unfamiliar (compare (173)) is the $\hbar$-dominated

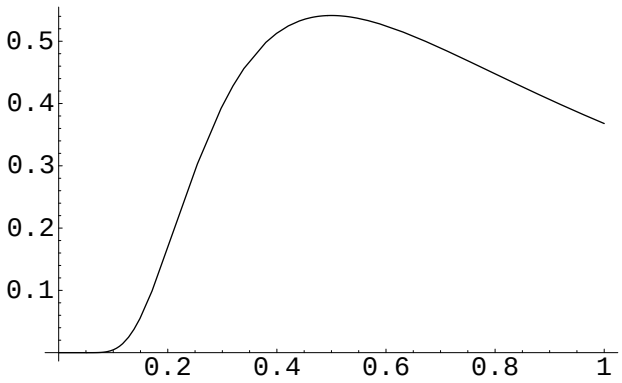

FIGURE 46: *Graph of the low-temperature heat capacity of a 1-dimensional quantum gas, based upon* (180)*, which has been written* $c = \theta^{-2}\exp\{-\theta^{-1}\}$ *with* $c \equiv C/N$ *and* $\theta \equiv 8kTm\ell^2/h^2$*. Remarkably, the heat capacity—which was stated at* (173) *to be constant—is shown here to vanish at low temperatures. And so also do its derivatives to all orders! The approximation used is evidently is reliable only for* $\theta \ll 0.5$*. Here* c *runs* $\uparrow$*,* θ *runs* $\rightarrow$*.*

structure of the low-temperature heat capacity

$$C_\ell(T) = \Big(\frac{\partial U}{\partial T}\Big)_{\ell,\,N} = N\cdot\alpha^2 e^{-\alpha}$$
$$= N\cdot\Big(\frac{1}{8kT}\frac{h^2}{m\ell^2}\Big)^2\exp\Big\{-\frac{1}{8kT}\frac{h^2}{m\ell^2}\Big\} \qquad (180)$$

which is plotted in Figure 46. In the essential respects described in the caption, the low-temperature heat capacity of a quantum gas resembles that of a system of quantum oscillators (Figure 40). We have touched here on what is, in fact, a *general* phenomenon (low-temperature failure of the Law of Dulong & Petit) that contributed importantly to the early development of quantum mechanics.[101]

12. Statistical mechanics of classical systems. Statistical mechanics came into the world as a thermodynamically motivated outgrowth of *classical* mechanics. Its invention contributed promptly and directly to the train of thought (mainly Planck's) that led to the development of quantum mechanics ... and in that sense "rendered classical mechanics obsolete." In electing to use quantum mechanical examples to illustrate the process

$$\text{microphysics} \longrightarrow Z\text{-construction} \longrightarrow \text{thermodynamics}$$

I have perpetrated an anachronism, but for a simple reason: quantum systems (of the sort we have considered) have—as our token model had—*discrete energy*

[101] We will have occasion to return to this subject. In the meantime, see Chapter 6 in Mendelssohn.[29]

spectra: the "number of accessible states" is in such cases just that—a *number*, determined by *counting*. And it is, in general, **easier to count than to measure**, easier to ennumerate than to mensurate. The classical theory is, for precisely that reason and in several respects, formally more awkward than its quantum counterpart, but it presents problems that abundantly repay close consideration.

Think classically about a macroscopic hunk of stuff. We imagine it to consist of N particles, bound together by certain characteristic forces, each particle tracing a trajectory in physical 3-space. The stuff, regarded as a dynamical system, has $3N$ degrees of freedom. Gibbs recognized that—for his novel purposes—the language of choice for describing the internal dynamics of such a system was provided by Hamilton. Within the Hamiltonian formalism the **dynamical state** of the stuff is represented as a **point** $\{p_1,\ldots,p_{3N},x_1,\ldots,x_{3N}\}$ **in 6N-dimensional "phase space."** The state-point moves as described by the canonical equations

$$\left.\begin{aligned}\dot{x}_i &= +\frac{\partial H}{\partial p_i}\\ \dot{p}_i &= -\frac{\partial H}{\partial x_i}\end{aligned}\right\} \quad : \quad i = 1,2,\ldots,3N$$

where the "Hamiltonian" $H(p_1,\ldots,p_{3N},x_1,\ldots,x_{3N})$ describes the mechanical design/constitution of the stuff in question. One has

$$\text{total energy } E \text{ of the system} = H(\text{momentary state-point})$$

The equation

$$H(p_1,\ldots,p_{3N},x_1,\ldots,x_{3N}) = E$$

identifies an **isoenergetic hypersurface** Σ_E within the phase space Γ, and the energy-conserving dynamical motion of the state-point inscribes a curve $\mathcal{C}$ on that hypersurface. The set $\{\Sigma_E\}$ of all such surfaces (which obviously cannot intersect) lends an "onion-like" structure to phase space: see Figure 47.

Our knowledge of the *location* of the state-point within Γ is necessarily statistical. Let

$$P(p_1,\ldots,p_{3N},x_1,\ldots,x_{3N})\frac{dp_1dx_1dp_2dx_2\cdots dp_{3N}dx_{3N}}{h^{3N}} \equiv P(p,x)\left(\tfrac{dpdx}{h}\right)^{3N}$$

denote the probability that the system will be found within the differential neighborhood of the indicated state-point. Here h is a constant that has been introduced from dimensional necessity[102]

$$[h] = [p\cdot x] = \text{action} \quad : \quad \text{value arbitrary}$$

[102] In its absence P would acquire the N-dependent dimension $(\text{action})^{-3N}$. Classical physics supplies, however, no universally-available natural candidate for the *value* of h.

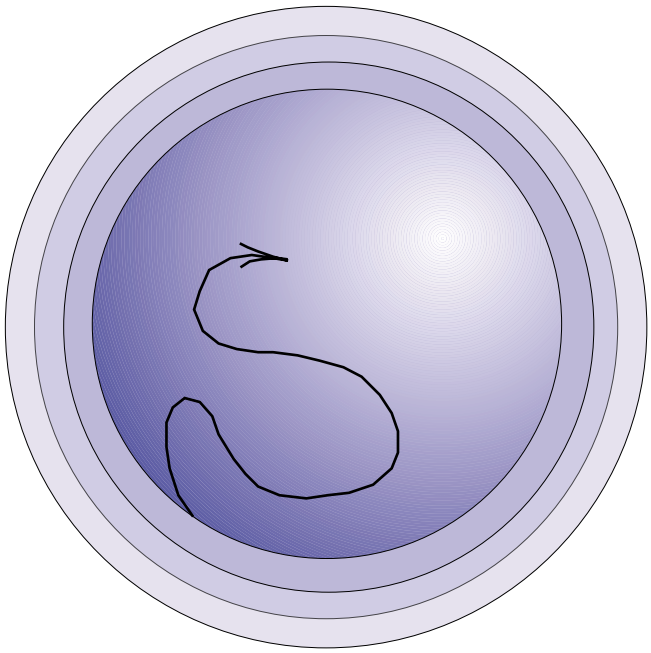

FIGURE 47: *Highly schematic attempt to represent the curve $\mathcal{C}$ inscribed dynamically on an isoenergetic hypersurface Σ_E in the very-high-dimensional phase space of a many-body system. Notice that, because the equations of motion are of first order, such curves can never intersect (though they can, in principle, close upon themselves: the system motion would then be periodic.) The figure refers to a situation that pertains whether or not the system has thermalized . . . and that fact raises a deep problem: it would take an ensemble of such figures to represent the assumption fundamental to statistical mechanics, yet the principles of that subject apply successfully to individual systems, represented by individual figures.*

We interpret the classical upshot of (134) to be that if the system can be considered to have thermalized at temperature T then

$$P(p_1,\ldots,p_{3N},x_1,\ldots,x_{3N};T,\boldsymbol{\alpha}) = \frac{1}{Z(T,\boldsymbol{\alpha})}\, e^{-H(p_1,\ldots,p_{3N},x_1,\ldots,x_{3N};\boldsymbol{\alpha})/kT} \tag{181}$$

Here $\boldsymbol{\alpha}$ refers to all the parameters (container-volume, electric & magnetic field strengths, *etc.*: see again page 128) that are subject to our control and $Z(T,\boldsymbol{\alpha})$

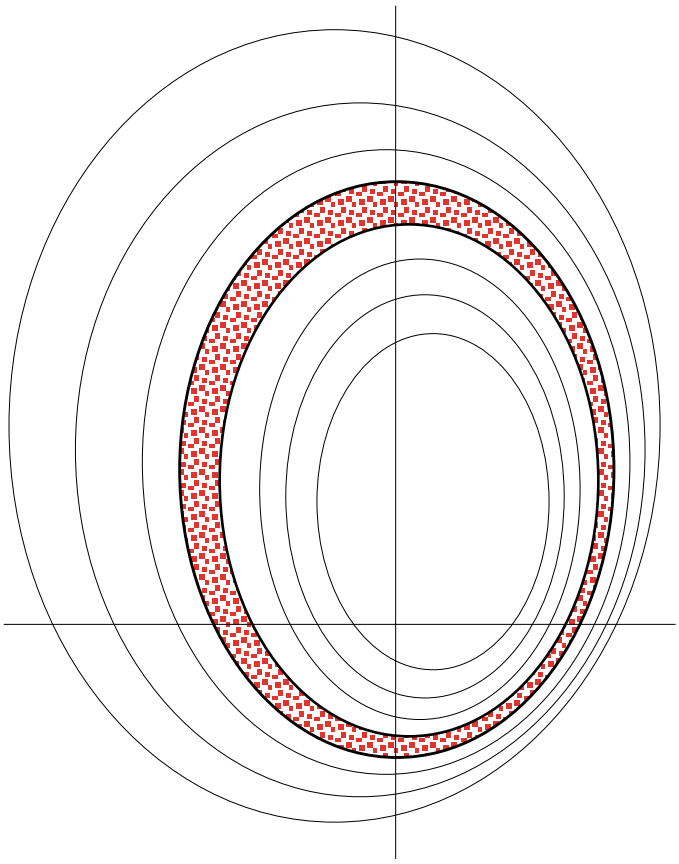

FIGURE 48: *Isoenergetic onion in high-dimensional phase space. Highlighted is the hypervolume bounded by Σ_E and Σ_{E+dE}. In the text I write $\Sigma_E(\boldsymbol{\alpha})$ to emphasize that the placement of the surfaces depends on the values assigned to the control parameters.*

is fixed by the normalization condition:

$$Z(T,\boldsymbol{\alpha}) \equiv \iint\cdots\int_{\text{all of phase space}} e^{-H(p_1,\ldots,p_{3N},x_1,\ldots,x_{3N};\boldsymbol{\alpha})/kT} \left(\tfrac{dpdx}{h}\right)^{3N} \tag{182}$$

