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THE KNOTS OF QUANTUM THERMODYNAMICS

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> *. . . The law that entropy always increases—the second law of thermodynamics—holds, I think, the supreme position among the laws of Nature. If someone points out to you that your pet theory of the universe is in disagreement with Maxwell's equations—then so much the worse for Maxwell's equations. If it is found to be contradicted by observation—well, these experimentalists do bungle things sometimes. But if your theory is found to be against the second law of thermodynamics I can give you no hope; there is nothing for it but to collapse in deepest humiliation. . . .*
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> —SIR ARTHUR EDDINGTON[1]

Several years ago, in the course of intense discussions with one of us concerning research problems of mutual interest, our colleague Wolfgang Yourgrau repeatedly employed the colorful term "knots"—perhaps an allusion to the story of Gordius of Phrygia—to denote challenging fundamental dilemmas in the conceptual fabric of physical theory. The galaxy of foundations problems he investigated during his remarkably productive life included, among many other interests, topics in quantal, statistical, and thermal physics. Issues both old and new which arise in efforts to unify these sciences surely qualify as excellent specimens of Professor Yourgrau's knots in natural philosophy. Hence, to honor his memory, we offer an essay on the knots of quantum thermodynamics. In order to focus mainly upon what Yourgrau used to call "tough science" as opposed to historiographic or metalinguistic analysis, we shall not dwell on the epistemological aspects but proceed immediately to the mathematical foundations of our subject.

1. SOME MATHEMATICAL NOTIONS AND NOTATIONS

To establish a mathematical framework in which to expose conflicts between quantum mechanics and thermodynamics, we begin by stating three postulates of quantum theory. The statements are essentially those given by Margenau and Park.[2]

P.1. Systems. With every physical system there is associated a complex, separable, complete inner product space, a Hilbert space $\mathcal{H}$. The Hilbert space associated with a composite system of two distinguishable systems A,B which are associated with Hilbert spaces $\mathcal{H}_A$, $\mathcal{H}_B$, respectively, is the direct product space $\mathcal{H}_A \otimes \mathcal{H}_B$.

P.2. State Preparations. To every reproducible preparation scheme Π for a physical system there corresponds a nonnegative definite, self-adjoint, unit trace operator ρ on $\mathcal{H}$ which contains all physical predictions regarding data gathered immediately subsequent to that preparation (cf. P.3). The trace class operator ρ, called the density operator or statistical operator, thus represents the state of the quantum system prepared in the manner Π.

P.3. Observables, Measurements, Data, and Ensembles. Some continuous, linear, self-adjoint operators $\{A, B, \dots\}$ on $\mathcal{H}$ correspond to observables of the system. The arithmetic mean value A of the data yielded by measurements of observable A on an ensemble of systems prepared in the manner Π with associated density operator ρ is given by the continuous linear functional of A

$$\langle A \rangle = \mathrm{Tr}(\rho A) \tag{1}$$

All the density operators for the system, referred to in P.2., are elements of $T(\mathcal{H})$, the real Banach space of all self-adjoint trace class operators on $\mathcal{H}$. Within this space $T(\mathcal{H})$ there is a set of nonnegative definite ("positive") operators on $\mathcal{H}$. This set is called the positive cone $V^+(\mathcal{H})$ in $T(\mathcal{H})$. The positive cone $V^+(\mathcal{H})$ is not a subspace of $T(\mathcal{H})$ since a positive operator multiplied by a negative real scalar does not yield a positive operator.

Contained in $V^+(\mathcal{H})$ is a convex set $V_1^+(\mathcal{H})$ of positive operators with unit trace. The elements of this set are the density operators corresponding to all possible preparations of the system.

The extreme elements of $V_1^+(\mathcal{H})$ are called the pure states of the system. The pure state density operators are elementary projectors onto one-dimensional subspaces of $\mathcal{H}$. Thus the pure states correspond to vectors (rays) in $\mathcal{H}$, e.g., an eigenvector or any linear superposition of eigenvectors of observable A corresponds to a pure state. The methods used to determine the density operator associated with a preparation Π will be considered below.

The standard quantum mechanical observables are represented by elements of $B(\mathcal{H})$, the space of all continuous, linear, self-adjoint operators on $\mathcal{H}$. The phraseology of P.3 recognizes not only the fact that not all elements of $B(\mathcal{H})$ correspond to observables (an aspect of superselection rules) but also the converse proposition that there are observable properties of some systems which do not correspond to operators in $B(\mathcal{H})$. Included in the latter category are functions of two or more noncommuting observables[3] and, of particular interest in the present context, such thermodynamic properties as temperature and entropy. The space $B(\mathcal{H})$ is a real Banach space with the operator norm

$$\|A\|_B = \sup_{\|x\|=1} \|Ax\|, \qquad A \in B(\mathcal{H}) \tag{2}$$

The third postulate also emphasizes the conventional interpretation of $\langle A \rangle$ as the arithmetic mean of the results of measurements of A on an ensemble of identically prepared systems. When the link is made between quantum mechanics and certain features of thermodynamics, we shall find it necessary sometimes to reinterpret the linear functional $\mathrm{Tr}(\rho A)$ so that its referent shifts from an ensemble of quantal systems to a single thermodynamic system.

For a complete physical theory, the three postulates already stated must be supplemented by a causal law. In conventional quantum theory there is the standard dynamical postulate which asserts that the time evolution of a system is given by a one-parameter unitary group $\{\Lambda_t\}$ of transformations of $T(\mathcal{H})$ into $T(\mathcal{H})$. However, as we shall soon see, this elegant rule is inadequate to describe all phenomena contemplated when quantum mechanics and thermodynamics are unified.

In the canonical version of quantum statistical thermodynamics, thermal equilibrium states are represented by density operators having the familiar form

$$\hat{\rho} = \frac{\exp(-\beta H)}{\mathrm{Tr}\,\exp(-\beta H)} \tag{3}$$

where H is the energy operator. For any quantum state ρ, the statistical analog for internal energy U is given by

$$U = \mathrm{Tr}(\rho H) \tag{4}$$

and the entropy is expressed as

$$S(\rho) = -k\mathrm{Tr}(\rho \ln \rho) \tag{5}$$

When (5) is maximized subject to constraint (4), the unique result is the canonical state (3), with inverse temperature β uniquely determined by (4).

