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Paul Bracken

The University of Texas Rio Grande Valley, paul.bracken@utrgv.edu

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Recommended Citation

Paul Bracken (November 17th 2020). Classical and Quantum Integrability: A Formulation That Admits Quantum Chaos, A Collection of Papers on Chaos Theory and Its Applications, Paul Bracken and Dimo I. Uzunov, IntechOpen, DOI: 10.5772/intechopen.94491. Available from: <https://www.intechopen.com/chapters/74091>

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Entropy in Quantum Mechanics and Applications to Nonequilibrium Thermodynamics

Paul Bracken

Abstract

Classical formulations of the entropy concept and its interpretation are introduced. This is to motivate the definition of the quantum von Neumann entropy. Some general properties of quantum entropy are developed, such as the quantum entropy which always increases. The current state of the area that includes thermodynamics and quantum mechanics is reviewed. This interaction shall be critical for the development of nonequilibrium thermodynamics. The Jarzynski inequality is developed in two separate but related ways. The nature of irreversibility and its role in physics are considered as well. Finally, a specific quantum spin model is defined and is studied in such a way as to illustrate many of the subjects that have appeared.

Keywords: classical, quantum, partition function, temperatures, entropy, irreversible

1. Introduction

The laws of thermodynamics are fundamental to the present understanding of nature [1, 2]. It is not surprising then to find they have a very wide range of applications beyond their original scope, such as to gravitation. The analogy between properties of black holes and thermodynamics could be extended to a complete correspondence, since a black hole in free space had been shown to radiate thermally with a temperature $T = \kappa/2\pi$, where κ is the surface gravity. One should be able to assign an entropy to a black hole given by $S_H = A_H/4$ where A_H is the surface area of the black hole [3]. In the nineteenth century, the problem of reconciling time asymmetric behavior with time symmetric microscopic dynamics became a central issue in this area of physics [4]. Lord Kelvin wrote about the subjection of physical phenomenon to microscopic dynamical law. If then the motion of every particle of matter in the universe were precisely reversed at any instant, the course of nature would be simply reversed for ever after [5]. Physical processes, on the other hand, are irreversible, such as conduction of heat and diffusion processes [6, 7]. It subsequently became apparent that not only is there no conflict between reversible microscopic laws and irreversible microscopic behavior, but there are extremely strong reasons to expect the latter from the former. There are many reasons; for example, there exists a great disparity between microscopic

and macroscopic scales and the fact that the events we observe in the macroworld are determined not only by the microscopic dynamics but also by the initial conditions or state of the system.

In the twentieth century, it became clear that the microworld was described by a different kind of physics along with mathematical ideas that need not be taken into account in describing the macroworld. This is the subject of quantum mechanics. Even though the new quantum equations have similar symmetry properties as their classical counterparts, it also reveals numerous phenomena that can contribute at this level to the problems mentioned above. These physical phenomena which play various roles include the phenomenon of quantum entanglement, the effect of decoherence in general, and the theory of measurements as well.

The purpose of this is to study the subject of entropy as it applies to quantum mechanics [8, 9]. Its definition is to be relevant to very small systems at the atomic and molecular level. Its relationship to entropies known at other scales can be examined. It is also important to relate this information from this new area of physics to the older and more established theories of thermodynamics and statistical physics [10–15]. To summarize, many good reasons dictate that the arrow of time is specified by the direction of increase of the Boltzmann entropy, the von Neumann macroscopic entropy. To relate the quantum Boltzmann approach to irreversibility to measurement theory, the measuring apparatus must be included as a part of the closed quantum mechanical system.

2. Entropy and quantum mechanics

Boltzmann's great insight was to connect the second law of thermodynamics with phase space volume. This he did by making the observation that for a dilute gas, $\log |\Gamma_M|$ is proportional up to terms negligible compared to the system size, to the thermodynamic entropy of Clausius. He then extended his insight about the relation between thermodynamic entropy and $\log |\Gamma_M|$ to all macroscopic systems, no matter what their composition. This gave a macroscopic definition of the observationally measurable entropy of equilibrium macroscopic systems. With this connection established, he generalized it to define an entropy for systems not in equilibrium.

Clearly, the macrostate $M(\mathbf{x})$ is determined by \mathbf{x} , a point in phase space, and there are many such points, in fact a continuum, which correspond to the same M . Let Γ_M then be the region in Γ consisting of all microstates \mathbf{x} corresponding to a given macrostate M . Boltzmann associated with each microstate \mathbf{x} of a macroscopic system M a number S_B , which depends only on $M(\mathbf{x})$, such that up to multiplicative and additive constants is given by

$$S(\mathbf{x}) = S_B(M(\mathbf{x})) = k_B \log |\Gamma_M|. \quad (1)$$

This S is called the Boltzmann entropy of a classical system. The constant $k_B = 1.38 \cdot 10^{-16}$ erg/K is called Boltzmann's constant, and if temperature is measured in ergs instead of Kelvin, it may be set to one. Boltzmann argued that due to large differences in the sizes of Γ_M , $S_B(\mathbf{x}_t)$ will typically increase in a way which explains and describes the evolution of physical systems towards equilibrium.

The approach of Gibbs, which concentrates primarily on probability distributions or ensembles, is conceptually different from Boltzmann's. The entropy of Gibbs for a microstate \mathbf{x} of a macroscopic system is defined for an ensemble density $\rho(\mathbf{x})$ to be

$$S_G(\rho) = -k_B \int_{\Gamma} \rho(\mathbf{x}) \log(\rho(\mathbf{x})) d\mathbf{x}. \quad (2)$$

In (2), $\rho(\mathbf{x})$ is the probability for the microscopic state of the system to be found in the phase space volume element $d\mathbf{x}$. Suppose $\rho(\mathbf{x})$ is taken to be the generalized microcanonical ensemble associated with a macrostate M

$$\rho_M(\mathbf{x}) = \begin{cases} |\Gamma_M|^{-1}, & \mathbf{x} \in \Gamma; \\ 0, & \text{otherwise.} \end{cases} \quad (3)$$

Then clearly

$$S_G(\rho_M) = k_B \log |\Gamma_M| = S_B(M). \quad (4)$$

The probability density for the system in the equilibrium macrostate $\rho_{M_{eq}}$ is the same as that for the microcanonical and equivalent to the canonical or grandcanonical ensemble when the system is of macroscopic size. The time development of S_B and S_G subsequent to some initial time when $\rho = \rho_M$ is very different unless $M = M_{eq}$ when there is no further systematic change in M or ρ . In fact, $S_G(\rho)$ never changes in time as long as \mathbf{x} evolves according to Hamiltonian evolution, so ρ evolves according to the Liouville equation. Then S_G does not give any indication that the system is evolving towards equilibrium. Thus the relevant entropy for understanding the time evolution of macroscopic systems is S_B and not S_G .