The integral is a computational monstrosity, but simplifies if one takes into account the fact that the exponential is constant on isoenergetic surfaces: what I will call "layer-by-layer onion integration" then supplies

$$= \int_{\text{all allowed } E\text{-values}} e^{-E/kT} g(E,\boldsymbol{\alpha})\, dE \tag{183}$$

where (see the figure)

$$g(E,\boldsymbol{\alpha})\, dE \equiv \left\{ \begin{array}{l} \text{dimensionless phase hypervolume between} \\ \text{the hypersurfaces } \Sigma_E(\boldsymbol{\alpha}) \text{ and } \Sigma_{E+dE}(\boldsymbol{\alpha}) \end{array} \right. \tag{184}$$

Evidently $g(E,\boldsymbol{\alpha})$ lends classical meaning to the **density of states** (page 123), and $Z(E,\boldsymbol{\alpha})$ is its Laplace transform.

In many cases of physical interest (molecular gases, for example) the constituent particles of the system present themselves (at least if temperature and pressure are not too extreme) as loose aggregates of little bound systems ("molecules"). In such cases

$$H = H_{\text{molecule }\#1} + H_{\text{molecule }\#2} + \cdots + H_{\text{molecule }\#\mathcal{N}} + \text{molecular interaction term}$$

where each molecular term depends upon its own relatively small set of variables. In such cases—owing entirely to an elementary property of the exponential—the monster integral (182) assumes (at least in the approximation that the interaction term can be neglected) the form

$$Z(T,\boldsymbol{\alpha}) = \prod_{\text{molecules}} Z_{\text{molecular}}(T,\boldsymbol{\alpha}) \tag{185}$$

where $Z_{\text{molecular}}$ requires integration over just a few variables.[103] Carrying this train of thought to its limit, we arrive at the case in which the "molecules" are in fact non-interactive point particles. We arrive, in short, at this ...

EXAMPLE: Classical statistical mechanics of ideal gas. Let N non-interactive, identical but distinguishable mass points m be confined to the interior of a box of volume V. The Hamiltonian of such a system reads

$$H(p_1,\ldots,p_{3N},x_1,\ldots,x_{3N}) = \sum_{i=1}^{N}\left\{\tfrac{1}{2m}(p_{i1}^2+p_{i2}^2+p_{i3}^2)+U(x_{i1},x_{i2},x_{i3})\right\}$$

where the "wall potential"

$$U(x_1,x_2,x_3) = \begin{cases} 0 & \text{inside the box} \\ \infty & \text{outside the box} \end{cases}$$

Immediately

$$\begin{aligned} Z(T,V) &= \left[\tfrac{1}{h^3}\iiint_{-\infty}^{+\infty} e^{-\frac{1}{2mkT}(p_1^2+p_2^2+p_3^2)}\,dp_1dp_2dp_3 \right. \\ &\qquad \left. \cdot \iiint_{-\infty}^{+\infty} e^{-U(x_1,x_2,x_3)/kT}dx_1dx_2dx_3\right]^N \\ &= (V/h^3)^N \cdot \left[\int_{-\infty}^{+\infty} e^{-\frac{1}{2mkT}p^2}\,dp\right]^{3N} \\ &= (V/h^3)^N \cdot \left[\sqrt{2\pi mkT}\right]^{3N} \\ &= \left[V\cdot\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right]^N \end{aligned} \tag{186}$$

[103] Instances of this **factorization principle** were encountered already at (143), (156) and (167).

We note in passing that if we wrote $V = \ell^3$ then this 3-dimensional classical result would become

$$\begin{aligned} &= \Big(\big[2\pi m \ell^2 kT/h^2 \big]^{\frac{N}{2}} \Big)^3 \qquad (187) \\ &= \left[\begin{array}{l} Z \text{ obtained at (168) for a 1-dimensional quantum} \\ \text{gas that is neither too cold nor too confined} \end{array} \right]^3 \end{aligned}$$

Proceeding now in the familiar way from (138/139/141), we have

$$\begin{aligned} U(T,V,N) &= kT^2 \frac{\partial}{\partial T} \log Z \\ &= \tfrac{3}{2} NkT \qquad (188.1) \end{aligned}$$

$$\begin{aligned} S(T,V,N) &= k \log Z + \frac{1}{T} U \\ &= Nk \Big\{ \log V + \tfrac{3}{2} \log \Big(\frac{2\pi mkT}{h^2} \Big) \Big\} + \tfrac{3}{2} Nk \\ &= Nk \big\{ \tfrac{3}{2} \log T + \log V \big\} + S_0 \qquad (188.2) \\ &\qquad\qquad S_0 \equiv \tfrac{3}{2} Nk \Big\{ \log \Big(\frac{2\pi mk}{h^2} \Big) + 1 \Big\} \\ F(T,V,N) &= -kT \log Z \\ &= -NkT \Big\{ \log V + \tfrac{3}{2} \log \Big(\frac{2\pi mkT}{h^2} \Big) \Big\} \qquad (188.3) \end{aligned}$$

from which follow

$$p \equiv -\Big(\frac{\partial F}{\partial V} \Big)_{T,\,N} = \frac{NkT}{V} \quad : \quad \text{equation of state} \qquad (188.4)$$

and the statement

$$\begin{aligned} C_V \equiv \Big(\frac{\partial U}{\partial T} \Big)_{V,\,N} &= N \cdot \tfrac{3}{2} k \quad : \quad \text{remains constant even as } T \downarrow 0 \qquad (188.5) \\ &= (\text{number of mechanical degrees of freedom}) \cdot \tfrac{1}{2} k \end{aligned}$$

These are identical to statements extracted earlier from the phenomenology of ideal monomolecular gases,[104] but have been obtained here by the methods of statistical mechanics from a classical micromechanical model. Note, however, in connection with (188.2) ... that at (28) we were obliged on dimensional grounds to set

$$S_0 = -Nk \big\{ \tfrac{3}{2} \log T_0 + \log V_0 \big\}$$

but lacked reason to assign any particular *values* to the "fiducial coordinates" T_0 and V_0, for which reason the *value of* S_0 *remained indeterminate*. It is, in this light, remarkable that the statistical mechanical argument proceeds to its end *without reference to a fiducial point*—this because

$$\Big[\frac{mk}{h^2} \Big] = \frac{\text{mass} \cdot \text{energy/temperature}}{(\text{action})^2} = \frac{1}{(\text{volume})^{\frac{2}{3}} \cdot \text{temperature}}$$

—but *value of* S_0 *remains still indeterminate because the classical theory ascribes no particular value to* h.

[104] See (28) on page 42, where the "monomolecular" requires us to set $c = \frac{3}{2} k$.

EXAMPLE: Same song, different orchestration. Suppose we had elected to proceed directly from (182), without reference to the factorization principle (185). The $6N$-fold integral can in the present instance be written in the alternative factored form

$$Z = \tfrac{1}{h^{3N}}\left[\iint\cdots\int_{3N\text{-dimensional hyperbox}} dx_1 dx_2\cdots dx_{3N}\right] \cdot\left[\iint\cdots\int_{-\infty}^{+\infty} e^{-\frac{1}{2mkT}(p_1^2+p_2^2+\cdots+p_{3N}^2)} dp_1 dp_2\cdots dp_{3N}\right]$$

and it is obvious that the top line supplies $(V/h^3)^N$. Writing

$$p_1^2+p_2^2+\cdots+p_{3N}^2 = 2mE$$

we observe that Σ_E is a hypersphere of radius $\sqrt{2mE}$ in $3N$-dimensional momentum-space. It becomes natural therefore to work in **hyperspherical coordinates**: we expect then to have have

$$Z = (V/h^3)^N \cdot \int_0^\infty e^{-\frac{1}{2mkT}p^2}\, \mathcal{S}_{3N}(p)\, dp \tag{189.1}$$

where[105]

$$\begin{aligned}\mathcal{S}_n(p) &\equiv \text{surface area of an } n\text{-dimensional sphere of radius } p\\ &= \frac{n\sqrt{\pi^n}}{\Gamma\left(1+\frac{n}{2}\right)}p^{n-1}\\ &= \frac{d}{dp}\mathcal{V}_n(p) \quad : \quad \mathcal{V}_n(p) \equiv \text{volume of such a sphere}\end{aligned} \tag{189.2}$$