The quantal version (5) of the famous Gibbsian entropy formula was derived originally by von Neumann[4] using the admittedly obscure notion of semipermeable membranes for different pure quantum states. However, the form of $S(\rho)$ given above can be obtained in other ways[5,6]; and we shall assume, as is customary with students of this subject, that (5) is correct. The recent exhaustive study by Hatsopoulos and Gyftopoulos[7–10] of the foundations of thermodynamics and its relationship to quantum mechanics contains an especially cogent alternative derivation of (5).

The mathematical form of the quantum mechanical entropy gives rise to important consequences for the entropy of composite systems. Consider two interacting systems A and B with associated Hilbert spaces $\mathcal{H}_A$ and $\mathcal{H}_B$. The state of the composite system of two distinguishable systems is assumed to be an operator defined on $\mathcal{H}_A \otimes \mathcal{H}_B$, i.e., $\rho_{AB} \in V_1^+(\mathcal{H}_A \otimes \mathcal{H}_B)$. The entropy calculated from this state is

$$S_{AB} = -k\mathrm{Tr}(\rho_{AB} \ln \rho_{AB}) \tag{6}$$

The reduced density operator for system A is customarily defined by

$$\rho_A = \mathrm{Tr}_B(\rho_{AB}) \tag{7}$$

where Tr_B denotes the trace over $\mathcal{H}_B$. Therefore $\rho_A \in V_1^+(\mathcal{H}_A)$. The entropy calculated from ρ_A is

$$S_A = -k\mathrm{Tr}(\rho_A \ln \rho_A) \tag{8}$$

For system B there are of course expressions for ρ_B and S_B similar to (7) and (8).

The interesting inequality

$$S_{AB} \leq S_A + S_B \tag{9}$$

is referred to as the subadditivity of entropy.[11] The equality holds if and only if

$$\rho_{AB} = \rho_A \otimes \rho_B \tag{10}$$

When this is the case, systems A and B are uncorrelated.

Since the mean value of the observable A for a system described by ρ is given by the linear functional

$$A = \mathrm{Tr}(\rho A) \tag{11}$$

where $\rho \in V_1^+(\mathcal{H})$ and $A \in B(\mathcal{H})$, it is tempting, and indeed some authors[12,13] do this, to consider entropy to be the mean value of the operator $\eta = -k \ln \rho$. However, there are difficulties encountered in making this identification. The operator η is not an element of $B(\mathcal{H})$ for all $\rho \in V_1^+(\mathcal{H})$. To see this, note via (2) that the norm of the operator η is

$$\|\eta\|_B = \sup_{\|x\|=1} \|\eta x\| = \sup_{\|x\|=1} \|-k \ln \rho x\| \tag{12}$$

Consider the case where ρ is pure, i.e., ρ is an extreme element of the convex set $V_1^+(\mathcal{H})$. Then there exists an eigenvector $x_0 \in \mathcal{H}$, $\|x_0\| = 1$ with eigenvalue $\alpha = 0$. The norm of the vector ηx_0 is unbounded:

$$\|\eta x_0\| = \langle \eta x_0, \eta x_0 \rangle^{1/2} = [k^2(\ln \alpha)^2]^{1/2} \rightarrow \infty \qquad \text{as } \alpha \rightarrow 0 \tag{13}$$

Nevertheless the entropy is well defined for the state $\rho_0 = |x_0\rangle\langle x_0|$ in the sense that

$$\lim_{\alpha \rightarrow 0} (-k\alpha \ln \alpha) \rightarrow 0 \tag{14}$$

Hence η, being unbounded, is not an element of $B(\mathcal{H})$ and does not qualify under P.3 as a quantal observable. Therefore entropy cannot rigorously be interpreted as the average value of a quantal observable.

A second peculiarity of the entropy functional involves its time evolution. In conventional quantum mechanics the time evolution is governed by a one-parameter unitary group of transformations on $T(\mathcal{H})$, a typical group element of which will be denoted by U_t. Through the correspondence $\sigma \rightarrow \mathrm{Tr}(\sigma A)$ we identify $B(\mathcal{H})$ with the dual of $T(\mathcal{H})$. Through this duality the transformation U_t induces a dual transformation U_t^* on $B(\mathcal{H})$. The state $\rho_t \in T(\mathcal{H})$ is related to the state $\rho_{t+s} \in T(\mathcal{H})$ by

$$\rho_{t+s} = U_s \rho_t \tag{15}$$

The average value of an observable $A \in B(\mathcal{H})$ at time $t + s$ is given by

$$\langle A \rangle_{t+s} = \mathrm{Tr}(\rho_{t+s}A) = \mathrm{Tr}(U_s\rho_t A) \tag{16}$$

This gives the time evolution of the average value in the so-called Schrödinger picture; i.e., the states change in time and the operators, unless explicit functions of time, remain fixed. The duality between $T(\mathcal{H})$ and $B(\mathcal{H})$ provides the time evolution of the average value in the Heisenberg picture; i.e.,

$$\langle A \rangle_{t+s} = \mathrm{Tr}(U_s\rho_t A) = \mathrm{Tr}(\rho_t U_s^* A) \tag{17}$$

All of this is standard and well known.

The problem with the entropy functional is that in the Schrödinger picture the state ρ depends on time but in the Heisenberg picture ρ is independent of time. Therefore the rate of change of the entropy is identically zero in the Heisenberg picture. When the time evolution is given by a unitary group, as in conventional quantum mechanics, no inconsistency arises since the entropy functional is invariant under unitary transformation, i.e.,

$$S(\rho_{t+s}) = S(\rho_t) \qquad \text{when } \rho_{t+s} = U_s\rho_t \tag{18}$$

So $dS(\rho)/dt \equiv 0$ in the Schrödinger picture also.

The reason for this invariance is that the value of $S(\rho)$ depends on the eigenvalues of ρ, which are invariant under unitary transformation. Thus we arrive at the long known but insufficiently appreciated result that *the unitary time evolution of conventional quantum mechanics is incapable of predicting a change in entropy*. This proposition leads immediately to one of the most disconcerting knots in physics.

