STEEPEST ENTROPY ASCENT IN QUANTUM THERMODYNAMICS

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Quantum Thermodynamics [1] is a unified quantum theory that includes within a single uncontradictory nonstatistical structure the whole of Quantum Mechanics and Classical Equilibrium Thermodynamics, as well as a general description of nonequilibrium states, their entropy, and their irreversible motion towards stable equilibrium. Quantum Thermodynamics postulates that a system has access to a much broader set of states than contemplated in Quantum Mechanics. Specifically, for a system that is strictly uncorrelated from any other system, namely, a system for which Quantum Mechanics contemplates only states that are described by a state vector $|\Psi\rangle$, Quantum Thermodynamics postulates that in addition to the quantum mechanical states there exist many other states that cannot be described by a vector $|\Psi\rangle$ but must be described by a self-adjoint, unit-trace, nonnegative-definite linear operator ρ that we call the state operator.

In contrast with the density operators used in Statistical Mechanics to characterize either a heterogeneous ensemble of identical uncorrelated systems that are generally distributed over a range of different states, or a homogeneous ensemble of identical systems that are correlated with some other system such as a heat bath or a reservoir, we emphasize that the state operators in Quantum Thermodynamics are used to characterize a homogeneous ensemble of identical uncorrelated systems each of which is exactly in the same state as all the others. In other words, state operators ρ in Quantum Thermodynamics describe the uncorrelated states of a system, in the same sense as the state vectors $|\psi\rangle$ in Quantum Mechanics describe the uncorrelated states of a system. Clearly, all the states of Quantum Mechanics form a subset of the states contemplated in Quantum Thermodynamics, namely, the subset of idempotent states operators ρ such that $\rho^2 = \rho = |\psi\rangle\langle\psi|$.

Postulating the augmentation just cited of the set of conceivable states of an uncorrelated system allows a unification of mechanics and thermodynamics at the fundamental microscopic level [2]. Entropy emerges as a state property much in the same way in which energy is understood to be a state property. Energy is represented by the state functional $\mathrm{Tr}H\rho$ where H is the Hamiltonian of the system. Entropy is represented by the state functional $-k\mathrm{Tr}\rho\ln\rho$ where k is the Boltzmann constant [2]. Among all the different states ρ with a given value $\langle E\rangle$ of the energy, i.e., such that $\mathrm{Tr}H\rho = \langle E\rangle$, the value of the entropy spans from zero for the idempotent quantum mechanical states to a maximum value for the classical thermodynamical state $\rho = \exp(-\beta H)/\mathrm{Tr}\exp(-\beta H)$, where β is uniquely determined by $\langle E\rangle$. State operators with values of the entropy between zero and the maximum value represent states that, in general, are nonequilibrium and are not contemplated either in Quantum Mechanics or in Classical Thermodynamics.

Because the nonidempotent state operators represent nonmechanical states, the description of their time evolution cannot be derived from the laws of mechanics. Specifically, it cannot be derived from the unitary evolution generated by the Schroedinger equation $d|\psi\rangle/dt = -iH|\psi\rangle/\hbar$. Quantum Thermodynamics postulates that the time evolution of the state operator ρ is given in general by the solution of a general equation of motion [1] which for a

single material constituent has the form

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H,\rho] - \frac{1}{\tau}F(\rho),\qquad(1)$$

where the operator $F(\rho)$ is given explicitly in [1] and can be visualized geometrically [3] as the projection of the gradient of the entropy functional $-kTr\rho\ln\rho$ onto the hyperplane generated by the normalization functional $Tr\rho$, the energy functional $TrH\rho$ and, for a field with number operator N (with $[N,H] = 0$), the number-of-particle functional $TrN\rho$.

The coefficient τ in Equation 1 cannot be inferred other than from experiments on the relaxation of nonequilibrium states. Mathematically, all the general results that we summarize below unfold identically whether τ is a universal constant, a constant that depends on the system, or any positive functional of ρ. At present, we have not found a way to estimate τ on the basis of available experimental data. However, we have discussed specific implications of Equation 1 which should in principle be experimentally verifiable [4].

The operator $F(\rho)$ has many interesting features. It reduces to the null operator whenever $\rho^2 = \rho$, namely, for each quantum mechanical state. Equation 1 maintains idempotent any initially idempotent state operator and, therefore, all the unitary evolutions of mechanical states generated by the Schroedinger equation are also solutions of Equation 1. Thus, we conclude that Quantum Thermodynamics contains the whole of Quantum Mechanics. But it is more general, because for the nonmechanical states, i.e., for $\rho^2 \neq \rho$, $F(\rho)$ does indeed contribute to the time evolution. The two terms in Equation 1 compete with each other in the sense that $-i[H,\rho]/\hbar$ tends to "pull" ρ in a direction tangent to the local constant entropy hypersurface whereas $-F(\rho)/\tau$ tends to "pull" ρ in the local direction of steepest entropy ascent while maintaining it on a constant energy and constant number of particles hyperplane.