Mathematica has no difficulty with the integral and, after a `FullSimplify` command, supplies

$$Z = (V/h^3)^N \cdot \left(2\pi mkT\right)^{\frac{3}{2}N}$$

... which is precisely (186). The point of this little *tour de force* is that (189) places us in position to write, after a change of variable,

$$Z(T,V,N) = \int_0^\infty g(E;V,N)\, e^{-\frac{E}{kT}}\, dE \tag{190}$$

with

$$\begin{aligned} g(E;V,N) &\equiv (V/h^3)^N \frac{3N\sqrt{\pi^{3N}}}{\Gamma\left(1+\frac{3N}{2}\right)}(2mE)^{\frac{3N-1}{2}}(m/2E)^{\frac{1}{2}}\\ &= \left\{\begin{array}{l}\textbf{classical density of states}\\ \text{function for this system}\end{array}\right.\end{aligned}$$

To recover (186) from the result that *Mathematica* reports to be the value of the integral (190) one needs only to know that $\Gamma(x)/\Gamma(1+x) = 1/x$,

[105] See §8 in "Construction & physical application of the fractional calculus" (1997) and references cited there.

and this, we saw on page 106, is an identity fundamental to the theory of the gamma function. The preceding calculation provides an illustration of the "onion integration" technique described on page 147, and it directs our attention to some illuminating physical geometry:

13. Hyper-dimensional geometry and the classical meaning of entropy. Let $\mathcal{V}_E$ signify the phase-volume interior to the isoenergetic surface Σ_E:

$$\mathcal{V}_E \equiv \iint\cdots\int_{\text{interior of } \Sigma_E} dx_1 dp_1 \cdots dx_N dp_N \tag{191}$$

where to reduce notational clutter I have taken N to refer now not (as formerly) to the number of particles but to the number of mechanical degrees of freedom. Dimensionally

$$\big[\mathcal{V}_E\big] = (\text{action})^N$$

The "number of states interior to Σ_E" will be taken to be the dimensionless number defined

$$\mathcal{N}_E \equiv \frac{\mathcal{V}_E}{h^N} \tag{192}$$

Though $\mathcal{N}_E$ has a literal/integral meaning in quantum mechanics, its classical meaning is—owing to the fact that the numerical value of h has become arbitrary—somewhat fanciful (rather like "number of lines of force" in classical electrodynamics). From

$$\mathcal{N}_{E+dE} - \mathcal{N}_E = \frac{d\mathcal{N}_E}{dE}dE$$

we conclude that the classical density of states at energy E can be described

$$g(E) = \frac{d\mathcal{N}_E}{dE} = \frac{1}{h^N}\frac{d\mathcal{V}_E}{dE} \tag{193}$$

Now some elementary hypergeometrical observations: the volume of an N-cube of radius R (*i.e.*, of side-length $2R$) can be described

$$V_N(R) = C_N^{\text{cube}} \cdot R^N \quad \text{with} \quad C_N^{\text{cube}} \equiv 2^N$$

so

$$\frac{V_N(r)}{V_N(R)} = (r/R)^N \tag{194}$$

For N-spheres one has $C_N^{\text{sphere}} = \sqrt{\pi^N}/\Gamma\big(1+\frac{N}{2}\big)$ but arrives at volume ratio that is again given by (194). A glance at Figure 49 brings us to the valuable insight that

> The volume of a convex N-blob lies mainly near its surface,
> and lies ever nearer as N increases.

To sharpen that insight we look (Figure 50) to an N-box with

- exterior radius R
- interior radius $r = \lambda R$, where $\lambda = 1 - \epsilon$
- wall thickness $w = R - r = \epsilon R \ll R$

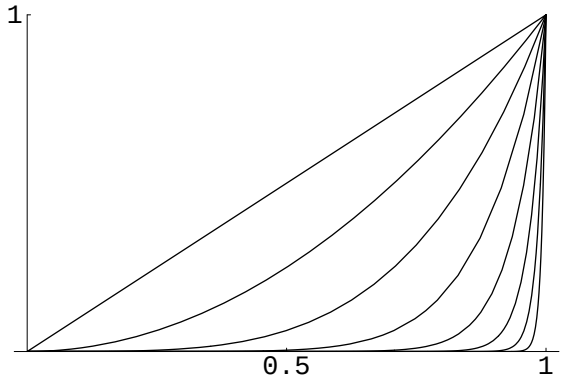

FIGURE 49: *Graphs of* $(r/R)^N$ *for* $N = 1, 2, 4, 8, 16, 32, 64, 128$. *Returning with this elementary information to* (194)*, we are brought to the conclusion that "the volume of a hypercube/hypersphere lies mainly quite near its surface."*

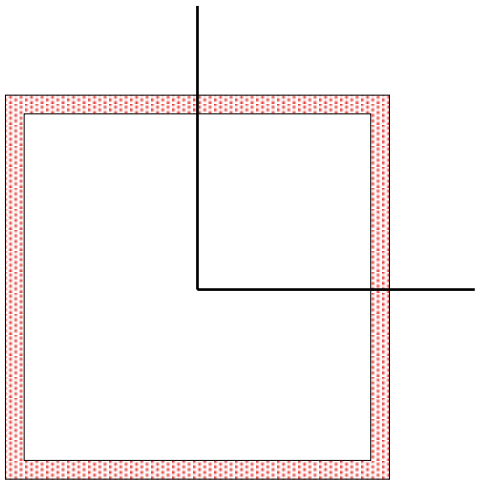

FIGURE 50: *Thin-walled "N-box," with most of its dimensions left to the imagination. However thin the walls may be, as* N *ascends in value it becomes evermore vividly the case that*

$$\textit{wall volume} \gg \textit{enclosed volume}$$

Immediately

$$\frac{\text{enclosed volume}}{\text{wall volume}} = \frac{\lambda^N}{1-\lambda^N} = \lambda^N\Big\{1+\lambda^N+\lambda^{2N}+\cdots\Big\}$$
$$\approx \lambda^N \quad : \quad N \text{ large enough that } \lambda^N \ll 1$$

So—counterintuitively—

$$\lim_{N\uparrow\infty} \frac{\text{enclosed volume}}{\text{wall volume}} = 0$$

An identical result pertains to *spherical* N-boxes. It is not clear what one means by the "higher-dimensional analog of an arbitrary 3-blob," so is in the general case not clear how to give meaning to the "dimensional inflation process." But it is pretty clear that we can expect quite generally to have

$$\frac{\text{enclosed hyperblob volume}}{\text{wall volume}} \sim 0 \text{ if } N \text{ is very large}$$

so if your assignment is to paint a hyperblob you might as well simply *fill* it with paint: doing so will require scarcely more paint!

It is easiest to comprehend very large/small numbers when they are expressed in base 10. Let us therefore write

$$Q \equiv \frac{\text{enclosed hyperblob volume}}{\text{wall volume}} = 10^{-q}$$

Then $Q = \lambda^N$ supplies

$$\begin{aligned} N \log_{10} \lambda &= -q \\ \lambda &= 10^{-q/N} \\ &= 1 - (q/N)\log 10 + \tfrac{1}{2!}\big[(q/N)\log 10\big]^2 - \cdots \\ &\equiv 1 - \epsilon \end{aligned}$$

whence

$$\epsilon \approx \frac{q \log 10}{N} = \frac{2.30259\, q}{N}$$

if $\big[(q/N)\log 10\big] \ll 1$. Suppose, for example, that $\lambda = \frac{100}{101}$; *i.e.*, that wall thickness adds 1% to the radius of the blob. Then $q = 6 \Rightarrow N = 1388.45$, which is to say:

$$Q = \left(\tfrac{100}{101}\right)^{1388.45} = 10^{-6} \;:\; \begin{cases} \text{if } N \geqslant 1389 \text{ then wall volume} \\ \text{exceeds enclosed volume by a} \\ \text{factor of more than a million} \end{cases}$$

Let N increase with Q held constant: then λ grows ever closer to $10^0 = 1$. If wall volume is to exceed enclosed volume by "only" a factor of a million in the case $N = 10^{20}$—still "small" by thermodynamic standards—then the walls must be *exceedingly thin*: $\epsilon = 2.30259 \times 6 \times 10^{-20}$.

Return now, in the light of the preceding discussion, to the high-dimensional phase space of a many-body system. The phase volume (which is to say: the "number of state points") contained within the "onion layer" bounded on the inside by $\Sigma_{E-\Delta E}$ and on the outside by Σ_E accounts (unless ΔE is made *too* small) for very nearly all of the *total* volume contained within Σ_E (which is to say: for an overwhelming majority of *all* the state points interior to Σ_E). The

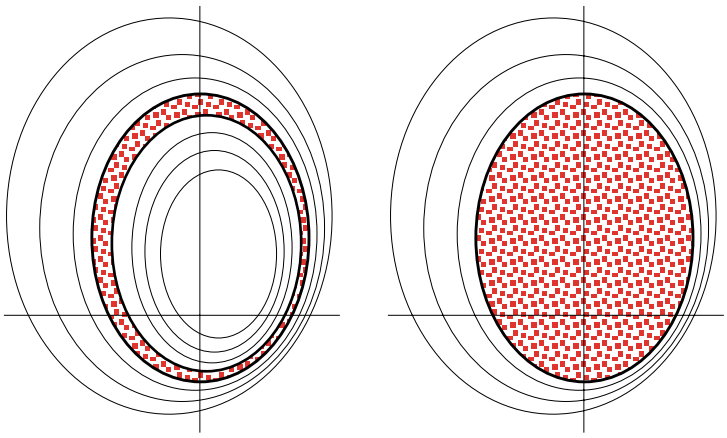

FIGURE 51: *On the left: the phase volume ("onion layer") bounded by the isoenergetic surfaces* Σ_E *and* $\Sigma_{E-\Delta E}$*. The shaded region provides a local/global representation of the* density *with which state points are sprinkled on to* Σ_E*. In high dimension we expect the figure on the right to provide essentially that same information.*

seeming implication is that—appearances notwithstanding—the figures shown above refer to essentially *identical populations of state points*. It becomes plausible, therefore, to write

$$S = k \log \frac{\mathcal{V}_{\langle E\rangle}}{h^N} \tag{195}$$

How does this work out in an illustrative case?