2. THE SECOND LAW KNOT

The temporal invariance of $S(\rho)$ under unitary evolution places mechanics and thermodynamics in a logical confrontation rather like the celebrated incompatibility of Galilean-Newtonian mechanics and Maxwellian electrodynamics from which emerged the theory of relativity. In particular, if the Second Law of Thermodynamics is to be retained as a basic principle of physics, then either quantum mechanics or statistical thermodynamics or both must be modified.

The Second Law mathematically characterizes thermal equilibrium in a closed system as the state which maximizes $S(\rho)$ subject to subsidiary constraints. It is generally understood also to entail that spontaneous processes of evolution toward thermal equilibrium do in fact occur, and that for closed systems the entropy never decreases.

Now, if the Second Law stands in conflict with quantum mechanics, might we reasonably consider abandonment of that law as a fundamental axiom of physics? We think not; indeed we shall proceed on the premise that the Second Law, like the great conservation laws, deserves a rather sacrosanct position in the hierarchy of physical principles. Our introductory quotation from the writings of A. S. Eddington forcefully conveys this viewpoint, but of course we cannot claim that Sir Arthur would have espoused any of the unorthodoxies advocated in the present essay.

Unitary quantum dynamics cannot be saved by denying the existence of motions in which closed systems gain entropy unless we are willing to deny the most elementary triumphs of the Second Law. Consider for example a composite system whose constituents A and B are initially uncorrelated, noninteracting, and separately in thermal equilibrium with distinct inverse temperatures, β_A, β_B. The total initial density operator is then

$$\rho_0 = \hat{\rho}_A \otimes \hat{\rho}_B \tag{19}$$

where $\hat{\rho}_A$, $\hat{\rho}_B$ are each of the canonical form (3). If internal constraints are lifted, interaction occurs, and eventually the composite system evolves to a unique state of mutual equilibrium, viz.,

$$\rho_\infty = \hat{\rho}_{AB} \tag{20}$$

where $\hat{\rho}_{AB}$ has the canonical form (3) with one final inverse temperature β_{AB}. This familiar model, which might refer to an experience as commonplace as equilibration following submergence of a piece of warm lead in a cup of cool water, is of course consonant with the Second Law since $S(\rho_\infty)$ is the maximum value the entropy functional can attain under the given circumstances. However, in general we also find in this situation that $S(\rho_\infty) > S(\rho_0)$, so that the motion $\rho_0 \to \rho_\infty$ cannot be understood within the framework of unitary mappings provided by conventional quantum theory. In other words, no conceivable Hamiltonian can generate the motion which in fact occurs as the lead cools and the water warms.

Throughout the past century the literature of physics has offered a variety of rationalizations for this paradox, so that some physicists when exposed to the problem viscerally reject it as heresy. Many others adhere to one or more of the standard explanations briefly described and criticized below; the literature citations given in each case exemplify a school of thought but are not exhaustive.

(a) *The Second Law and the entropy concept are subjective or "anthropomorphic," the entropy increase representing essentially the growing obsolescence of past knowledge rather than an objective dynamical process.*[14–17]

Despite our genuine appreciation of the methodology of information theory, we believe nevertheless that the thermodynamic entropy of a closed system rises independently of the informational state of the observer.

(b) *Thermodynamically closed systems are mechanically open in some sense and are therefore mechanical subsystems for which $S(\rho)$ is not invariant.*[18–22]

This alleged openness of thermodynamically isolated systems has been associated with various causes, including quantal uncertainties at the boundary, random external fields, and even cosmological asymmetries. In our opinion, all of these ideas share the same flaw, viz., that in any bounded mechanical system obeying a unitary law of motion the total entropy is invariant and, since the overall motion is quasiperiodic,[23] the entropy of a subsystem calculated using (7) and (8) will also be quasiperiodic and hence exhibit no Second-Law unidirectionality.

Consider for example a system A with surroundings B, prepared initially in an uncorrelated pure state

$$\rho_{AB}(0) = |\psi_A\rangle\langle\psi_A| \otimes |\psi_B\rangle\langle\psi_B| \tag{21}$$

When (21) is substituted into (6), (7), and (8), we find that

$$S_{AB}(0) = S_A(0) = S_B(0) = 0 \tag{22}$$

However, as the composite system A plus B evolves unitarily, S_{AB} remains invariant; but both S_A and S_B may increase as interactions breed correlations between A and B. This peculiar result is of course consistent with the subadditivity property (9).

Superficially, mechanical subsystem A seems to be undergoing a process of the kind contemplated by the Second Law. Unfortunately this is merely an illusion, for the motion of A plus B is ultimately periodic, so that eventually S_A and S_B decrease again to zero. Thus the Second-Law behavior of A is only temporary, and highly dependent upon the choice of an initial condition like (22) which captures S_A during an ascent phase.

(c) Irreversible phenomena should be treated by invoking special limit procedures or redefinitions of S, but without altering conventional unitary quantum dynamics.[24–27]

Included in this broad category are theories based on such notions as coarse-graining or the thermodynamic limit and the abstract theories of ergodicity and mixing, incisive analyses of which could easily fill a book. However, we do wish to record in particular our skepticism toward demonstrations that entropy may increase indefinitely but only in infinite-volume, infinite-population assemblies. Even if rigorously correct, such propositions can hardly be germane to the physical problem, since realistic systems in which entropy is observed to increase are in fact finite.

(d) Even though the Second Law is not a universal theorem of mechanics, nevertheless we tend to observe only entropy-increasing situations because by our very nature we encounter or create only systems with highly improbable initial conditions.[28,29]

A particularly dramatic statement of this view was given by Landé[30]:

> In ordinary life and in thermodynamics we deal with finite systems which deliberately are brought into a state of high entropy by branching them off from the rest of the universe. Here we have indeed, at least for a limited time span, a parallelism of time and entropy—which does not prove any such parallelism in general, ... We happen to live in a very improbable state of the world which develops into a more probable state. But if ours were not a very improbable world, there would not be any "we" to speculate about it.

This approach incorporates features of both (a) and (b), as well as a philosophical perspective which, though intriguing, is scientifically infertile, since it confers upon the Second Law knot a rather dogmatic mantle of inevitability. We prefer to believe that the knot will eventually be untied by the development of a more comprehensive dynamics in which entropy-increasing processes occur as natural motions. The question of man's relation to the universe would play no role in such a theory.