From the standpoint of mathematics, these expressions for classical entropies can be unified under the heading of the Boltzmann-Shannon-Gibbs entropy [16]. A very general form of entropy which includes those mentioned can be defined in a mathematically rigorous way. To do so, let (Ω, A, μ) be a finite measure space, ν a probability measure that is absolutely continuous with respect to μ , and its Radon-Nikodym derivative $d\nu/d\mu$ exists. The generalized BSG entropy is defined to be

$$S_{BSG} = \int \frac{d\nu}{d\mu} \cdot \log \left(\frac{d\nu}{d\mu} \right) d\nu, \quad (5)$$

when the integrand is integrable.

This includes the classical Boltzmann-Gibbs entropy when $d\mu$ and $d\nu$ are given by

$$d\mu = \frac{d^{3N}p d^{3N}q}{h^{3N}}, \quad d\nu = \rho^{cl} d\mu. \quad (6)$$

It also includes the Shannon entropy appearing in information theory in which

$$\Omega = \{1, 2, \dots\}, \quad \mu(\{1\}) = \mu(\{2\}) = \dots = 1, \quad \nu(\{i\}) = 1. \quad (7)$$

In this case, (5) gives the entropy to be

$$S = - \sum_i \rho_i \log(\rho_i). \quad (8)$$

In attempting to translate these considerations to the quantum domain, it is immediately clear that a perfect analogy does not exist.

Although the situation is in many ways similar in quantum mechanics, it is not identical. The irreversible incompressible flow in phase space is replaced by the unitary evolution of wave functions in Hilbert space and velocity reversal of x by

complex conjugation of the wave function. The analogue of the Gibbs entropy (2) of an ensemble is the von Neumann entropy of a density matrix ρ :

$$S_{vN}(\rho) = -k_B \text{Tr}(\rho \log \rho). \quad (9)$$

This formula was given by von Neumann. It generalizes the classical expression of Boltzmann and Gibbs to the realm of quantum mechanics. The density matrix with maximal entropy is the Gibbs state. The range of S_{vN} is the whole of the extended real line $[0, \infty]$, so to every number ζ with $0 < \zeta \leq \infty$, there is a density matrix ρ such that $S_{vN}(\rho) = \zeta$. Like the classical $S_G(\rho)$, this does not alter in time for an isolated system evolving under Schrödinger evolution. It has value zero whenever ρ represents a pure state. Similar to $S_G(\rho)$, it is not most appropriate for describing the time symmetric behavior of isolated macroscopic systems. The Szilard engine composed of an atom is an example in which the entropy of a quantum object is made use of. von Neumann discusses the macroscopic entropy of a system, so a macrostate is described by specifying values of a set of commuting macroscopic observable operators \hat{A} , such as particle number, energy, and so forth, to each of the cells that make up the system corresponding to the eigenvalues a_α , an orthogonal decomposition of the system's Hilbert space \mathcal{H} into linear subspaces $\hat{\Gamma}_\alpha$ in which the observables \hat{A} take the values a_α . Let Π_α the projection into $\hat{\Gamma}_\alpha$. von Neumann then defines the macroscopic entropy of a system with density matrix $\tilde{\rho}$ as

$$\tilde{S}_{mac}(\tilde{\rho}) = k_B \sum_{\alpha=1}^N p_\alpha(\tilde{\rho}) \log |\hat{\Gamma}_\alpha| - k_B \sum_{\alpha=1}^N p_\alpha(\tilde{\rho}) \log p_\alpha(\tilde{\rho}). \quad (10)$$

Here, $p_\alpha(\tilde{\rho})$ is the probability of finding the system with density matrix $\tilde{\rho}$ in the microstate M_α

$$p_\alpha(\tilde{\rho}) = \text{Tr}(\Pi_\alpha \tilde{\rho}), \quad (11)$$

and $|\hat{\Gamma}_\alpha|$ is the dimension of $\hat{\Gamma}_\alpha$. An analogous definition is made for a system which is represented by a wave function Ψ ; simply replace $p_\alpha(\rho)$ by $p_\alpha(\Psi) = \langle \Psi, \Pi_\alpha \Psi \rangle$. In fact, $|\Psi\rangle\langle\Psi|$ just corresponds to a particular pure density matrix. von Neumann justifies (10) by noting that

$$\tilde{S}_{mac}(\rho) = -k_B \text{Tr}[\tilde{\rho} \log \tilde{\rho}] = S_{vN}(\tilde{\rho}), \quad (12)$$

for

$$\tilde{\rho} = \sum_{\alpha} \frac{p_\alpha}{|\hat{\Gamma}_\alpha|} \Pi_\alpha, \quad (13)$$

and $\tilde{\rho}$ is macroscopically indistinguishable from ρ .

A correspondence can be made between the partitioning of classical phase space Γ and the decomposition of Hilbert space \mathcal{H} and to define the natural quantum analogues to Boltzmann's definition of $S_B(M)$ in (1) as

$$\hat{S}_B(M_\alpha) = k_B \log |\hat{\Gamma}_{M_\alpha}| \quad (14)$$

where $|\hat{\Gamma}_{M_\alpha}|$ is the dimension of $\hat{\Gamma}_{M_\alpha}$. With definition (14) the first term on the right of (10) is just what would be stated for the expected value of the entropy of a

classical system of whose macrostate we were unsure. The second part of (10) will be negligible compared to the first term for a macroscopic system, classical or quantum, and going to zero when divided by the number of particles.

Note the difference that in the classical case, the state of the system is described by $\mathbf{x} \in \Gamma_\alpha$ for some α , so the system is always in one of the macrostates M_α . For a quantum system described by ρ or Ψ , this is not the case. There is no analogue of (1) for general ρ or Ψ . Even when the system is in a macrostate corresponding to a definite microstate at t_0 , only the classical system will be in a unique macrostate at time t . The quantum system will in general evolve into a superposition of different macrostates, as is the case in the Schrödinger Cat paradox. In this wave function, Ψ corresponding to a particular macrostate evolves into a linear combination of wave functions associated with very different macrostates. The classical limit is obtained by a prescription in which the density matrix is identified with a probability distribution in phase space and the trace is replaced by integration over phase space. The superposition principle excludes partitions of the Hilbert space: an orthogonal decomposition is all that is relevant.