For a classical particle in a 1-dimensional box we have

$$\begin{aligned}\mathcal{V}_E &= \ell^N \cdot \text{volume of } N\text{-sphere of radius } \sqrt{2mE} \\ &= \ell^N \frac{\sqrt{\pi^N}}{\Gamma\big(1+\frac{N}{2}\big)}\big(\sqrt{2mE}\,\big)^N \end{aligned} \tag{196}$$

which at $E \to \langle E\rangle = N\cdot\frac{1}{2}kT$ becomes

$$\mathcal{V}_{\langle E\rangle} = \frac{\big[\sqrt{\pi m\ell^2 NkT}\,\big]^N}{\Gamma\big(1+\frac{N}{2}\big)}$$

The conjectured relation (195) would on this basis supply

$$S = k\Big\{\tfrac{1}{2}N\log\big[2\pi m\ell^2 kT/h^2\big] + \tfrac{N}{2}\log\tfrac{N}{2} - \log\Gamma\big(1+\tfrac{N}{2}\big)\Big\}$$

But by Stirling's formula[106] $\log\Gamma\big(1+\frac{N}{2}\big) \sim \big(1+\frac{N}{2}\big)\log\frac{N}{2} - \frac{N}{2} + \frac{1}{2}\log\frac{4\pi}{N} + \cdots$

[106] Or see "Barnes' asymptotic expansion" at **43:6:8** in J.Spanier & K.Oldham, *An Atlas of Functions* (1987).

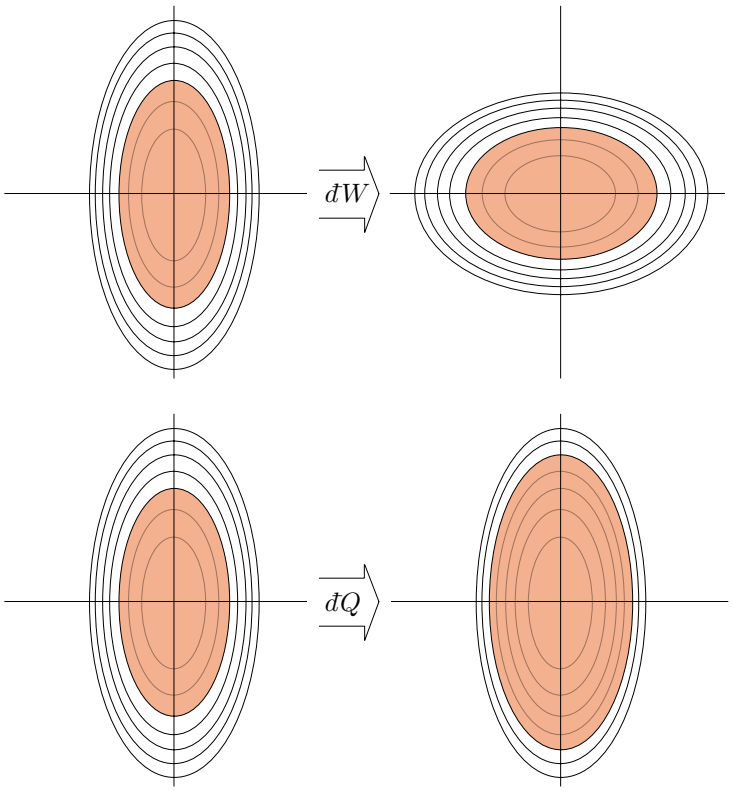

FIGURE 52: *Figures based upon the classical relation* (195) *between hypervolume and entropy. The equation*

$$H(p_1, \ldots, x_1, \ldots; \alpha_1, \ldots) = E$$

defines the surfaces Σ_E*. Tickling the control parameters* $\boldsymbol{\alpha}$ *alters the shape of those surfaces. The upper figure refers to the adiabatic (i.e., isentropic or volume-preserving) performance of work, the lower figure to pure heating (i.e., to an injection of energy subject to the shape-preserving condition* $đW = 0$*).*

so we have

$$\begin{aligned} S &\sim k\Big\{\tfrac{1}{2}N\log\left[2\pi m\ell^2 kT/h^2\right] + \tfrac{N}{2}\Big\} + \tfrac{N}{2}\log\tfrac{N}{2} - \big(1+\tfrac{N}{2}\big)\log\tfrac{N}{2} - \tfrac{1}{2}\log\tfrac{4\pi}{N} \\ &\downarrow \\ &= N\cdot\tfrac{1}{2}k\Big\{\log\left[2\pi m\ell^2 kT/h^2\right] + 1\Big\} \quad \text{for large values of } N \end{aligned}$$

which agrees precisely with the result achieved at (170) for a *quantum* mechanical particle-in-a-box.

Equation (195) establishes a classical relationship

$$\text{entropy} \;\Leftrightarrow\; \text{a hypergeometric aspect of the microphysics}$$

that serves very well the needs both of intuitive understanding and graphical representation: see Figure 52.

14. Energy fluctuation & the macro/microcanonical distinction. The mechanical state point of the isolated system $\mathfrak{S}$ that sits before us on the lab bench traces a curve $\mathcal{C}$ on some specific isoenergetic hypersurface Σ_E (see again Figure 47). It might therefore seem odd to pretend that the system has been drawn from a macrocanonical *ensemble* of systems in which the energy is exponentially graded, and in which non-zero probability is assigned to the possibility that the state point of $\mathfrak{S}$ lies off the surface Σ_E. The **microcanonical ensemble** was invented to remove that seeming "difficulty."

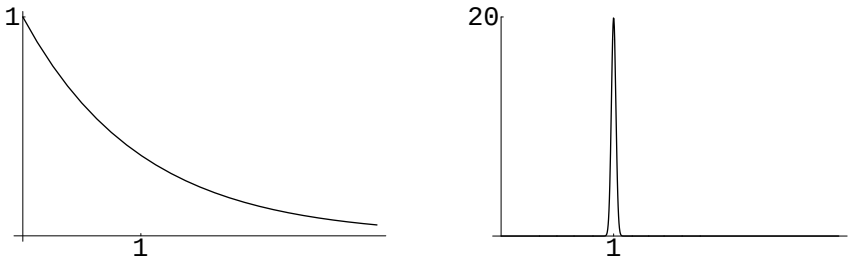

FIGURE 53: *At left: the exponentially graded energy distribution characteristic of a macrocanonical ensemble of systems (and—within any individual thermalized system—of the Boltzmann distribution). At right: the sharply localized energy distribution characteristic of a microcanonical ensemble of systems.*

All members of a microcanonical ensemble have the same sharply defined energy E. The ensemble is represented by state points sprinkled onto Σ_E. The laws of motion cause the state points to move around on Σ_E, but if the local density of points is set equal to the *fraction of the time* that any given state point spends in the vicinity of each Σ_E-point then the distribution as a whole will become time-independent: time-averaging over the career of any individual system becomes equivalent—**ergodic hypothesis**—to averaging (at any instant) over the microcanonical ensemble.

To establish contact with thermodynamics we write

$$U = \langle E \rangle = \int E\,\delta(E - \mathcal{E})\,dE = \mathcal{E} \tag{197.1}$$

$$S = k \log\left[\varepsilon_0 \frac{1}{h^N} \frac{d\mathcal{V}_\mathcal{E}}{d\mathcal{E}}\right] \tag{197.2}$$

$$\frac{1}{T} = \frac{\partial S}{\partial U} \tag{197.3}$$

Here $\mathcal{E}$ is some arbitrarily-selected energy value, having at the moment nothing to do with temperature, (197.2) embodies the idea first encountered at (193),[107] ε_0 is an "energy" of arbitrary value (its introduction is forced by a dimensional consideration), and it is *via* (197.3) that temperature enters the picture. Note that the microcanonical formalism gets along—is obliged to get along—without reference to the partition function (which in the *macro*canonical formalism is the central object).

Let us consider how the microcanonical program plays out in a concrete case—taken to be (once again) the case of a "classical 1-dimensional ideal gas." At (196) we had

$$\frac{1}{h^N}\mathcal{V}_\mathcal{E} = \ell^N \frac{\sqrt{\pi^N}}{\Gamma\left(1+\frac{N}{2}\right)}\left(\sqrt{2m\mathcal{E}/h^2}\,\right)^N$$

so

$$\varepsilon_0 \frac{1}{h^N}\frac{d\mathcal{V}_\mathcal{E}}{d\mathcal{E}} = \frac{\left[\ell\sqrt{2\pi m\mathcal{E}/h^2}\,\right]^N}{\Gamma\left(1+\frac{N}{2}\right)}\frac{N}{2\mathcal{E}}\varepsilon_0$$

gives

$$S = Nk\log\left[\ell\sqrt{2\pi m\mathcal{E}/h^2}\,\right] - k\log\Gamma\left(1+\tfrac{N}{2}\right) + k\log\left(N\varepsilon_0/2\mathcal{E}\right)$$

which by (197.3) supplies

$$\frac{1}{T} = \frac{(N-1)k}{2\mathcal{E}} \qquad \text{whence} \qquad \mathcal{E} = (N-1)kT \approx \tfrac{1}{2}NkT$$

Returning with this information to the preceding description of S and borrowing from page 154 the asymptotic expansion of $\log\Gamma\left(1+\frac{N}{2}\right)$, we obtain

$$\begin{aligned} S &\sim N\cdot\tfrac{1}{2}k\Big\{\log\left[2\pi m\ell^2\tfrac{N}{2}kT/h^2\right]+1\Big\} - k\left(1+\tfrac{N}{2}\right)\log\tfrac{N}{2} + k\log\left[\varepsilon_0/kT\right] \\ &\downarrow \\ &= N\cdot\tfrac{1}{2}k\Big\{\log\left[2\pi m\ell^2 kT/h^2\right]+1\Big\} + k\log\left[\varepsilon_0/kT\right] \end{aligned}$$

for large values of N. Comparison with the result obtained macrocanonically at the bottom of page 155 suggests that the dangling term is an artifact of the method: it would disappear if we justify setting $\varepsilon_0 = kT$.