(e) *The entropy of thermodynamic systems rises due to repeated measurements, each followed by a discontinuous state change in accordance with the projection postulate of quantum mechanics.*[20,28]

This idea, a variant of (b) in which the randomizing environment is imagined in some sense to perform measurements, is based upon a popular but discredited quantum theory of measurement in which wave packet reduction is a key concept.

It was first shown by von Neumann[4] that the entropy of a system cannot decrease under the projection postulate transformation, and thereafter various authors have attempted to explain irreversibility using the projection postulate. While it is true that the entropy can increase and the energy can be conserved under the projection postulate transformation, it is not true that the transformation drives the system to the canonical state.

According to the projection postulate, an energy measurement results in the transformation of the density operator,

$$\rho \to \rho' = \sum_n P_n \rho P_n \tag{23}$$

where P_n is the projection operator onto the eigenspace corresponding to energy eigenvalue E_n. If the energy spectrum is nondegenerate, the elementary projectors are

$$P_n = |n\rangle\langle n| \tag{24}$$

where $H|n\rangle = E_n|n\rangle$.

The energy is conserved under this transformation if

$$U \equiv \mathrm{Tr}(\rho H) = \mathrm{Tr}\left(\sum_n P_n \rho P_n H\right) \tag{25}$$

To show that (25) holds, we note that $[P_n, H] = 0$ so that

$$\mathrm{Tr}\left(\sum_n P_n \rho H P_n\right) = \mathrm{Tr}\left(\sum_n P_n^2 \rho H\right) = \mathrm{Tr}(\rho H) = U \tag{26}$$

The matrix for ρ' is diagonal in the energy representation and its diagonal elements are the same as those of ρ, i.e.,

$$\langle m|\rho'|l\rangle = \langle m\left|\left(\sum_n \left(\left|n\rangle\langle n\right|\rho\left|n\rangle\langle n\right|\right)\right|l\right\rangle = \langle m|\rho|m\rangle\delta_{ml} \tag{27}$$

It is possible to change the diagonal elements of ρ' if another observable A is measured which does not commute with H, but then energy would not be conserved in general.

Let $\overline{P}_n$ be the projector onto the subspace associated with the eigenvalue a_n of A, $[A,H] \neq 0$,

$$\overline{P}_n = |a_n\rangle\langle a_n| \tag{28}$$

where $A|a_n\rangle = a_n|a_n\rangle$. The projection postulate transformation is

$$\rho' \rightarrow \rho'' = \sum_n \overline{P}_n \rho' \overline{P}_n \tag{29}$$

The energy in the state ρ'' is

$$U'' = \mathrm{Tr}(\rho'' H) = \mathrm{Tr}\left(\sum_n \overline{P}_n \rho' \overline{P}_n H\right) \tag{30}$$

In general $U'' \neq U$.

In the approach to equilibrium of a closed thermodynamic system, the energy is conserved as the entropy increases. The projection postulate can lead to a stationary state with the energy conserved, but unless the diagonal elements of the initial state happen to be already those of the final maximum-entropy canonical state, the projected state will not be canonical. Therefore this theory cannot explain the general validity of the Second Law of thermodynamics.

Having rejected all of the foregoing attempts to reconcile the contradiction between the Second Law and the invariance of $S(\rho)$ under unitary evolution, we now explore an alternative interpretation of that dilemma. Rather than clinging to the tradition of Hamiltonian mechanics from which the unitary dynamical postulate of orthodox quantum theory evolved, let us suppose the latter is simply incomplete. It must therefore be replaced with a new principle of motion encompassing not only the familiar unitary evolutions of conventional quantum theory but also the nonunitary evolutions required to describe thermodynamical processes.

This possibility has been suggested by several authors,[31–34] but the most persuasive arguments are to be found in the work of Hatsopoulos and Gyftopoulos,[7–10] who argue quite conclusively that some as yet unknown, nonunitary principle of quantal motion must be devised in order to achieve a satisfactory unification of thermodynamics and quantum mechanics into one uncontradictory science.

Motivated either by these thermodynamic considerations or by the desire to obtain phenomenological descriptions of the evolution of subsystems, various authors[18,19,35–38] have considered mathematical generalizations of quantum dynamics in which the laws of motion do not conserve S. These efforts have generally featured nonunitary mappings which are elements of linear semigroups, thus assuring the applicability of a substantial body of standard mathematical structures. This approach has yielded several interesting contributions to the quantum dynamics of subsystems, where entropy may rise or fall but energy need not be conserved. Moreover, Band and Park[32–34] found that for 2-level quantum systems there exist linear maps—independent of the initial density operator—which describe energy-conserving, entropy-increasing processes. The latter would be an essential feature of a unified theory of quantum thermodynamics.

Unfortunately, the present authors[39] have discovered that for N-level systems with $N > 2$, there are no linear maps describing energy-conserving, entropy-increasing motion. Consequently the search for a new principle of motion can expect no assistance from the mathematical theory of linear semigroups.

Although the correct equation of motion for ρ is not known at this point, we can give a list of necessary conditions that such an equation must satisfy. Consider a closed system with energy operator H and density operator ρ. Let $\rho(s)$ be related to $\rho(s + t)$ by a nonlinear mapping Γ_t,

$$\rho(s + t) = \Gamma_t\rho(s) \tag{31}$$

It is desirable to assume Γ_t is an element of a one-parameter semigroup G of nonlinear transformations. The usual semigroup property

$$\Gamma_s \circ \Gamma_t = \Gamma_{s+t} \in G \tag{32}$$

is required if it is assumed that time is homogeneous. Then any time s can be taken as the initial time $s = 0$, so that (31) becomes

$$\rho(t) = \Gamma_t\rho(0) \tag{33}$$

Being nonlinear, this transformation cannot be written in matrix form, but it is still mathematically possible[40] to obtain an equation of motion for $\rho(t)$ in terms of a nonlinear infinitesimal generator F of the semigroup:

$$\frac{d\rho(t)}{dt} = F\rho(t) \tag{34}$$

The conditions to be satisfied by the generalized evolution are that it (i) maintain positivity, (ii) maintain self-adjointness, (iii) preserve the trace,

$$\frac{d}{dt}[\mathrm{Tr}(\rho)] = \mathrm{Tr}\left(\frac{d\rho}{dt}\right) = \mathrm{Tr}(F\rho) = 0 \tag{35}$$

(iv) conserve the energy,

$$\frac{dU}{dt} = \mathrm{Tr}\left(\frac{d\rho}{dt}H\right) = \mathrm{Tr}(F\rho H) = 0 \tag{36}$$

and (v) increase the entropy,

$$\frac{dS}{dt} = -k\mathrm{Tr}\left(\frac{d\rho}{dt}\ln\rho\right) = -k\mathrm{Tr}(F\rho\ln\rho) \geq 0 \tag{37}$$

with equality if and only if $\rho = \hat{\rho}$, the canonical state.