2.1 Properties of entropy functions

Entropy functions have a number of characteristic properties which should be briefly described in the quantum case. The set of observables will be the bounded, self-adjoint operators with discrete spectra in a Hilbert space. The set of normal states can be taken to be the density operators or positive operators of trace one.

The entropy functional satisfies the following inequalities. Let $\lambda_i > 0$ and $\sum_i \lambda_i = 1$. Then S has the concavity property:

$$S\left(\sum_i \lambda_i \rho_i\right) \geq \sum_i \lambda_i S(\rho_i), \quad (15)$$

with equality if all λ_i are equal.

Subadditivity holds with equality if and only if $\rho_i \rho_j = 0, i \neq j$

$$S\left(\sum_i \lambda_i \rho_i\right) \leq \sum_i \lambda_i S(\rho_i) - \sum_i \lambda_i \log \lambda_i. \quad (16)$$

and

$$S\left(\sum_i \lambda_i \rho_i\right) \leq S(T_B \rho) \leq S(\rho) - \sum_k p_k \log p_k \quad (17)$$

where the first equality holds iff $T_B \rho = \rho$ and the second iff $S(\rho_k) = S(\rho)$ for all k . The conditional entropy is defined to be

$$S(\rho_1 | \rho_2) = \text{Tr}(\rho_1 \log \rho_1 - \rho_1 \log \rho_2). \quad (18)$$

The formal expression will be interpreted as follows. If A, B are positive traceless operators with complete orthonormal sets of eigenstates $|a_i\rangle$ and $|b_i\rangle$, using a resolution of identity, $\sum_i \langle a_i | A \log A | a_i \rangle = \sum_{i,j} \langle a_i | A | b_j \rangle \langle b_j | \log A | a_i \rangle = \sum_{i,j} a_i \langle a_i | b_j \rangle \log a_i \langle b_j | a_i \rangle$ so that

$$\begin{aligned}
 \sum_j \langle b_j | A \log A - A \log B + B - A | b_j \rangle &= \sum_j \langle a_i | A \log A - A \log B + B - A | a_i \rangle \\
 &= \sum_{i,j} |\langle a_i | b_i \rangle|^2 (a_i \log a_i - a_i \log b_j + b_j - a_i) = S(A|B).
 \end{aligned}
 \tag{19}$$

Concavity of the function $x \log x$ ensures the terms of the final sum are nonnegative. In order that $S(\rho_1|\rho_2) < \infty$, it is necessary that $\pi_{\rho_1} \leq \pi_{\rho_2}$ where $\pi_W = \text{supp } W$ is the support projection of W , so $\rho_1 < \rho_2$. From the definition, $S(\rho_1|\rho_2) \geq 0$ with equality if $\rho_1 = \rho_2$. If $\lambda \rho_1 \leq \rho_2$, for some $\lambda \in (0, 1)$, $S(\rho_1|\rho_2) \leq -\log \lambda$ from operator monotony of $\log z$. If $\rho = \sum_i \lambda_i \rho_i$, then

$$S(\rho) = \sum_i \lambda_i S(\rho_i) + \sum_i \lambda_i S(\rho_i|\rho), \tag{20}$$

which gives (15) and (16). If T is a trace-preserving operator, then $\rho < T\rho$, and

$$S(T\rho) = S(\rho) + S(\rho|T\rho). \tag{21}$$

This is to say that T is entropy-increasing.

The concept of irreversibility is clearly going to be relevant to the subject at hand, so some thoughts related to it will be given periodically in what follows. A possible way to account for irreversibility in a closed system in nature is by the various types of course-graining. There are also strong reasons to suggest the arrow of time is provided by the direction of increase of the quantum form of the Boltzmann entropy. The measuring apparatus should be included as part of the closed quantum mechanical system in order to relate the quantum Boltzmann approach to irreversibility to the concept of a measurement. Let S_c be a composite system consisting of a macroscopic system S coupled to a measuring instrument \mathcal{I} , so $S_c = S + \mathcal{I}$, where \mathcal{I} is a large but finite N -particle system. A set of course-grained mutually commuting extrinsic variables are provided whose eigenspaces correspond to the pointer positions of \mathcal{I} . von Neumann's picture of the measurement process is basic to the approach, but according to which, the coupling of S to \mathcal{I} leads to the following effects. A pure state of S described by a linear combination $\sum_\alpha c_\alpha \psi_\alpha$ of its orthonormal energy eigenstates is converted into a statistical mixture of these states for which $|c_\alpha|^2$ is the probability of finding the system in state ψ_α . It also sends a certain set of classical or intercommuting, macroscopic variables \mathcal{M} of \mathcal{I} to values indicated by pointer readings that indicate which of the states is realized.

There is an amplification process of the $S - \mathcal{I}$ coupling where different microstates of S give rise to macroscopically different states of \mathcal{I} . If \mathcal{I} is designed to have readings which are in one-to-one correspondence with the eigenstates of S , it may be assumed index α of its microstates goes from 1 to n . Denote the projection operator for subspace \mathcal{K} by Π_α , then

$$\Pi_\alpha \Pi_\beta = \Pi_\alpha \delta_{\alpha\beta}, \quad \sum_\alpha \Pi_\alpha = 1_{\mathcal{K}_\alpha}, \tag{22}$$

and each element of the abelian subalgebra of \mathcal{B} takes the form with M_α scalars

$$M = \sum_\alpha M_\alpha \Pi_\alpha. \tag{23}$$

Define the projection operators:

$$\pi_\alpha = 1 \otimes \Pi_\alpha, \quad \alpha = 1, \dots, n. \quad (24)$$

Suppose A is measured on system S , initially in a state of the composite system described by a density matrix ρ . The value p_α is obtained with probability $\tau_\alpha = \text{Tr}(\rho\pi_\alpha)$. After the measurement, the state of the composite system is accounted for by the density matrix:

$$\rho_\alpha = \frac{1}{\tau_\alpha} \pi_\alpha \rho \pi_\alpha. \quad (25)$$

This is a mixture of states in each of which A has a definite value.