The microcanonical formalism tends to be computationally awkward, but does lend valuable perspective to the deep question *How do mechanical systems manage to achieve states of thermal equilibrium, and what does it mean for them to do so*?

The objection that the macrocanonical formalism asks us to contemplate an ensemble with exponentially smeared energies—even though the system in

[107] We have, in effect, let the state points contained within an "onion layer" (left side of Figure 51) rain down upon $\Sigma_\mathcal{E}$.

front of us possesses an energy that is (if not precisely known to us) sharply defined and conserved—has less force than might naively be supposed. For consider the expression

$$\begin{aligned}
\langle (E-\langle E\rangle)^2\rangle &= \langle E^2\rangle - \langle E\rangle^2 \\
&= \tfrac{1}{Z}\int E^2 e^{-\beta E} g(E)\,dE - \left[\tfrac{1}{Z}\int E e^{-\beta E} g(E)\,dE\right]^2 \\
&= \frac{1}{Z}\frac{\partial^2 Z}{\partial\beta^2} - \left[\frac{1}{Z}\frac{\partial Z}{\partial\beta}\right]^2 \\
&= \frac{\partial^2 \log Z}{\partial\beta^2} \\
&= \left(-kT^2\frac{\partial}{\partial T}\right)\left(-kT^2\frac{\partial}{\partial T}\right)\log Z \\
&= kT^2\Big(\frac{\partial U}{\partial T}\Big)_{V,N} && \text{by (138), page 127} \\
&= kT^2 C_V && \text{by (63.1), page 65}
\end{aligned}$$

For an ideal monomolecular gas we therefore—fairly typically—have

$$\frac{\sqrt{\langle E^2\rangle - \langle E\rangle^2}}{\langle E\rangle} = \frac{\sqrt{kT^2\cdot\frac{3}{2}Nk}}{\frac{3}{2}NkT} = \frac{1}{\sqrt{\frac{3}{2}N}}$$

$$\downarrow$$

$$= 0 \quad \text{as } N \text{ becomes large} \qquad (198)$$

We conclude that the energy distribution within a macrocanonical ensemble of realistically-sized many-body systems is in fact very tightly localized at an energy set by the temperature, that in this respect the macro-micro distinction comes very close to being a "distinction without a difference." But in practical terms there is a world of difference, for "evaluate the partition function Z"—an instruction special to and central to the macrocanonical formalism—is a very sharply posed problem, susceptible to attack by a great variety of well-oiled techniques.

Evidently the functional identity of the macro/micro formalisms can be understood as a manifestation of the hypergeometrical point developed in §13.

Equation (198) provides an instance of a **fluctuation formula**, where the word "fluctation" refers not (as most commonly) to a process that takes place in time but a result of *ranging over an ensemble*. Similar formulæ describe pressure fluctuations, density fluctuations, etc.[108] Note that all such formulæ refer to statistical properties of thermalized systems that lie beyond the reach of classical thermodynamics. This is the sort of thing that Gibbs had in mind when he alluded[109] to the power of statistical mechanics to supply "new results."

[108] For a good discussion see Chapter 5 in D. ter Haar's superb text, *Elements of Statistical Mechanics* (1954).

[109] See again the passage quoted on page 129.

15. Classical estimation of energy at a specified temperature: the equipartition principle. In introductory texts one sometimes encounters the assertion that "temperature is a measure of the average kinetic energy of the individual molecules" that collectively comprise the thermalized system in question.[110] Such a conception of "temperature" would, however, make it impossible to assign a temperature to thermalized radiation (no molecules), and anyway can be criticized on the ground that it puts the cart before the horse: better to say that "temperature *determines* the average kinetic energy ..." Concerning temperature itself, we might adopt the view that " 'temperature' is the name given to the parameter that controls the shape of the macrocanonical distribution function," but would confront then the circumstance that the macrocanonical ensemble is itself a convenient fiction: had we elected to work with a *micro*canonical ensemble then no question of "distribution shape" arises. In the latter context we find ourselves *forced* to assign to "temperature" what is arguably its deepest meaning

$$(\text{temperature})^{-1} = \left(\frac{\partial S}{\partial U}\right)_{\text{all else}}$$

and to speak (as on the preceding page) of the "energy set by the temperature."

Which brings us back to our point of departure: *Within a molecular system, what is the energy (per molecule) set by the temperature?* An answer was provided by the celebrated **equipartition principle**. It was evidence of some perplexing violations of that principle that provided major impetus toward the development of quantum mechanics, and resolution of those difficulties that provided some of the most convincing early support of the young quantum theory.

Max Born[111] has presented an argument that captures the essence of the equipartition principle in the smallest possible nutshell, and proceeds as follows: Suppose the Hamiltonian of a classical system $\mathfrak{S}$ has the form

$$H(p_1, p_2, \ldots, x_1, x_2, \ldots) = ap_1^n + \mathcal{H}(p_2, \ldots, x_1, x_2, \ldots)$$

Then

$$\langle ap_1^n \rangle = \frac{\int\cdots\int ap_1^n e^{-\beta H} dp_1 dx_1 dp_2 dx_2 \cdots}{\int\cdots\int e^{-\beta H} dp_1 dx_1 dp_2 dx_2 \cdots} = \frac{\int ap_1^n e^{-\beta a p_1^n} dp_1}{\int e^{-\beta a p_1^n} dp_1}$$

NOTE: The h-factors above and below cancel, so have been omitted.

$$= -\frac{\partial}{\partial \beta} \log \mathcal{Z}$$

[110] See, for example, Douglas C. Giancoli, *Physics for Scientists & Engineers* (3rd edition 2000), page 487.

[111] *Natural Philosophy of Cause & Chance* (1949), Appendix 26, page 188.

with

$$\mathcal{Z} \equiv \int\cdots\int e^{-\beta a p_1^n}\, dp_1 = \begin{cases} \infty & : \quad n = 1,3,5,\ldots \\ \dfrac{2\Gamma\left(\frac{n+1}{n}\right)}{(a\beta)^{1/n}} & : \quad n = 2,4,6,\ldots \end{cases}$$

Immediately

$$\begin{aligned} \langle a p_1^n \rangle = \frac{1}{n\beta} &= \tfrac{1}{n} kT \quad : \quad n = 2,4,6,\ldots \\ &= \tfrac{1}{2} kT \quad \text{in the physically interesting case } n = 2 \end{aligned}$$

I present now a generalized variant of the preceding argument. Suppose the system Hamiltonian has the form

$$H = \mathcal{T}(p_1, p_2, \ldots p_\nu, x_1, x_2, \ldots, x_\nu) + \mathcal{V}(x_1, x_2, \ldots, x_\nu)$$

and that $\mathcal{T}$ is homogeneous of degree n in the momenta. By Euler's homogeneous function theorem (35) we then have

$$\mathcal{T} = \tfrac{1}{n} \sum_{j=1}^{\nu} p_j \frac{\partial \mathcal{T}}{\partial p_j} \equiv \tfrac{1}{n}\, \boldsymbol{p}\cdot\boldsymbol{\nabla}_p \mathcal{T}$$

Therefore (omitting h-factors for the same reason as before)

$$\langle \mathcal{T} \rangle \equiv \tfrac{1}{nZ} \int_\Gamma e^{-\beta H} \boldsymbol{p}\cdot\boldsymbol{\nabla}_p \mathcal{T}\, (dp\, dx)^\nu$$

But

$$\begin{aligned} e^{-\beta H} \boldsymbol{p}\cdot\boldsymbol{\nabla}_p \mathcal{T} &= e^{-\beta H} \boldsymbol{p}\cdot\boldsymbol{\nabla}_p H \\ &= -\beta^{-1} \boldsymbol{\nabla}_p \cdot \left(e^{-\beta H} \boldsymbol{p}\right) + \beta^{-1} e^{-\beta H} \left(\boldsymbol{\nabla}_p \cdot \boldsymbol{p}\right) \\ &= -\beta^{-1} \boldsymbol{\nabla}_p \cdot \left(e^{-\beta H} \boldsymbol{p}\right) + \nu \beta^{-1} e^{-\beta H} \end{aligned}$$

so

$$\begin{aligned} \langle \mathcal{T} \rangle &= \frac{\nu}{n\beta} - \frac{1}{n\beta Z} \int \left\{ \int \boldsymbol{\nabla}\cdot \left(e^{-\beta H} \boldsymbol{p}\right) (dp)^\nu \right\} (dx)^\nu \\ &= \frac{\nu}{n\beta} - \frac{1}{n\beta Z} \int \left\{ \int_{\text{momentum boundary}} e^{-\beta H} \boldsymbol{p}\cdot\boldsymbol{d\sigma} \right\} (dx)^\nu \end{aligned}$$