These five conditions are not independent; (ii), (iii), and (v) together imply (i). To see that this is plausible, note that the entropy functional (5) may be expressed in terms of the eigenvalues $\{r_i\}$ of ρ as

$$S(\rho) = -k \sum_i r_i \ln r_i \tag{38}$$

a nonnegative definite form for all density operators, i.e., for each $\rho \in V_1^+(\mathcal{H})$. Moreover, for a self-adjoint, unit trace $\rho \notin V_1^+(\mathcal{H})$, at least one r_i would be negative and (38) would then be complex. Thus if an equation of motion satisfies (ii), (iii), and (v) for all t and the initial state $\rho(t_0)$ is an element of $V_1^+(\mathcal{H})$, then $\rho(t) \in V_1^+(\mathcal{H})$ for all t; i.e., condition (i) is automatically fulfilled. Of course, there are positive evolutions for which (37) is not satisfied so (i), (ii), and (iii) together do not imply (v).

The equation of motion

$$\frac{d\rho}{dt} = -i[H,\rho] + \frac{1}{\lambda}(\hat{\rho} - \rho) \tag{39}$$

with $\lambda > 0$ provides an example satisfying all conditions. In (39) $\hat{\rho}$, the canonical state, is determined uniquely by

$$\mathrm{Tr}(\hat{\rho}H) = \mathrm{Tr}(\rho H) \tag{40}$$

It is easy to show that (39) satisfies conditions (ii) and (iii) and (40) can be used to show that (iv) is satisfied. That (39) satisfies (v) is a bit more difficult to show, but once this is established we know from the preceding discussion that (i) is satisfied.

Substituting (39) into (37) gives

$$\begin{aligned} -k\mathrm{Tr}\left(\frac{d\rho}{dt}\ln\rho\right) &= -k\mathrm{Tr}(-i[H,\rho]\ln\rho) \\ &\quad + \frac{-k}{\lambda}\mathrm{Tr}[(\hat{\rho} - \rho)\ln\rho] \geq 0 \end{aligned} \tag{41}$$

Since the trace is invariant under cyclic permutations and since $[\ln\rho,\rho] = 0$, the first term on the right-hand side of the equality vanishes. Since $k, \lambda > 0$, the second term will be greater than zero if

$$[-\mathrm{Tr}(\rho\ln\rho)] - [-\mathrm{Tr}(\hat{\rho}\ln\rho)] \leq 0 \tag{42}$$

To show that (42) holds, we recall that for all ρ satisfying (40),

$$-\mathrm{Tr}(\hat{\rho}\ln\hat{\rho}) \geq -\mathrm{Tr}(\rho\ln\rho) \tag{43}$$

with equality if and only if $\rho = \hat{\rho}$. It follows that

$$[-\mathrm{Tr}(\rho\ln\rho)] - [-\mathrm{Tr}(\hat{\rho}\ln\rho)] \leq [-\mathrm{Tr}(\hat{\rho}\ln\hat{\rho})] - [-\mathrm{Tr}(\hat{\rho}\ln\rho)] \tag{44}$$

Using Klein's inequality in the form

$$[-\mathrm{Tr}(\sigma\ln\sigma)] - [-\mathrm{Tr}(\sigma\ln\sigma')] \leq 0 \tag{45}$$

for $\sigma, \sigma' \in V_1^+(\mathcal{H})$, with $\sigma = \hat{\rho}$ and $\sigma' = \rho$ we obtain from (44)

$$[-\mathrm{Tr}(\rho \ln \rho)] - [-\mathrm{Tr}(\hat{\rho} \ln \rho)] \leq 0 \tag{46}$$

which is precisely (42) and therefore (v) is satisfied by (39).

Although there is no physical justification for the specific equation of motion (39), it does have some attractive properties. We can express (39) in terms of the infinitesimal generator F of a semigroup of nonlinear transformations,

$$\frac{d\rho}{dt} = -i[H,\rho] + \frac{1}{\lambda}[\hat{\rho}(\rho) - \rho] = F\rho \tag{47}$$

The equivalence relation in $V_1^+(\mathcal{H})$ which partitions $V_1^+(\mathcal{H})$ into equivalence classes $[\rho U]$ of states ρ with the same energy U induces a partitioning of the semigroup G. The generator F depends on the state of the system through (40). Since F thus depends on the energy of the system there is a unique generator F for each equivalence class $[\rho U]$.

An equation of the form (47) would be applicable not only to closed systems but would also be useful for describing at least approximately an open thermodynamic system exchanging energy with some other system, in which case F would have an implicit dependence on time through $U(t)$. If the energy of the system changes slowly with respect to the characteristic relaxation time λ of the system, then the system would be very nearly in a canonical state at all times, fulfilling the classic definition of a reversible quasistatic process. The dependence of F on U is therefore desirable since it allows one to account, within the framework provided by the equation of motion, for the rapid or slow removal of constraints on the system.

All of this detail regarding possible generalized evolutions is of course conjectural; the correct principle of motion with sufficient structure to complete the theory of quantum thermodynamics and thereby to untie the Second Law knot remains to be discovered.

3. Knots in the State Concept

For a quantum mechanical system the state corresponds to a density operator $\rho \in V_1^+(\mathcal{H})$. For every reproducible preparation Π of the system there is a density operator ρ. The state of a system at any time t can be obtained by measuring the average values at time t of a quorum[41,42] of observables for the system. However, it would not be necessary to measure the average values of a quorum if one knew the state, ρ_{AB}, of the composite system consisting of system A plus preparation device B, since the state ρ_A could then be obtained from the composite state ρ_{AB} using (7).