The term $-i[H,\rho]/\hbar$ maintains invariant the entropy functional by maintaining invariant each of the eigenvalues of the state operator ρ. If H is time-dependent, then this term describes an adiabatic exchange of energy between the system and some other external systems during which the two systems remain uncorrelated. The adiabatic rate of energy change, $Tr(dH/dt)\rho$, depends on the rate of change of the Hamiltonian operator H. Even if H is time-dependent, the term $-F(\rho)/\tau$ does not contribute to changing the value of the energy functional $TrH\rho$, but for most nonidempotent states it increases the value of the entropy functional $-Tr\rho\ln\rho$. Interestingly, the rate of entropy increase is independent of the rate of change dH/dt of the Hamiltonian operator and, therefore, adiabatic energy exchanges can be made to approach reversibility, i.e., vanishing entropy production, in the limit of very fast changes of the Hamiltonian.

The magnitude of the rate of entropy increase is a nonlinear function of ρ which goes to zero smoothly at many states, including the idempotent states, the equilibrium states, and the limit cycles. It is therefore interesting to note that if a state is very close to, say, an idempotent state, then the term $-F(\rho)/\tau$ may be so small compared to the term $-i[H,\rho]/\hbar$ that its effect may be negligible for a long time, during which the evolution may seem dominated by the unitary term $-i[H,\rho]/\hbar$. According to Equation 1, however, all the idempotent states, the limit cycles, and the less-than-maximum-entropy equilibrium states are unstable in the sense of Lyapunov, i.e., arbitrarily close to each one of them there is a trajectory that after some finite time (perhaps very long) carries the state to a finite distance. The only equilibrium states that are stable in the sense of Lyapunov are the maximum entropy states $\rho = \exp(-\beta H)/Tr\exp(-\beta H)$, i.e., the equilibrium states of classical thermodynamics.

From the results just summarized it follows that if we postulate that the uncorrelated states of a system are described by state operators ρ that are not

necessarily idempotent and evolve in time according to Equation 1, then we obtain a quantum theory that when restricted to the idempotent state operators reduces to the whole of Quantum Mechanics, and when restricted to the maximum entropy state operators, which turn out to be the only stable equilibrium states -- a conclusion that is equivalent to the second law of thermodynamics [2], reduces to the whole of Equilibrium Thermodynamics.

Moreover, the theory implies general conclusions on the nature of the nonequilibrium states and their irreversible, energy conserving but entropy increasing, motion towards stable equilibrium. A general state operator ρ can always be written as

$$\rho = B \exp(-\sum_j f_j X_j), \tag{2}$$

where the self-adjoint linear operators X_1, X_2, ..., X_j, ... form a fixed set spanning the real space of all self-adjoint linear operators, the coefficients f_1, f_2, ..., f_j, ... are real numbers, and B is an idempotent, self-adjoint linear operator. In terms of this expression, the entropy functional

$$S = -kTr\rho\ln\rho = k\sum_j f_j TrX_j\rho = k\sum_j f_j \langle X_j \rangle \tag{3}$$

so that

$$kf_j = \partial S/\partial \langle X_j \rangle \Big|_{\langle X_{i \neq j} \rangle}, \tag{4}$$

and the coefficient f_i can be interpreted as a generalized affinity associated with the observable represented by operator X_i.

The particular structure of the dissipative term $-F(\rho)/\tau$ in the equation of motion of Quantum Thermodynamics is such that its contribution to the rate of change $dTrX_j\rho/dt$ of the mean value of observable X_j can be written as $-TrX_j F(\rho)/\tau = \sum_i f_i L_{ji}(\rho)$, thus implying the existence of linear interrelations between the dissipative contribution to the rate of change of $\langle X_j \rangle$ and the generalized affinities f_i. The coefficients $L_{ji}(\rho)$ may be interpreted as generalized conductivities. The explicit structure of the functionals $L_{ji}(\rho)$ is such that $L_{ji}(\rho) = L_{ij}(\rho)$ and the symmetric matrix $[L_{ij}(\rho)]$ is nonnegative definite. Thus, we conclude that the particular structure of the dissipative term in Equation 1, when coupled with the general expression for nonequilibrium states given by Equation 2, implies a general result that we may identify with an extension of Onsager's reciprocity principle to all nonequilibrium states. We emphasize that this result follows directly with no further assumptions from the specific structure of the operator $-F(\rho)/\tau$, which implies the existence of an endogenous irreversible dynamical tendency of nonequilibrium states to follow the local direction of steepest entropy ascent. The complete dynamical behavior results from the competition between the endogenous irreversible tendency towards the direction of steepest entropy ascent, contributed by the term $-F(\rho)/\tau$ in the equation of motion, and the reversible Hamiltonian tendency towards a unitary evolution, contributed by the term $-i[H,\rho]/\hbar$.

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