The transformation $\rho \rightarrow \tilde{\rho} = \sum_\alpha \pi_\alpha \rho \pi_\alpha$ may be viewed as a loss of information contained in non-diagonal terms $\psi_\alpha \rho \pi_{\alpha'}$ with $\alpha \neq \beta$ in $\sum_{\alpha\alpha'} \pi_\alpha \rho \pi_{\alpha'}$. When a sequence of measurements is carried out and a time evolution is permitted to occur between measurements leads one to assign to a sequence of events $\pi_{\alpha_1}(t_1)\pi_{\alpha_2}(t_2)\cdots\pi_{\alpha_n}(t_n)$ the probability distribution:

$$\mathcal{P}(\alpha) = \text{Tr}(\pi_{\alpha_1}(t_n)\cdots\pi_{\alpha_1}(t_1)\rho\pi_{\alpha_1}(t_1)\cdots\pi_{\alpha_n}(t_n)), \quad (26)$$

where $\rho = \rho(0)$, over the set of histories, where the π_k satisfy (22) with Π replaced by the π . Let us define

$$D(\alpha', \alpha) = \text{Tr}(\pi_{\alpha_1}(t_1)\cdots\pi_{\alpha_n}(t_n)\rho\pi_{\alpha_n}(t_n)\cdots\pi_{\alpha_1}(t_1)). \quad (27)$$

The following definition can now be stated. A history is said to *decohere* if and only if

$$D(\alpha, \alpha') = \delta_{\alpha, \alpha'} \rho_\alpha. \quad (28)$$

A state is called decoherent with respect to the set of π_α if and only if

$$\pi_\alpha \rho(0) \pi_\beta = 0, \quad \alpha \neq \beta. \quad (29)$$

This implies that $\text{Tr}(\pi_{\alpha'} \rho \pi_\alpha A) = 0$ for all $\alpha \neq \alpha'$, which is equivalent to $[\pi_\alpha, \rho] = 0$ for all α . In contrast to infinite systems where there is no need to refer to a choice of projections, decoherent mixed states over the macroscopic observables can be described by relations between the density matrix and the projectors. They would be of the form $\rho_m = |\Psi\rangle\langle\Psi|$ with $|\Psi\rangle = \sum_\alpha \lambda_\alpha \pi_\alpha \Phi_\alpha$ such that $\sum_\alpha |\lambda_\alpha|^2 = 1$ and $\Phi_\alpha \in \mathcal{H}$ and satisfy

$$\sum_{\alpha \neq \alpha'} (\pi_{\alpha'} \rho_m \pi_\alpha + \pi_\alpha \rho_m \pi_{\alpha'}) \neq 0. \quad (30)$$

The relative or conditional entropy between two states $S(\rho_1|\rho_2)$ was defined in (18), and it plays a crucial role. It is worth stating a few of its properties, as some are necessary for the theorem:

$$S(\rho_1|\rho_2) \geq 0. \quad (31)$$

$$S(\rho_1|\rho_2) = 0, \quad \rho_1 = \rho_2. \quad (32)$$

$$S(\lambda\rho_1 + (1-\lambda)\rho_2|\lambda\sigma_1 + (1-\lambda)\sigma_2) \leq \lambda S(\rho_1|\sigma_1) + (1-\lambda)S(\rho_2|\sigma_2). \quad (33)$$

When γ is a completely positive map, or embedding

$$S(\rho_1 \cdot \gamma | \rho_2 \cdot \gamma) \leq S(\rho_1 | \rho_2). \quad (34)$$

The last two inequalities are known as joint concavity and monotonicity of the relative entropy. The following result may be thought of as a quantum version of the second law.

Theorem: Suppose the initial density matrix is decoherent at zero time (29) with respect to π_α and have finite entropy

$$\begin{aligned} \rho(0) &= \sum_{\alpha} \pi_{\alpha} \rho(0) \pi_{\alpha}, \\ S(\rho(0)) &= -k_B \text{Tr}(\rho(0) \log(\rho(0))) < \infty, \end{aligned} \quad (35)$$

and it is not an equilibrium state of the system. Let $\rho(t_f)$, for $t_f > 0$, be any subsequent state of the system, possibly an equilibrium state. Then for an automorphic, unitary time evolution of the system between $0 \leq t \leq t_f$

$$S(0) \leq S(t_f), \quad (36)$$

where $S(0) = S(t_f)$ if and only if $(\mathbf{e}) \sum_{\alpha < \beta} \pi_{\alpha} \rho(t_f) \pi_{\beta} + \pi_{\beta} \rho(t_f) \pi_{\alpha} = 0$.

Proof: Set $\rho'(t_f) = \sum_{\alpha} \pi_{\alpha} \rho(t_f) \pi_{\alpha} = \rho(t_f) \cdot \gamma$, so ρ' is obtained from ρ by means of a completely positive map. It follows that

$$\begin{aligned} S(\rho'(t_f) | \rho'(0)) &= -S(\rho'(t_f)) - k_B \sum_{\alpha} \text{Tr}(\rho(t_f) \pi_{\alpha} \log(\rho(0)) \pi_{\alpha}) \\ &= -S(t_f) - k_B \text{Tr}(\rho(t_f) \log(\rho(0))) \leq S(\rho(t_f) | \rho(0)) = -S(\rho(0)) - \text{Tr}(\rho(t_f) \log(\rho(0))). \end{aligned} \quad (37)$$

The first equality uses the cyclic property of the trace and the definition of ρ' . The second equality uses decoherence of $\rho(0)$, and the next inequality is a consequence of (34). The evolution is unitary and hence preserves entropy which is the last equality. This implies that $S(t) \geq S(0)$ and the equality condition (e) follows from (32). \square

Of course, entropy growth as in the theorem is not necessarily monotonic in the time variable. For this reason, it is usual to refer to fixed initial and final states. For thermal systems, a natural choice of the final state is the equilibrium state of the system. It is the case in thermodynamics that irreversibility is manifested as a monotonic increase in the entropy. Thermodynamic entropy, it is thought, is related to the entropy of the states defined in both classical and quantum theory. Under an automorphic time evolution, the entropy is conserved. One application of an environment is to account for an increase. A type of course-graining becomes necessary together with the right conditions on the initial state to account for the arrow of time. In quantum mechanics, the course-graining seems to be necessary and may be thought of as a restriction of the algebra and can also be interpreted as leaving out unobservable quantum correlations. This may, for example, correspond to decoherence effects important in quantum measurements. Competing effects arise such as the fact that correlations becoming unobservable may lead to entropy increase. There is also the effect that a decrease in entropy might be due to nonautomorphic processes. Although both effects lead to irreversibility, they are not cooperative but rather contrary to one another. The observation that the second law does hold implies these nonautomorphic events must be rare in comparison with time scales relevant to thermodynamics.