To apply this in practice would require information about the interactions between the preparation device and the system and the states $\rho_A(0)$, $\rho_B(0)$ when A and B are initially brought together. If A and B are initially uncorrelated and the evolution of the composite system is given by the mapping Γ_t, then the state of A at time t is

$$\rho_A(t) = \mathrm{Tr}_B[\Gamma_t \rho_A(0) \otimes \rho_B(0)] \tag{48}$$

The concept of measuring a quorum of observables was introduced to avoid the above assumption and therefore circumvent the problem of knowing the entire history of the system of interest. However, the definition of the state of A as a partial trace is useful if one agrees never to ask questions concerning the *joint* observables defined on $\mathcal{H}_A \otimes \mathcal{H}_B$. The average values of joint observables depend on correlations between A and B and this information is lost in the operation of taking the partial trace.

Conventional quantum mechanics requires only that a preparation Π be reproducible to have associated with it a state ρ_A of the prepared system. For quantum thermodynamics, however, it was discovered recently that an additional restriction must be placed on the preparation. Hatsopoulos and Gyftopoulos[7–10] were the first authors to point out the need for a distinction between two types of reproducible preparations, referred to as ambiguous and unambiguous. The original definitions of these new concepts are expressed in terms of time correlations of average values. Instead of quoting those definitions, we may readily illustrate this newest quantal knot by contrasting two reproducible preparations which are both acceptable in ordinary quantum mechanics but only one of which is acceptable in quantum thermodynamics.

We consider in particular preparations $\{\Pi_i | i = 1,2, \ldots\}$ each of which when repeated generates an ensemble characterized by canonical density operator

$$\hat{\rho}_i = \frac{\exp(-\beta_i H)}{\mathrm{Tr}[\exp(-\beta_i H)]} \tag{49}$$

where β_i is determined by the mean energy U_i through

$$U_i = \mathrm{Tr}(\hat{\rho}_i H) \tag{50}$$

Since $\hat{\rho}_i$ is the thermodynamic equilibrium state, the corresponding preparation scheme Π_i may essentially entail waiting until the closed system with internal energy U_i spontaneously attains stable thermal equilibrium. An alternate procedure would be to couple the system to a thermostat with temperature $T_i = 1/k\beta_i$ until mutual equilibrium is achieved, then isolate the system.

Consider next a preparation Π_0 which combines Π_1 and Π_2 by some operational rule. For example, if the flip of a coin results in heads, a system is generated by Π_1 and if tails results, a system is prepared in the manner Π_2. We choose Π_1 and Π_2 such that the mean energy associated with Π_0 is

$$U_0 = \tfrac{1}{2}U_1 + \tfrac{1}{2}U_2 \tag{51}$$

but $\hat{\rho}_0 \neq \hat{\rho}_2$ so that $\beta_1 \neq \beta_2$.

Let the preparation Π_3 be such that

$$U_3 \equiv \mathrm{Tr}(\hat{\rho}_3 H) = U_0 \tag{52}$$

In general $\beta_3 \neq \beta_1$, $\beta_3 \neq \beta_2$.

The preparation Π_0 is ambiguous where Π_3 is unambiguous. If some thermodynamic property, e.g., temperature or adiabatic availability, is measured on systems prepared by Π_0 one will find two results, sometimes T_1, sometimes T_2 for the temperature. Any system prepared by Π_3 will, upon measurement, yield the temperature T_3. On the other hand, if the quantum mechanical energy observable H is measured on systems prepared by Π_0 and by Π_3 no distinction is possible since the result of each measurement is an eigenvalue of H and the arithmetic means of these results are the same for Π_0 and Π_3.

This distinction between ambiguous and unambiguous preparations is an attempt to illustrate the difference between quantum observables and thermodynamic properties. There are measurable properties of systems, such as temperature and entropy, which are not the mean values of some quantum mechanical operators. This difference is present even in Gibbs' original approach where the temperature is related to the modulus of the distribution and is not the average value of a function of phase.

The temperature of a single thermodynamic system is, however, related to the average value of a quantum mechanical operator H. In conventional quantum mechanics the average value of H refers to the arithmetic mean of the results of measurements of H on an ensemble of identically prepared systems. In quantum statistical thermodynamics, $\mathrm{Tr}(\rho H)$ is interpreted as the internal energy of a single system prepared in the manner Π with the associated density operator ρ. An ensemble is necessary to determine the ρ associated with preparation Π, but once ρ is known it applies to *each* system prepared by Π as far as *thermodynamic* properties are concerned. The density operator ρ will predict with certainty the entropy of a single system prepared in the manner Π, but it cannot predict with certainty the result of a measurement of the quantum mechanical energy of a single system prepared in the manner Π. It is this difference in the predictive power of ρ which necessitates the distinction between ambiguous and unambiguous preparations. Systems prepared by an unambiguous preparation all share the same values for thermodynamic quantities; thus, such an ensemble is thermodynamically "homogeneous" even though its density operator may have the form traditionally associated with inhomogeneous quantal ensembles (mixtures).

Requiring that preparations be unambiguous has important implications concerning the interpretation of the canonical state. Consider an ensemble of identical N-level systems prepared by the ambiguous preparation Π_m. We take Π_m such that each system in the ensemble is prepared in an energy eigenstate associated with energy eigenvalue E_i and such that the relative frequency of occurrence p_i of systems in state E_i is

$$p_i = \frac{\exp(-\beta E_i)}{\mathrm{Tr}[\exp(-\beta H)]} \tag{53}$$

The density operator representing the preparation Π_m is the incoherent mixture

$$\check{\rho} = \frac{\sum_{i=1}^{N} \exp(-\beta E_i)\,|E_i\rangle\langle E_i|}{\sum_{i=1}^{N} \exp(-\beta E_i)} = \frac{\exp(-\beta H)}{\mathrm{Tr}[\exp(-\beta H)]} \tag{54}$$

Now consider a second ensemble prepared by an unambiguous preparation $\mathbf{\Pi}_c$ of the kind described under (50) which prepares identical N-level systems in the canonical equilibrium state

$$\hat{\rho} = \frac{\exp(-\beta H)}{\operatorname{Tr}[\exp(-\beta H)]} \tag{55}$$

By construction, any system from the ensemble prepared by $\mathbf{\Pi}_m$ has come from an identifiable pure subensemble and hence the entropy is zero for each system. On the other hand, any system taken from the ensemble prepared by $\mathbf{\Pi}_c$ is in thermal equilibrium with nonzero entropy.