Under conditions that cause the surface term to vanish[112] we therefore have

$$\begin{aligned} \langle \mathcal{T} \rangle = \tfrac{\nu}{n} kT \quad \text{giving} \quad U &= \tfrac{\nu}{n} kT + \langle \mathcal{V} \rangle \\ &\Downarrow \\ &= \nu \cdot \tfrac{1}{n} kT \quad \text{in absence of a potential} \end{aligned} \tag{199}$$

$$U_{\text{free particles in a 1-box}} = \tfrac{1}{2} kT \tag{200.1}$$

$$U_{\text{free particles in a 3-box}} = \tfrac{3}{2} kT \tag{200.2}$$

[112] This—because the "momentum boundary" lies at infinity—was seen above to entail $n = 2, 4, 6, \ldots$

If we assume the Hamiltonian to have the more specialized design

$$H = \mathcal{T}(p_1, p_2, \ldots p_\nu) + \mathcal{V}(x_1, x_2, \ldots, x_\nu)$$

and assume moreover that

- $\mathcal{T}$ is homogeneous of degree n in the momenta
- $\mathcal{V}$ is homogeneous of degree m in the (Cartesian) coordinates

then the $\langle \mathcal{V} \rangle$-term in (199) yields to similar analysis, and we obtain

$$U = \nu \cdot \left(\tfrac{1}{n} + \tfrac{1}{m}\right) kT$$

which entails

$$\begin{aligned} U_{\text{1-dimensional harmonic oscillators}} &= N \cdot \left(\tfrac{1}{2} + \tfrac{1}{2}\right) kT = NkT \\ U_{\text{2-dimensional harmonic oscillators}} &= 2N \cdot \left(\tfrac{1}{2} + \tfrac{1}{2}\right) kT = 2NkT \\ U_{\text{1-dimensional quartic oscillators}} &= N \cdot \left(\tfrac{1}{2} + \tfrac{1}{4}\right) kT = \tfrac{3}{4} NkT \end{aligned} \tag{200.3}$$

Equations (200.1) and (200.2) illustrate the source of the rubric

"$\frac{1}{2}kT$ per degree of freedom per particle"

which is the upshot of the "equipartition principle." We note, however, that while a 1-dimensional oscillator has only one mechanical degree of freedom, it carries a full kT of energy ... of which half is kinetic, half potential.

Each of the preceding results assigns (by T-differentiation) a *constant* value to the heat capacity C, and the constant values obtained from (200.1) and (200.3) are in fact in precise agreement with the high-temperature reported at (173) and (162). But at low temperatures those heat capacities $C(T)$ are found (see again Figures 40 & 46)—for quantum mechanical reasons—to depart from constancy, and in fact to drop to zero. It was the discovery by late 19th Century experimentalists that *T-dependent heat capacities are the rule, not the exception* that alerted theorists to the fact that there was something fishy about the purported "equipartition principle," but their attempts to resolve the problem by classical means were oddly desultory, and were in any event not met with much success. Only with the development of quantum mechanics did the issue begin to achieve a measure of clarity: see Figure 54.[113]

In the preceding discussion we have traced the equipartition principle (also, if somewhat misleadingly, called the "equipartition *theorem*") to statements that emerge when kinetic/potential energy are **averaged over a macrocanonical ensemble**.[114] In 1870 Rudolph Clausius observed that statements of similar

[113] See Stephen G. Brush, *The Kind of Motion We Call Heat: A History of the Kinetic Theory of Gases in the* 19th *Century* (1976), page 86 and §§10.8 & 9.

[114] The equipartition principle was already old by the time Gibbs invented the macrocanonical ensemble, so the discussion has been rooted in anachronism.

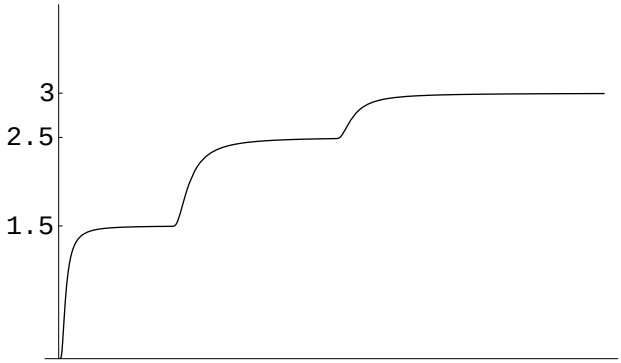

FIGURE 54: *Highly schematic representation of the heat capacity of a diatomic gas. At moderately low temperatures the molecules behave like point masses, and carry* $\frac{3}{2}kT$ *of energy. Only at*

$$T \approx T_{\text{rotational}} \equiv \frac{\text{energy of lowest rotational mode}}{k}$$

do the rotational degrees of freedom come into play, contributing an additional $\frac{2}{2}kT$*. Finally, at*

$$T \approx T_{\text{vibrational}} \equiv \frac{\text{energy of lowest vibrational mode}}{k}$$

the vibrational degree of freedom becomes active, and contributes a final $\frac{1}{2}kT$*. Thus do thermodynamic measurements—of heat capacity and of other system-attributes—provide a non-spectroscopic view of features of the quantum mechanical energy spectrum. At high temperatures we expect quantum effects to be washed out, and all systems to behave more or less classically. After all, at* sufficiently *high temperatures all systems* vaporize! *In any event, what we see in the figure is a kind of* **staged implementation of the equipartition principle***, with quantum mechanics in control of the switches.*

formal appearance can be extracted from the basic principles of mechanics by a process that involves **averaging over time**. He himself did not do much with the idea, but in the hands of others it soon became basic to the theory of real gases. His work—to which I now turn—is of interest also because it invites one to *conflate* ensemble averages and time averages, to consider them to be interchangeable ... which is the idea basic to ergodic theory.

Let $q^1, q^2, \ldots, q^n$ be generalized coordinates of a mechanical system with Lagrangian $L(\dot{q}, q)$ of the form

$$L(\dot{q}, q) = T(\dot{q}, q) - U(q)$$

Introducing

$$W(t) \equiv p_i(t)\, q^i(t)$$

where $\sum_i$ is understood and where the conjugate momenta p_i are defined in the usual way

$$p_i \equiv \frac{\partial L}{\partial \dot{q}^i}$$

we study the time-average of $\frac{d}{dt}W(t)$. "Time-average" will be taken to have the standard meaning

$$\overline{f} \equiv \tfrac{1}{\tau}\int_0^\tau f(t)\, dt \equiv \text{time-average of } f(t) \text{ on the indicated interval}$$

Immediately

$$\begin{aligned}\dot{W} &= \frac{\partial L}{\partial \dot{q}^i}\, \dot{q}^i + q^i \frac{d}{dt}\frac{\partial L}{\partial \dot{q}^i} \\ &= \frac{\partial T}{\partial \dot{q}^i}\, \dot{q}^i + \frac{\partial L}{\partial q^i}\, q^i \quad \text{by Lagrange's equations}\end{aligned}$$

so

$$\overline{\dot{W}} = \tfrac{1}{\tau}\int_0^\tau \frac{dW(t)}{dt}\, dt = \frac{W(\tau) - W(0)}{\tau} = \overline{\frac{\partial T}{\partial \dot{q}^i}\, \dot{q}^i} + \overline{\frac{\partial L}{\partial q^i}\, q^i} \tag{201}$$

With Clausius we observe that

$$\frac{W(\tau) - W(0)}{\tau} \text{ can be considered to vanish} \tag{202}$$

under either of the following circumstances:

- the system is periodic, and τ is its period, for then $W(\tau) = W(0)$;
- the system, though aperiodic, has the property that $W(\tau)$ is bounded (as would happen if, for example, the q's were Cartesian and referred to a spatially confined system: "particles in a box"); we then realize (202) in the limit $\tau \uparrow \infty$.

In either event, we can bring (202) to (201) to obtain the **virial theorem**

$$\overline{\frac{\partial T}{\partial \dot{q}^i}\, \dot{q}^i} + \overline{\frac{\partial L}{\partial q^i}\, q^i} = 0 \tag{203}$$

—the time averages being taken over a period (finite or infinite).

If $T(\dot{q}, q)$ is homogeneous of degree 2 in the velocities $\dot{q}$ then, by Euler's theorem,

$$\frac{\partial T}{\partial \dot{q}^i}\, \dot{q}^i = 2T$$

and we have

$$\overline{T} \equiv \text{time-averaged kinetic energy} = -\tfrac{1}{2}\overline{\frac{\partial L}{\partial q^i}\, q^i}$$

More briefly,

$$\overline{T} = \overline{\mathcal{V}} \tag{204.1}$$

where

$$\mathcal{V} \equiv -\tfrac{1}{2}\frac{\partial L}{\partial q^i}\,q^i = -\tfrac{1}{2}Q_i\,q^i \tag{204.2}$$

defines what Clausius called the "virial." Here the Q_i are what in mechanics are called the "components of generalized force," and $\sum_i$ is again understood. If (as will be the case in inertial *Cartesian* coordinates) $T(\dot{q}, q)$ is actually q-independent then

$$\downarrow$$
$$= +\tfrac{1}{2}\frac{\partial U}{\partial q^i}\,q^i$$

It is interesting to note in this connection that <u>if U is homogeneous of degree n</u> then

$$\downarrow$$
$$= \tfrac{n}{2}\,U$$

and the virial theorem reads

$$\overline{T} = \tfrac{n}{2}\,\overline{U} \tag{205}$$

which has obvious and familiar applications[115] to (for example)

- the theory of oscillators ($n = 2$)
- the Kepler problem ($n = -1$)

and in the case $n = -2$ supplies the curious result $\overline{E} = \overline{T} + \overline{U} = 0$.[116]

Consider now the case of a **classical gas**. The kinetic energy function is of the form

$$T = T(\dot{\boldsymbol{x}}_1, \dot{\boldsymbol{x}}_2, \ldots, \dot{\boldsymbol{x}}_N) = \sum_{j=1}^{3N} \tfrac{1}{2} m \dot{x}_j^2$$

where $\boldsymbol{x}_i$ describes the position of the i^{th} molecule. The virial theorem (204) supplies

$$\overline{T} = -\tfrac{1}{2}\sum_{i=1}^{N} \overline{\boldsymbol{F}_i \cdot \boldsymbol{x}_i} \tag{206}$$

---

[115] See H. Pollard, *Mathematical Introduction to Celestial Mechanics* (1966), page 44. An ingenious application of the virial theorem to the theory of static structures has been described by J. C. Maxwell (see *Scientific Papers*, Volume II, page 410.)