3. Quantum mechanics and nonequilibrium thermodynamics

Some aspects of equilibrium thermodynamics are examined by considering an isothermal process. Since it is a quasistatic process, it may be decomposed into a sequence of infinitesimal processes. Assume initially the system has a Hamiltonian $H(\gamma)$ in thermal equilibrium at a temperature T . Boltzmann's constant is set to one. The state is given by the Gibbs density operator ρ . This expression can also be written in terms of the energy eigenvalues ε_n and eigenvectors $|n\rangle$ of H . The probability of finding the system in state $|n\rangle$ is

$$p_n = \langle n|\rho|n\rangle = \frac{e^{-\beta\varepsilon_n}}{Z}. \quad (38)$$

The average external energy U of the system is given as

$$U = \langle U \rangle = \text{Tr}(H\rho) = \sum_n \varepsilon_n p_n. \quad (39)$$

When the parameter γ is changed to $\gamma + d\gamma$, both ε_n and p_n as well as U change to

$$dU = \sum_n [d\varepsilon_n p_n + \varepsilon_n dp_n]. \quad (40)$$

Each instantaneous infinitesimal process can be broken down into a part which is the work performed; the second is the heat transformed as the system relaxes to equilibrium. This breakup motivates us to define

$$\delta W = \sum_n (d\varepsilon_n) p_n, \quad \delta Q = \sum_n \varepsilon_n dp_n, \quad (41)$$

so $dU = \delta Q + \delta W$, and δ is used to indicate that heat and work are not exact differentials. The free energy of the system is defined to be $F = -T \log Z$, so $dF = \sum_n (d\varepsilon_n) p_n$ which means

$$\delta W = dF. \quad (42)$$

By integrating over the infinitesimal segments, we find W is

$$W = \Delta F = \Delta U - Q. \quad (43)$$

Inverting Eq. (38) for p_n , we can solve for

$$\varepsilon_n = -T \log(Z p_n). \quad (44)$$

Substituting into the relation for δQ , we get two terms, one proportional to $\log(Z)$ and the other to $\log(p_n)$. The term with $\log(Z)$ when the p_k satisfy $\sum_k p_k = 1$ is

$$-T \sum_n \log(Z) dp_n = -T \log(Z) d\left(\sum_n p_n\right) = 0, \quad (45)$$

It remains to study

$$\delta Q = -T \sum_n dp_n \log(p_n). \quad (46)$$

By the chain rule

$$d\left(\sum_n p_n \log(p_n)\right) = \sum_n dp_n \log(p_n) + \sum_n dp_n = \sum_n dp_n \log(p_n). \quad (47)$$

So δQ is not a function of the state but is related to the variation of something that is. Define the entropy S as usual from (9), $S = -\sum_n p_n \log(p_n)$, and arrive at

$$\delta Q = T dS. \quad (48)$$

This relation only holds for infinitesimal processes. For finite and irreversible processes, there may be additional terms to the entropy change. This has been quite successful at describing many different types of physical system [17–19].

A deep insight has come recently into the properties of nonequilibrium thermodynamics which could be achieved by regarding work as a random variable. For example, consider a process in which a piston is used to compress a gas in a cylinder. Due to the nature of the gas and its chaotic motion, each time the piston is pressed, the gas molecules exert a back reaction with a different force. This means the work needed to achieve a given compression changes each time something is carried out.

Usually a knowledge of nonequilibrium processes is restricted to inequalities such as the Jarzynski inequality. He was able to show by interpreting work W as a random variable that an inequality can be obtained, even for a process performed arbitrarily far from equilibrium.

Suppose the system is always prepared in the same state initially. A process is carried out and the total work W performed is measured. Repeating this many times, a probability distribution for the work $\mathcal{P}(W)$ can be constructed. An average for W can be computed using $\mathcal{P}(W)$ as

$$\langle W \rangle = \int \mathcal{P}(W) dW. \quad (49)$$

Jarzynski showed that the statistical average of $e^{-\beta W}$ satisfies

$$\langle e^{-\beta W} \rangle = e^{-\beta \Delta F}, \quad (50)$$

where $\Delta F = F(T, \gamma_f) - F(T, \gamma_i)$. It holds for a process performed arbitrarily far from equilibrium. Now the inequality $W \geq \Delta F$ is contained in (50) and can be realized by applying Jensen's inequality, which states that $\langle e^{-\beta W} \rangle \geq e^{-\beta \langle W \rangle}$.

In macroscopic systems, individual measurements are usually very close to the average by the law of large numbers. For microscopic systems, this is usually not true. In fact, the individual realizations of W may be smaller than ΔF . These cases would be local violations of the second law but for large systems become extremely rare. If the function $\mathcal{P}(W)$ is known, the probability of a local violation of the second law is

$$\mathcal{P}(W < \Delta F) = \int_{-\infty}^{\Delta F} \mathcal{P}(W) dW. \quad (51)$$

To get (50) requires detailed knowledge of the system's dynamics, be it classical, quantum, unitary, or whatever.

Consider nonunitary quantum dynamics. Initially, the system has Hamiltonian $H_i = H(\gamma_i)$. The system was in thermal equilibrium with a bath at temperature T . The initial state of the system is the Gibbs thermal density matrix (38). Let ε_n^i and $|n\rangle$ denote the initial eigenvalues and eigenvectors of H_i as ε_n^i is obtained with probability $p_n = e^{-\beta\varepsilon_n^i} / Z$.

Immediately after this measurement, γ changes from $\gamma(0) = \gamma_i$ to $\gamma(\tau) = \gamma_f$ according to the rule $\gamma(t)$. If it is assumed the contact with the bath is very weak during this process, the state of the system evolves according to

$$|\psi(t)\rangle = U(t)|n\rangle, \quad (52)$$

where U is the unitary evolution operator which satisfies Schrödinger's equation, $i\partial_t U = H(t)U$, $U(0) = \mathbf{1}$.

The Hamiltonian is $H(\gamma_f)$ at the end and has energy levels ε_m^f , eigenvectors $|m\rangle$, so the probability ε_n^f measured is $|\langle m|\psi(\tau)\rangle|^2 = |\langle m|U(\tau)|n\rangle|^2$. This may be interpreted as the conditional probability a system in $|n\rangle$ will be in $|m\rangle$ after time τ .

No heat has been exchanged with the environment, so any change in the environment has to be attributed to the work performed by the external agent and is

$$W = \varepsilon_m^f - \varepsilon_n^i, \quad (53)$$

where both ε_n^i and ε_m^f are fluctuating and change during each realization of the experiment. The first ε_n^i is random due to thermal fluctuations and ε_m^f is random due to quantum fluctuations in W as a random variable by (53).