The two density operators $\check{\rho}$ and $\hat{\rho}$ have the same form, but the interpretation of each is fundamentally different. Requiring all preparations in quantum thermodynamics to be unambiguous eliminates preparations of the type $\mathbf{\Pi}_m$. The state of a system prepared in thermodynamic equilibrium is not some unknown energy eigenstate but is simply the entire mixture $\hat{\rho}$, the canonical state. By the state of a system we mean all the information concerning the average values of all observable properties of the system at the present time and all the information necessary to predict the average values in the future. Since $\check{\rho}$ applies only to the ensemble it cannot be used to predict the thermodynamic behavior of one system taken from the ensemble.

Another important consequence resulting from the elimination of preparations $\mathbf{\Pi}_m$ from the theory of quantum thermodynamics is that the popular use of transition probabilities to describe the approach to equilibrium is fallacious. A transition probability is a concept taken from perturbation theory and gives the total probability that a system in one energy eigenstate of the unperturbed Hamiltonian will make a transition to another energy eigenstate. The transition is induced or caused by the perturbation. If the system is not in an energy eigenstate, as is the case when the state is $\hat{\rho}$, then there are no transition probabilities defined.

An example of the use of transition probabilities in describing the approach to equilibrium is found in the theory of paramagnetic relaxation. It is imagined that there is some number N_+ of the spin systems in the eigenstate spin up (magnetic moment parallel to the applied field) and some number $N - N_+ = N_-$ in the eigenstate spin down. The interaction of the spins with the lattice is treated as a perturbation. An equation for the rate of change of N_+ is then written as

$$\frac{dN_+}{dt} = W(- \rightarrow +)N_- - W(+ \rightarrow -)N_+ \tag{56}$$

where $W(- \rightarrow +)$ is the probability of a transition from spin down to spin up, $W(+ \rightarrow -)$ is the probability of a transition from spin up to spin down. If V_{SL} is the perturbation Hamiltonian describing the spin-lattice interaction, then to first order,

$$W(- \rightarrow +) = W(+ \rightarrow -) \propto |\langle \mathrm{up} | V_{\mathrm{SL}} | \mathrm{down} \rangle|^2 \tag{57}$$

The rate equation above predicts the equilibrium numbers,

$$N_+ = N_- = N/2 \tag{58}$$

If the sample is at some finite temperature T, then $N_+ \neq N/2$ and the rate equation fails in its prediction. We attribute this failure to the fact that each spin system in the sample is not in some energy eigenstate but is in a mixed state.

If N_+ is interpreted as N times the average value of the projection operator onto the eigenspace of spin up, then the rate equation applies to the entire ensemble as if it were a single system, i.e., as if a single system were prepared by some unambiguous preparation. In this case the transition probabilities are not defined since the system is not in some unknown energy eigenstate.

We therefore conclude that the use of rate equations to describe relaxation to equilibrium cannot provide a fundamental understanding of the process. The fallacious character of the approach becomes clear when we realize it is necessary to reinterpret $W(- \rightarrow +)$ and $W(+ \rightarrow -)$ in order to predict the correct equilibrium state. It is customarily *assumed* that these probabilities are related by a Boltzmann factor,

$$\frac{W(- \rightarrow +)}{W(+ \rightarrow -)} = \exp(2\beta\epsilon) \tag{59}$$

where $\beta = 1/kT$ and ϵ is given by $H|\mathrm{up}\rangle = -\epsilon|\mathrm{up}\rangle$. This assumption is of course without justification and is in fact not compatible with the condition

$$W(+ \rightarrow -) = W(- \rightarrow +) \propto |\langle \mathrm{up}|V_{\mathrm{SL}}|\mathrm{down}\rangle|^2 \tag{60}$$

4. KNOTS ASSOCIATED WITH ZEROTH AND FIRST LAWS

The traditional aim of quantum statistical thermodynamics has been to account for the behavior of thermodynamic systems in terms of the laws of quantum mechanics; yet even the Zeroth and First Laws of thermodynamics when interpreted mechanically give rise to troublesome knots.

To demonstrate this we will briefly discuss an application of thermodynamics, i.e., a question to which thermodynamics is capable of yielding an answer, and then show the approximations necessary in mechanics to yield the same answer.

One of the fundamental problems of thermodynamics is to predict from the initial conditions the final conditions of two interacting systems. For example, if a piece of warm lead is placed in a cup of cool water, we may inquire as to the final (equilibrium) temperatures of the lead and the water. To solve the problem we rely on the Zeroth and First Laws of thermodynamics. The Zeroth Law states that two systems in equilibrium have equal temperatures, and furthermore that a third system at the same temperature is in equilibrium with the first two systems. Therefore in our example the final state is attained when the temperature of the lead is the same as the temperature of the water. We could also argue that the final equality of temperatures is a consequence of the Second Law since the total entropy of the two systems is maximum when the temperatures are equal.

The value of this final, common temperature can be predicted using the First Law, which states that the total energy of the composite system lead plus water is constant. The energy lost by the lead is gained by the water. If the energy of each as a function of temperature is known, it is then easy to calculate the final, common temperature. In order to verify that the final temperatures are indeed equal, one must separate the two systems, i.e., terminate the interaction. It is routinely assumed in thermodynamics that separating the systems affects neither the energies nor the temperatures of the two systems. Moreover, as commonly applied to composite systems, the First Law is a statement concerning the sum of the private energies and as such does not include the interaction energy. As is the case with the energy, in equilibrium the entropy is also regarded as an extensive thermodynamic quantity; thus the total entropy of the composite system is the sum of the private entropies of the constituent subsystems.