[116] For a derivation of the virial theorem based on Newtonian mechanics see, for example, H. Goldstein, *Classical Mechanics* (2nd edition 1980) §3–4: many applications are listed in Goldstein's index. H. C. Corben & P. Stehle (*Classical Mechanics*, 2nd edition 1960, page 164) provide a derivation in language of the Hamiltonian formalism. My own Lagrangian approach is closest in spirit to that of C. W. Kilmister, *Lagrangian Dynamics* (1967) page 33. For a statement of the **quantum mechanical virial theorem** (which is very closely related to "Ehrenfest's theorem") see E. Merzbacher, *Quantum Mechanics* (2nd edition 1970) page 168.

where $\boldsymbol{F}_i$ describes the net force experienced by the i^{th} molecule. If the gas is sufficiently dilute that the only molecular interactions of importance are 2-body interactions we expect to be able to write

$$\boldsymbol{F}_i = \boldsymbol{f}_i + \sum_{j\neq i} \boldsymbol{F}_{ij} \quad \text{where} \quad \begin{cases} \boldsymbol{f}_i & \text{describes the "wall force"} \\ \boldsymbol{F}_{ij} & \text{describes the force on } i^{\text{th}} \text{ by } j^{\text{th}} \end{cases}$$

Equation (206) then becomes

$$-\tfrac{1}{2}\sum_i \overline{\boldsymbol{f}_i\cdot\boldsymbol{x}_i} = \overline{T} + \tfrac{1}{2}{\sum_{i,\,j}}' \overline{\boldsymbol{F}_{ij}\cdot\boldsymbol{x}_i} \tag{207.1}$$

where the prime on the $\sum$ signifies that the cases $i = j$ are to be excluded (and can be dropped if we set $\boldsymbol{F}_{ii} = \boldsymbol{0}$). In the less explicit language of (204.1) we have

$$\begin{aligned} \overline{\mathcal{V}^{\text{wall}}} &= \overline{T} - \overline{\mathcal{V}^{\text{intermolecular}}} \\ \mathcal{V}^{\text{intermolecular}} &= \sum_{\text{pairs}} \mathcal{V}_{ij} \end{aligned} \tag{207.2}$$

It may be true that, as Clifford Truesdell has remarked,[117] "the purpose of statistical mechanics ... is to calculate time averages," but that, in all but a few favorable cases, is impossible to do. It is for that reason that we have recourse to the **ergodic hypothesis**, according to which time-averaging and averaging over a macrocanonical ensemble *give the same result*. On the strength of that hypothesis we allow ourselves, in place of (107.2), to write

$$\overline{\mathcal{V}^{\text{wall}}} = \big\langle T \big\rangle - \big\langle \mathcal{V}^{\text{intermolecular}} \big\rangle \tag{208}$$

The time-average that has been retained on the left falls into the "favorable case" category, for it is time-averaged wall forces that give rise to the notion of "pressure." We expect to have

$$\begin{aligned} \overline{\mathcal{V}^{\text{wall}}} \equiv -\tfrac{1}{2}\sum_i \overline{\boldsymbol{x}_i\cdot\boldsymbol{f}_i} &= \tfrac{1}{2}p\int_{\partial V} \boldsymbol{x}\cdot\boldsymbol{d\sigma} \\ &= \tfrac{1}{2}p\int_V \boldsymbol{\nabla}\cdot\boldsymbol{x}\, d^3x \\ &= \tfrac{3}{2}pV \end{aligned}$$

where the sign reversal at the first step reflects the fact that wall forces are inner-directed while the surface differential $\boldsymbol{d\sigma}$ is outer-directed. Drawing now

[117] P. Caldirola (editor), *Ergodic Theories* (1961), page 25.

upon the equipartition principle to write $\overline{T} = \frac{3}{2}kT$, we find that (208) can be expressed

$$\begin{aligned} pV &= NkT - \tfrac{2}{3}\big\langle \mathcal{V}^{\text{intermolecular}} \big\rangle \\ &= NkT + \tfrac{1}{3}{\sum_{i,\,j}}' \big\langle \boldsymbol{F}_{ij}\cdot\boldsymbol{x}_i \big\rangle \\ &\downarrow \\ &= NkT \quad \text{in the } \textit{absence} \text{ of intermolecular forces} \end{aligned} \tag{209}$$

Equation (209) plays a prominent role in the classical theory of real gases . . . as we will later have occasion to see. But I have achieved already my present objective, which was to demonstrate how collaborative interplay among

- the equipartition principle
- the virial theorem
- the ergodic hypothesis

can be used to produce a thermodynamic result.

16. Adiabatic invariants, entropy and quantization. We look finally to some "collaborative interplay" of a different sort. The story begins at the 1st Solvay Congress (Brussels, 1911) where Lorentz chanced to mention, within the context of a discussion of the emerging role of $\hbar$ in physics, that he had once asked Einstein "How does a simple pendulum behave when the suspending string is gradually shortened?" (see Figure 55) and that Einstein had responded that he "had once demonstrated that the ratio of the energy to frequency would remain constant if the string length were altered continuously and infinitely slowly." I find it a little surprising that the scholarly Lorentz had to ask Einstein about a question that had already been posed and resolved by Boltzmann (1866), by Clausius(1871) and by Rayleigh (1902), but it's good that he did . . . for his question (new audience, new context) stimulated the major effort that produced the **theory of adiabatic invariants**. The objective of that theory—which is a creation mainly of Paul Ehrenfest and his student, Jan Burgers—is to

> indentify those features/attributes of the motion of general periodic systems which *remain invariant under slow variation of the system parameters*.

The theory is fairly intricate.[118] It will serve my present purposes to quote without proof a couple of its typical results.

The state point (p, x) of an oscillator traces an ellipse in phase space.

[118] It exploits an idea ("action and angle variables") that had been introduced into celestial mechanics by C. E. Delauney (1816–1872) in 1846, the relevance of which had been pointed out by Karl Schwartschild (1873–1916) in a paper published on the very day of his death. A fairly detailed account of the theory, and extensive references, can be found in my CLASSICAL MECHANICS (1983), pages 382–423.

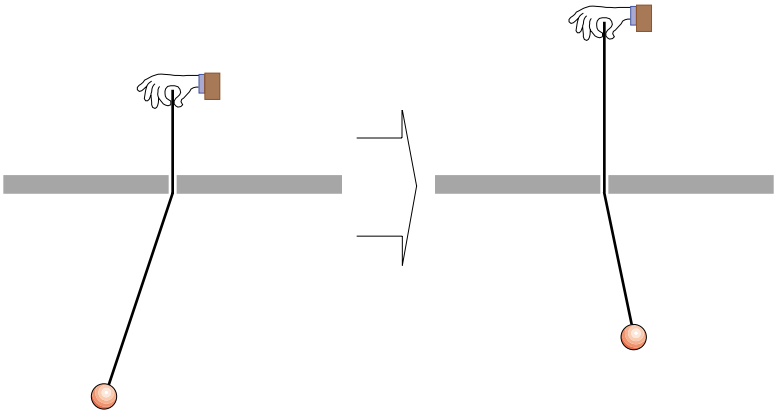

FIGURE 55: *The* LORENTZ PENDULUM PROBLEM. *The support string is shortened (which is to say:* $\omega = \sqrt{g/\ell}$ *is increased) in a time very long compared to the period of the pendulum. The procedure requires that work be done on the pendulum, so poses the question*: What can one say about the relationship of E_{final} to E_{initial}? *Curiously, it was sixty years before anyone thought to ask how the* phase *is affected by slow* cyclic *excursions in the space of control parameters.*

Immediately

$$x_{\text{intercept}} = \pm(\text{amplitude}) = \pm\sqrt{2E/m\omega^2}$$
$$p_{\text{intercept}} = \pm m\omega(\text{amplitude}) = \pm\sqrt{2mE}$$

so

$$\frac{|p_{\text{intercept}}|}{|x_{\text{intercept}}|} = m\omega$$

describes how the *shape* of the ellipse depends upon ω, while

$$\text{phase area } \oint p\,dx = \pi|x_{\text{intercept}}||p_{\text{intercept}}| = 2\pi(E/\omega)$$

describes how its *area* depends (for given ω) upon the energy. The theory devised by Ehrenfest establishes that, as Einstein had asserted (see Figure 56),

$$\oint p\,dx \text{ is adiabatically invariant}$$

Even more elementary is the example provided by a particle bouncing back and forth within a 1-dimensional box of length ℓ (Figure 57). The period is $\tau = 2m\ell/p = 1/f$ (where f denotes the *literal* frequency) so we have

$$\text{phase area } \oint p\,dx = 2p\ell = \tfrac{1}{2m}p^2 \cdot 4m\ell/p = 2(E/f) \tag{210}$$

which again, by general theory, is adiabatically invariant.