To get an expression for $\mathcal{P}(W)$ obtained by repeating the process several times, this is a two-step measurement process. From probability theory, if A, B are two events, the total probability $p(A|B)$ that both events have occurred is

$$p(A, B) = p(A|B)p(B), \quad (54)$$

where $p(B)$ is the probability B which occurs and $p(A|B)$ is the conditional probability B that has occurred. The probability of both events that have occurred is $|\langle m|U(\tau)|n\rangle|^2 p_n$. Since we are interested in the work performed, we write

$$\mathcal{P}(W) = \sum_{n,m} |\langle m|U(\tau)|n\rangle|^2 p_n \delta(W - (\varepsilon_m^f - \varepsilon_n^i)). \quad (55)$$

And some over all allowed events, weighted by their probabilities, and arrange the terms according to the values $\varepsilon_m^f - \varepsilon_n^i$. In most systems, there are present a rather large number of allowed levels, and even more allowed differences $\varepsilon_m^f - \varepsilon_n^i$. It is more efficient to use the Fourier transform

$$\mathcal{G}(y) = \langle e^{iyW} \rangle = \int_{-\infty}^{\infty} \mathcal{P}(W) e^{iyW} dW. \quad (56)$$

This has the inverse Fourier transform

$$\mathcal{P}(W) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dy \mathcal{G}(y) e^{-iyW}. \quad (57)$$

Using (55), we obtain that

$$\begin{aligned}
 \mathcal{G}(y) &= \sum_{n,m} |\langle m|U|n\rangle|^2 p_n e^{iy(\epsilon_m^f - \epsilon_n^i)} = \sum_{n,m} \langle n|U^\dagger e^{iy\epsilon_m^f} |m\rangle \langle m|U e^{-iy\epsilon_n^i} p_n |n\rangle \\
 &= \sum_{n,m} \langle n|U^\dagger e^{iyH_f} |m\rangle \langle m|U e^{-iyH_i} \rho |n\rangle = \text{Tr}(U^\dagger(\tau) e^{iyH_f} U(\tau) e^{-iyH_i} \rho).
 \end{aligned} \tag{58}$$

Hence, it may be concluded that

$$\mathcal{G} = \text{Tr}(U^\dagger(\tau) e^{iyH_f} U(\tau) e^{-iyH_i} \rho). \tag{59}$$

This turns out to be somewhat easier to work with than $\mathcal{P}(W)$, and (59) plays a similar role as Z in equilibrium statistical mechanics. From $\mathcal{G}(y)$, the statistical moments of W can be found by expanding

$$\mathcal{G}(y) = \langle e^{iyW} \rangle = 1 + iy\langle W \rangle - \frac{y^2}{2} \langle W^2 \rangle - \frac{y^3}{6} \langle W^3 \rangle + \dots \tag{60}$$

A formula for the quantum mechanical formula for the moments can be found as well. The average work is $\langle W \rangle = \langle H_f \rangle - \langle H_i \rangle$, where for any operator A , we have $\langle A \rangle_t = \text{Tr}(U^\dagger(t) A U(t) \rho)$ as the expectation value of A at time t . This follows from the fact that the state of the system at t is $\rho(t) = U(t) \rho U(t)^\dagger$. From the definition of \mathcal{G} , it ought to be the case that $\mathcal{G}(y = i\beta) = \langle e^{-\beta W} \rangle$. However, ρ in (38) and (59) yields

$$\mathcal{G}(i\beta) = \frac{1}{Z_i} \text{Tr}(U^\dagger e^{-\beta H_f} U) = \frac{1}{Z_i} \text{Tr}(e^{\beta H_f}) = \frac{Z_f}{Z_i}. \tag{61}$$

Using $Z = e^{-\beta F}$, (61) yields (50)

$$\mathcal{G}(iy) = \langle e^{-\beta W} \rangle = e^{-\beta \Delta F}. \tag{62}$$

Nothing has been assumed about the speed of this process. Thus inequality (50) must hold for a process arbitrarily far from equilibrium.

4. Heat flow from environment approach

There is another somewhat different way in which the Jarzynski inequality can be generalized to quantum dynamics. In a classical system, the energy of the system can be continuously measured as well as the flow of heat and work. Continuous measurement is not possible in quantum mechanics without disrupting the dynamics of the system [20].

A more satisfactory approach is to realize that although work cannot be continuously measured, the heat flow from the environment can be measured. To this end, the system of interest is divided into a system of interest and a thermal bath. The ambient environment is large, and it rapidly decoheres and remains at thermal equilibrium, uncorrelated and unentangled with the system. Consequently, we can measure the change in energy of the bath ($-Q$) without disturbing the dynamics of the system. The open-system Jarzynski identity is expressed as

$$\langle e^{-\beta W} \rangle = \langle e^{-\beta E_f} e^{\beta Q} e^{\beta E_i} \rangle = e^{-\beta \Delta F}. \tag{63}$$

For a system that has equilibrated with Hamiltonian H interacting with a thermal bath at temperature T , the equilibrium density matrix is $\rho = e^{\beta H} / Z = e^{-\beta F - \beta H}$,

where $\beta = 1/K_B T$. The dynamics of an open quantum system is described by a quantum operator $\tilde{\rho} = S\rho$, a linear trace-preserving, complete positive map of operators. Any such complete positive superoperator has an operator-sum representation

$$S\rho = \sum_{\alpha} A_{\alpha}\rho A_{\alpha}^{\dagger}. \quad (64)$$

Conversely, any operator-sum represents a complete positive superoperator. The set of operators $\{A_{\alpha}\}$ is often called Krauss operators. The superoperator is trace-preserving and conserves probability if $\sum_{\alpha} A_{\alpha}^{\dagger}A_{\alpha} = \mathbf{I}$. In the simplest case, the dynamics of an isolated quantum system is described by a single unitary operator $U^{\dagger} = U^{-1}$.

The interest here is in the dynamics of a quantum system governed by a time-dependent Hamiltonian weakly coupled to an extended, thermal environment. Let the total Hamiltonian be

$$H = H^S(t) \otimes \mathbf{I}^B + \mathbf{I}^S \otimes H^B + \varepsilon H^{int}, \quad (65)$$

where \mathbf{I}^S and \mathbf{I}^B are system and bath identity operators, $H^S(t)$ the system Hamiltonian, H^B the bath Hamiltonian, and H^{int} the bath-system interaction with ε a small parameter. Assume initially the system and environment are uncorrelated such that the initial combined state is $\rho^S \otimes \rho_{eq}^B$, where ρ_{eq}^B is the thermal density equilibrium matrix of the bath.