Now let us analyze the same type of problem—two systems interacting—with quantum statistical thermodynamics. Take two systems A and B with associated Hilbert spaces $\mathcal{H}_A$ and $\mathcal{H}_B$, respectively. The energy operator H and density operator ρ_{AB} for the composite system are defined on the tensor product space $\mathcal{H}_A \otimes \mathcal{H}_B$. The initial state is assumed to have the uncorrelated form

$$\rho_{AB}(0) = \rho_A(0) \otimes \rho_B(0) \tag{61}$$

We can, as discussed earlier, define the state of, say, system A at any time t as the reduced density operator ρ_A obtained by taking the trace over $\mathcal{H}_B$ of ρ_{AB}. In some cases H can be written as a sum of private energies plus an interaction term,

$$\begin{aligned} H &= H_A \otimes I_B + I_A \otimes H_B + V_{AB} \\ &= H_A + H_B + V_{AB} \end{aligned} \tag{62}$$

(The second equality gives the standard abbreviated form where identities and $\otimes$ symbols are suppressed.) Under these circumstances, we may define the private energy of A as

$$U_A(t) = \mathrm{Tr}[\rho_{AB}(H_A \otimes I_B)] = \mathrm{Tr}_A(\rho_A H_A) \tag{63}$$

Quantum statistical thermodynamics predicts that the equilibrium state $\hat{\rho}_{AB}$ for the composite system is the canonical state

$$\hat{\rho}_{AB} = \frac{\exp[-\beta(H_A + H_B + V_{AB})]}{\mathrm{Tr}\{\exp[-\beta(H_A + H_B + V_{AB})]\}} \tag{64}$$

with $\mathrm{Tr}(\hat{\rho}_{AB}H) = \mathrm{Tr}\{(\rho_A(0) \otimes \rho_B(0)H\}$.

The density operator $\hat{\rho}_{AB}$ cannot in general be factored into the tensor product of two canonical states. Further, we cannot at this point logically claim that the two systems A and B are at the same temperature because there is only a *single* (composite) system; but if the interaction energy is neglected compared to the private energies of the two systems A and B then the canonical operator can be factored into the tensor product of two canonical density operators with the same temperature parameter:

$$\hat{\rho}_{AB} = \frac{\exp(-\beta H_A)}{\mathrm{Tr}[\exp(-\beta H_A)]} \otimes \frac{\exp(-\beta H_B)}{\mathrm{Tr}[\exp(-\beta H_B)]} \equiv \hat{\rho}_A \otimes \hat{\rho}_B \tag{65}$$

Two independent systems can now be identified and the temperatures are indeed equal. Nevertheless, the statement of the equality of temperatures in equilibrium is only approximately true inasmuch as two temperatures can be defined and compared only if the interaction is neglected.

The First Law of Thermodynamics, viewed as conservation of the sum of private energies, is also an approximation. In thermodynamics, the entropy is maximized subject to the constraint that $U_A + U_B = \text{const}$. In quantum statistical mechanics the constraint is that the total energy is constant, i.e., $U_A + U_B + \langle V_{AB} \rangle \equiv \text{const}$. If $\langle V_{AB} \rangle \ll U_A + U_B$, then we recover the First Law of thermodynamics from quantum statistical thermodynamics.

That the entropy in equilibrium is additive over subsystems is also seen to be an approximation. The entropy of the composite system is calculated using (64); but from the subadditivity of entropy (9) we have

$$S_{AB} \leq S_A + S_B \tag{66}$$

with equality if and only if (65) were strictly true. Therefore the extensive property of entropy is an approximation. Evidently some familiar thermodynamical procedures are best interpreted as approximations; the art of thermodynamics is to know how to partition a system into subsystems so that these approximations are valid and the laws of thermodynamics apply.

As an example, consider two very thin sheets A and B. If we assume the interaction energy is proportional to the surface area in contact between two systems, then the thermodynamics of the composite system where the area of contact is the edges of the sheets will be different from the case where the contact is the faces of the sheets. In the first case $\langle V_{AB} \rangle \ll U_A + U_B$, but in the latter case $\langle V_{AB} \rangle$ need not be negligible compared to U_A and U_B. Simply stating that the sheets are brought into contact is not sufficient to determine if the normal methods of thermodynamics apply to the two sheets separately or only to the composite system viewed as one sheet.

Finally, we discuss an interesting knot connected with the concept of interaction as it is customarily interpreted in statistical thermodynamics. As we have seen, the interaction part of H needs to be present and large enough to provide a channel for the transfer of an appreciable amount of energy between the systems but at the same time must be, in some sense, small compared to the private energies of the interacting systems. It is not always clear what this criterion means. There are systems for which the H is not simply a sum of private energy operators onto which a small interaction term is added. If this is the case, then the interaction may not possess the properties described above. To illustrate this, consider the interaction of an N-particle gas G in a box compressed by a weight W in a gravitational field. The energy operator for W has the standard form

$$H_W = \frac{P^2}{2m} + mgZ \tag{67}$$

and the energy operator for G

$$H_G = H_G' + \sum_{i=1}^{N} V_{i\text{box}} \tag{68}$$

In this expression, H_G' contains all kinetic energies of the particles of the gas plus all interparticle potential energies V_{ij}, i.e.,

$$H_G' = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + \sum_{i,j=1}^{N} V_{ij} \tag{69}$$

The term $V_{i\text{box}}$ is the potential energy of the ith particle due to the walls of the box:

$$V_{i\text{box}}(x_i,y_i,z_i,Z) = V_0[1 - \Theta(x_0 - x_i)\Theta(x_i)\Theta(y_0 - y_i)\Theta(y_i)\Theta(Z - z_i)\Theta(z_i)] \tag{70}$$

where Θ is the Heaviside unit step function.

This potential energy contains both the position operators for the gas particle and the position operator of the weight, and is therefore an operator defined in the tensor product space $\mathcal{H}_G \otimes \mathcal{H}_W$, where $\mathcal{H}_G$, $\mathcal{H}_W$ are the Hilbert spaces associated with G, W respectively.

The total energy operator for the system is

$$H = H_G' \otimes I_W + I_G \otimes H_W + V_{GW} \tag{71}$$

where

$$V_{GW} = \sum_{i=1}^{N} V_{i\text{box}}(x_i,y_i,z_i,Z) \tag{72}$$

Clearly we cannot regard V_{GW} as being "small" in any sense. Indeed to neglect V_{GW} is to disregard the walls of the box, thereby making the system of gas plus weight fundamentally different. The point of this illustration is that we cannot give a general rule concerning the ignorability of the interaction between two systems. Whether V_{AB} can be neglected so that A and B may be regarded as separable in applying the laws of thermodynamics must be decided case by case.

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