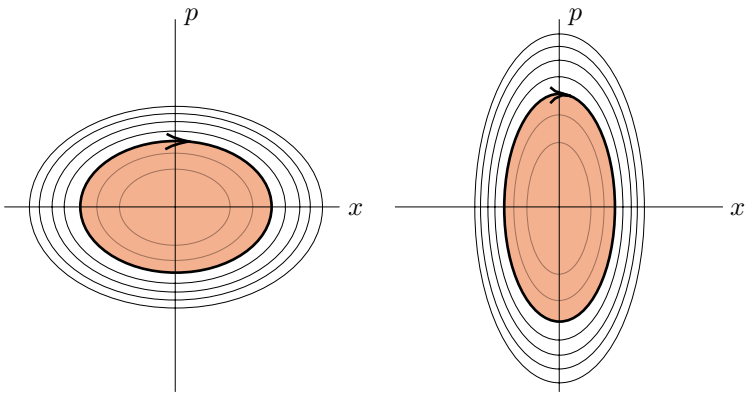

FIGURE 56: *Adjustment of ω alters the figure of the ellipse traced by an oscillator in phase space. The point remarked by Einstein—which had, in fact, been noticed already by many others before him—is that the area of the ellipse becomes invariant as the adjustment becomes quasi-static*:

$$\frac{\text{oscillatory period}}{\text{duration of } \omega\text{-adjustment process}} \ll 1$$

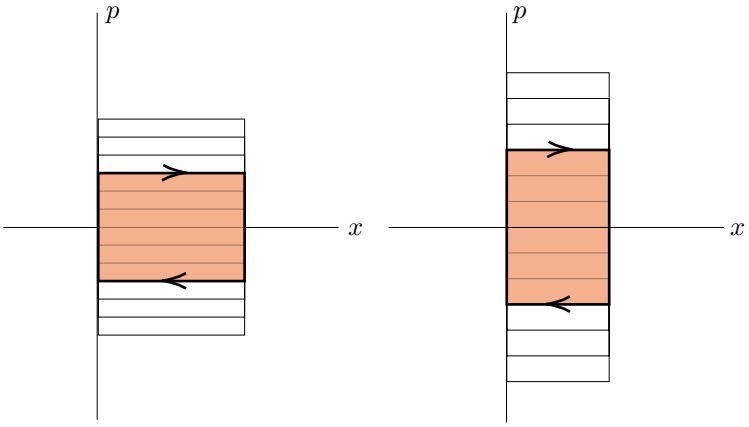

FIGURE 57: *The same idea, as it pertains to slow compression of the 1-dimensional box in which a particle is bouncing back and forth. The former ellipses have become rectangles.*

The point that engaged Ehrenfest's interest is that Planck's quantization procedure, as formulated by Bohr & Sommerfeld, can be expressed

$$\oint p\,dx = nh \quad : \quad n = 1, 2, 3, \ldots$$

—the seeming implication being that it is by *reaching into classical mechanics,*

isolating the adiabatic invariants and rendering them discrete that the $\hbar$-dependent aspects of the world are to be exposed. This idea was taken very seriously for about a decade ... up until the appearance (1925/26) of the work of Heisenberg and Schrödinger.[119]

Speaking now somewhat tentatively... for many-body systems we may plausibly expect "quantized adiabatic phase areas" to go over into "quantized adiabatic hypervolumes." But such hypervolumes we have learned to associate with entropy. Looking in this light back to (195) we see that Planck's discovery has served in effect

- to assign a specific physical value to the previously arbitrary constant h
- to identify entropy with a number that issues from counting (rather than from measuring)
- to conflate two previously distinct meanings of "adiabatic:"

"adiabatic" $\equiv$ "quasi-static" in mechanical usage
$\Updownarrow$
hypervolume-preserving
$\Updownarrow$
entropy-preserving
$\Updownarrow$
"adiabatic" in thermodynamic usage

Carrying this train of thought forward just a little bit ... it follows readily (by $E\ell^2 = (2p\ell)^2/8m$) from (210) that

$E\ell^2$ is an adiabatic invariant of the particle-in-a-box system (211)

Consider now (Figure 58) a thermally isolated N-molecular sample of ideal gas. Quasi-static manipulation of the volume of the gas is (owing to the thermal insulation) a necessarily *isentropic* process ($đQ = TdS = 0 \Rightarrow dS = 0$) so from the 1st law we have $dU = đW = -p\,dV$. Adiabatic compression ($dV < 0$) serves therefore to increase (and expansion to decrease) the value of U. For the gas sample in question $U = N\frac{3}{2}kT$ so that energy increase must show up as a temperature increase. Writing $\ell = V^{\frac{1}{3}}$ we conclude from (211) that

$TV^{\frac{2}{3}}$ is invariant under adiabatic compression/expansion

of the ideal gas sample, and that necessarily

$$S(T,V,N) = N \cdot f(TV^{\frac{2}{3}}) \quad : \quad f(\bullet) \text{ arbitrary}$$

This is structurally consistent with the statement

$$S(T,V,N) = \tfrac{3}{2}Nk\log\left\{\frac{T}{T_0}\left(\frac{V}{V_0}\right)^{\frac{2}{3}}\right\}$$

[119] See §10 and §16 in Max Born, *The Mechanics of the Atom* (1924).

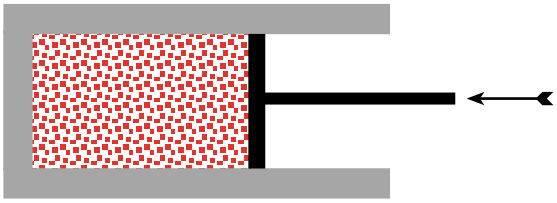

FIGURE 58: *Monomolecular gas in a thermally insulated chamber, being subjected to quasi-static compression.*

quoted at (28), and can in fact be used in conjunction with $\partial S/\partial U = 1/T$ to reproduce that sharper statement: we have

$$\Big(\frac{\partial S}{\partial T}\Big)\cdot\Big(\frac{\partial T}{\partial U}\Big) = Nf'(TV^{\frac{2}{3}})V^{\frac{2}{3}}\cdot\frac{2}{3Nk} = \frac{1}{T}$$

which can be written

$$f'(\xi) = \tfrac{3}{2}k/\xi \quad \text{with} \quad \xi \equiv TV^{\frac{2}{3}}$$

and which upon integration gives

$$f(\xi) - f(\xi_0) = \tfrac{3}{2}k\log\{\xi/\xi_0\}$$

Therefore

$$S(T,V,N) = \tfrac{3}{2}Nk\log\Big\{\frac{TV^{\frac{2}{3}}}{T_0V_0{}^{\frac{2}{3}}}\Big\} + S(T_0,V_0,N)$$

which is the sharp result we sought to establish.

The preceding argument supports the notion that there is—at least in such simple settings—a direct link between the

- classical mechanical and
- thermodynamic

conceptions of adiabatic invariance. But "reaching into classical mechanics and isolating the adiabatic invariants" is much more easily said than done.[120] The only generally feasible procedure appears to be to argue from thermodynamic evidence that $\mathcal{V}_E$ is an adiabatic invariant in the mechanical sense, should therefore be quantized, and that entropy can on this basis be expected to be the logarithm *of an integer*. But we can expect this insight to have observable consequences only at very low temperatures; *i.e.*, only when $\mathcal{V}_E$ is so small that its "pixelated" character has begun to become evident.

[120] Born ends his discussion of the "adiabatic hypothesis" with the observation that "[we are led, then,] to the conclusiuon that our method is, for the time being, only a formal scheme ... enabling us, in certain cases, to replace true quantum principles, which are as yet unknown, by calculations on a classical basis."

17. Concluding remarks. The material reviewed in the present chapter is due mainly to J. Willard Gibbs (1839–1903), though it was anticipated in part by the kinetic theorists (Clausius, Maxwell, and especially Boltzmann) and inspired probing critical commentary and extension by such people as Poincaré and Zermello. Gibbs became active as a thermodynamicist in the 1870's. He published in the Transactions of the Connecticut Academy of Arts & Sciences, to which he contributed a paper on "Graphical methods in the thermodynamics of fluids" in 1873, and shortly thereafter an important 300-page monograph "On the equilibria of heterogeneous substances." He was perfectly aware that Transactions was not likely to be seen in the places that mattered (there were at the time not many alternatives available to American scientists), so was careful to send reprints directly to Maxwell, Boltzmann and other leading figures. His work gained the warm admiration especially of Maxwell (1831–1879), but Maxwell saw only the thermodynamic publications: he did not live to see the birth of statistical mechanics. During the 1880's Gibbs concerned himself with celestial mechanics, the electromagnetic theory of light, the invention (in commonsensical reaction to the "quaternion debate" then raging) of vector analysis. But in 1889/90 he offered to students at Yale a "Short course on the *a priori* deduction of thermodynamics from the theory of probabilities." He worked on the development of statistical mechanics throughout the 1890's, but published almost nothing in the field prior to the appearance—in 1902, just a year before his death—of *Elementary Principles in Statistical Mechanics*, to which he attached the subtitle "The Rational Foundation of Thermodynamics." Gibbs did not live to see the infusion of quantum mechanical ideas into the field he had created.

There is much of value to be learned from the intricate history of this subject. ter Harr[108] provides an excellent introduction to the principal issues. Brush[113] provides a wonderfully detailed account of the thermodynamic and kinetic theoretic work that culminated in the invention of statistical mechanics, but has little to say about statistical mechanics itself, or about the contributions of Gibbs. Paul & (his wife) Tatiana Ehrenfest published in the Encyklopädie der mathematischen Wissenschaften (1912) a profound and influential critique of the work of Boltzmann and Gibbs which is available in English translation as *The Conceptual Foundations of the Statistical Approach in Mechanics* (1959). Readers with a mathematical turn of mind will also take great pleasure from A. I. Khinchin, *Mathematical Foundations of Statistical Mechanics* (1949).