By following the unitary dynamics of the combined total system for a finite time and measuring the final state of the environment, a quantum operator description of the system dynamics can also be obtained:

$$\begin{aligned} S(s,t)\rho^S &= \text{Tr}_B U(\rho^S \otimes \rho_{eq}^B)U^{\dagger} = \sum_{i,f} \langle b_f | U(\rho^S \otimes (\sum_i \frac{e^{-\beta\varepsilon_i^B}}{Z^B} |b_i\rangle\langle b_i|))U^{\dagger} | b_f \rangle \\ &= \frac{1}{Z^B} \sum_{i,f} e^{-\beta\varepsilon_i^B} \langle b_f | U | b_i \rangle \rho^S \langle b_i | U^{\dagger} | b_f \rangle. \end{aligned} \quad (66)$$

Here U is the unitary evolution operator of the total system

$$U = \exp\left(\frac{i}{\hbar} \int_s^t H(\tau) d\tau\right), \quad (67)$$

and Tr_B is the partial trace over the bath degrees of freedom, $\{\varepsilon_i^B\}$ are the energy eigenvalues, $\{|b\rangle\}$ is the orthonormal energy eigenvectors of the bath, and Z^B is the bath partition function. Assume the bath energy states are nondegenerate. Then (66) implies the Krauss operators for this dynamics are

$$A_{i,f} = \frac{1}{\sqrt{Z^B}} e^{-\beta\varepsilon_i^B/2} \langle b_f | U | b_i \rangle. \quad (68)$$

Suppose the environment is large, with a characteristic relaxation time short compared with the bath-system interactions, and the system-bath coupling ε is small. The environment remains near thermal equilibrium, unentangled and uncorrelated with the system. The system dynamics of each consecutive time

interval can be described by a superoperator derived as in (66) which can then be chained together to form a quantum Markov chain:

$$\rho(t) = S(t-1, t) \cdots S(s+1, s+2) S(s, s+1) \rho. \quad (69)$$

The Hermitian operator of a von Neumann-type measurement can be broken up into a set of eigenvalues λ_σ and orthonormal projection operators π_σ such that $H = \sum_\sigma \lambda_\sigma \pi_\sigma$. In a more general sense, the measured operator of a positive operator-valued measurement need not be projectors or orthonormal. The probability of observing the a -th outcome is

$$p_a = \text{Tr}(A_a \rho A_a^\dagger). \quad (70)$$

The state of the system after this interaction is

$$\tilde{\rho}_a = \frac{A_a \rho A_a^\dagger}{\text{Tr}(A_a \rho A_a^\dagger)}. \quad (71)$$

The result of the measurement can be represented by using a Hermitian map superoperator \mathcal{A} :

$$\mathcal{A} = \sum_\alpha a_\alpha A_\alpha \rho A_\alpha^\dagger. \quad (72)$$

An operator-value sum maps Hermitian operators into Hermitian operators:

$$[\mathcal{A}H]^\dagger = [a_\alpha A_\alpha H A_\alpha^\dagger]^\dagger = \sum_\alpha a_\alpha (A_\alpha^\dagger)^\dagger H^\dagger A_\alpha^\dagger = \mathcal{A}H. \quad (73)$$

In the other direction, any Hermitian map has an operator-value-mean representation. Hermitian maps provide a particularly concise and convenient representation of sequential measurements and correlation functions. For example, suppose Hermitian map \mathcal{A} represents a measurement at time 0, \mathcal{C} is a different measurement at time t , and the quantum operation S_t represents the system evolution between the measurements. The expectation value of a single measurement is

$$\langle a \rangle = \text{Tr}(\mathcal{A}\rho) = \sum_\alpha a_\alpha \text{Tr} A_\alpha \rho A_\alpha^\dagger = \sum_\alpha p_\alpha a_\alpha. \quad (74)$$

The correlation function $\langle b(t)a(0) \rangle$ can be expressed as

$$\langle b(t)a(0) \rangle = \text{Tr}(B S_t \mathcal{A} \rho(0)) = \sum_{\alpha, \beta} a_\alpha b_\beta \text{Tr} B_\alpha (S_t (A_\alpha \rho(0) A_\alpha^\dagger)) B_\beta^\dagger. \quad (75)$$

It may be shown that just as every Hermitian operator represents some measurement on the Hilbert space of pure states, every Hermitian map can be associated with some measurement on the Liouville space of mixed states.

A Hermitian map representation of heat flow can now be constructed under assumptions that the bath and system Hamiltonian are constant during the measurement and the bath-system coupling is very small. A measurement on the total system is constructed, and thus the bath degrees of freedom are projected out. This leaves a Hermitian map superoperator that acts on the system density matrix alone. Let us describe the measurement process and mathematical formulation together.

Begin with a composite system which consists of the bath, initially in thermal equilibrium weakly coupled to the system:

$$\rho^S \otimes \rho_{eq}^B. \quad (76)$$

Measure the initial energy eigenstate of the bath so based on (76):

$$(I^S \otimes |b_i\rangle\langle b_i|) (\rho^S \otimes \rho_{eq}^B) (I^S \otimes |b_j\rangle\langle b_j|). \quad (77)$$

Now allow the system to evolve together with the bath for some time:

$$U(I^S \otimes |b_i\rangle\langle b_i|) (\rho^S \otimes \rho_{eq}^B) (I^S \otimes |b_j\rangle\langle b_j|) U^\dagger. \quad (78)$$

Finally, measure the final energy eigenstate of the bath:

$$(I^S \otimes |b_i\rangle\langle b_f|) U(I^S \otimes |b_i\rangle\langle b_i|) (\rho^S \otimes \rho_{eq}^B) (I^S \otimes |b_j\rangle\langle b_j|) U^\dagger (I^S \otimes |b_f\rangle\langle b_f|). \quad (79)$$

Taking the trace over the bath degrees of freedom produces the final normalized system density matrix where trace over S gives the probability of observing the given initial and final bath eigenstates. Multiply by the Boltzmann weighted heat, and sum over the initial and final bath states to obtain the desired average Boltzmann weighted heat flow:

$$\langle e^{\beta Q} \rangle = \sum_{i,f} e^{-\beta(\epsilon_f^B - \epsilon_i^B)} \text{Tr}_S \text{Tr}_B (I^S \otimes |b_f\rangle\langle b_f|) U(I^S \otimes |b_i\rangle\langle b_i|) (\rho^S \otimes \rho_{eq}^B) (I^S \otimes |b_j\rangle\langle b_j|) U^\dagger (I^S \otimes |b_j\rangle\langle b_j|). \quad (80)$$

Replace the heat bath Hamiltonian by $I^S \otimes H^B = H - H^S(t) \otimes I^B - \epsilon H^{int}$. The total Hamiltonian commutes with the unitary dynamics and cancels. The interaction Hamiltonian can be omitted in the small coupling limit giving

$$\langle e^{\beta Q} \rangle = \text{Tr}_S \text{Tr}_B (e^{\beta H^S/2} \otimes I^S) U(e^{-\beta/2H^S} \otimes I^B) (\rho^S \otimes \rho_{eq}^B) (e^{-\beta H^S/2} \otimes I^B) U^\dagger (e^{\beta H^S/2} \otimes I^B) \quad (81)$$

Collecting the terms acting on the bath and system separately and replacing the Krauss operators describing the reduced dynamics of the system, the result is

$$\begin{aligned} \langle e^{\beta Q} \rangle &= \text{Tr}_S e^{\beta H^S/2} \left(\text{Tr}_B \left(U e^{-\beta H^S/2} \rho^S e^{-\beta H^S/2} \right) \otimes \rho_{eq}^B U^\dagger \right) e^{\beta H^S/2} \\ &= \text{Tr}_S \sum_{\alpha} e^{\beta H^S/2} A_{\alpha} e^{-\beta H^S/2} \rho^S e^{\beta H^S/2} A_{\alpha}^\dagger e^{-\beta H^S/2}. \end{aligned} \quad (82)$$

To summarize, it has been found that the average Boltzmann weighted heat flow is represented by

$$\langle e^{\beta Q} \rangle = \text{Tr} (\mathcal{R}^{-1} S \mathcal{R} \rho^S). \quad (83)$$

where S represents the reduced dynamics of the system. The Hermitian map superoperator \mathcal{R}_t is given by

$$\mathcal{R}_t \rho = e^{-\beta H_t/2} \rho e^{\beta H_t/2}. \quad (84)$$

The paired Hermitian map superoperators act at the start and end of a time interval. They give a measure of the change in the energy of the system over that interval. This procedure does not disturb the system beyond that already incurred by coupling the system to the environment. The Jarzynski inequality now follows by applying this Hermitian map and quantum formalism. Discretize the experimental time into a series of discrete intervals labeled by an integer t .

The system Hamiltonian is fixed within each interval. It changes only in discrete jumps at the boundaries. The heat flow can be measured by wrapping the superoperator time evolution of each time interval S_t along with the corresponding Hermitian map measurements $\mathcal{R}_t^{-1} S_t \mathcal{R}_t$. In a similar fashion, the measurement of the Boltzmann weighted energy change of the system can be measured with $\langle e^{-\beta \Delta E} \rangle = \text{Tr} \mathcal{R}_\tau S \mathcal{R}_\tau^{-1}$. The average Boltzmann weighted work of a driven, dissipative quantum system can be expressed as

$$\langle e^{-\beta W} \rangle = \text{Tr} \left(\mathcal{R}_\tau \prod_t (\mathcal{R}_t^{-1} S_t \mathcal{R}_t) \mathcal{R}_\tau^{-1} \rho_0^{eq} \right), \quad (85)$$

In (85), ρ_{eq}^t is the system equilibrium density matrix when the system Hamiltonian is H_t^S .

This product actually telescopes due to the structure of the energy change Hermitian map (84) and the equilibrium density matrix (65). This leaves only the free energy difference between the initial and final equilibrium ensembles, as can be seen by writing out the first few terms

$$\begin{aligned} \langle e^{-\beta W} \rangle &= \text{Tr} \left[\mathcal{R}_\tau (\mathcal{R}_\tau^{-1} S_\tau \mathcal{R}_\tau) \cdots (\mathcal{R}_2^{-1} S_2 \mathcal{R}_2) (\mathcal{R}_1^{-1} S_1 \mathcal{R}_1) \mathcal{R}_0^{-1} \rho_{eq}^0 \right] \\ &= \text{Tr} \left[\tau (\mathcal{R}_\tau^{-1} S_\tau \mathcal{R}_\tau) \cdots (\mathcal{R}_2^{-1} S_2 \mathcal{R}_2) (\mathcal{R}_1^{-1} S_1 \mathcal{R}_1) \frac{I}{Z(0)} \right] \\ &= \text{Tr} \left[\mathcal{R}_\tau (\mathcal{R}_\tau^{-1} S_\tau \mathcal{R}_\tau) \cdots (\mathcal{R}_2^{-1} S_2 \mathcal{R}_2) \left(\mathcal{R}_1^{-1} S_1 \rho_{eq}^1 \frac{Z(1)}{Z(0)} \right) \right] \\ &\quad \cdots = \frac{Z(\tau)}{Z(0)} = e^{-\beta \Delta F} = e^{-\beta \Delta F}. \end{aligned} \quad (86)$$

In the limit in which the time intervals are reduced to zero, the inequality can be expressed in the continuous Lindblad form:

$$\langle e^{-\beta W} \rangle = \text{Tr} \mathcal{R}(t) \exp \left[\int_0^t \mathcal{R}(\xi)^{-1} S(\xi) \mathcal{R}(\xi) d\xi \right] \mathcal{R}(0)^{-1} \rho_0^{eq} = e^{-\beta \Delta F}. \quad (87)$$

5. A model quantum spin system

A magnetic resonance experiment can be used to illustrate how these ideas can be applied in practice. A sample of noninteracting spin-1/2 particles are placed in a strong magnetic field B_0 which is directed along the z direction. Denote by $\sigma_j, j = x, y, z$ the usual Pauli matrices and $\mathbf{1}$ the 2×2 identity matrix. It is assumed the motion of the system is unitary. Then the spin is governed by the Hamiltonian:

$$H_0 = -\frac{1}{2} B_0 \sigma_z. \quad (88)$$

In units where \hbar is one, B_0 represents the characteristic precession frequency of the spin. Since H_0 is diagonal in the $|\pm\rangle$ basis that diagonalizes σ_z , the matrix exponential and partition function are given by

$$e^{-H/T} = \begin{pmatrix} e^{B_0/2T} & 0 \\ 0 & e^{-B_0/2T} \end{pmatrix}, \quad Z = \text{Tr} \left(e^{-H/T} \right) = 2 \cosh \left(\frac{B_0}{2T} \right), \quad (89)$$

If we set $\tilde{\sigma}$ to be the equilibrium magnetization of the system, $\tilde{\sigma} = \langle \sigma_x \rangle_{th}$, the thermal density matrix is

$$\rho = \rho_{th} = \frac{1}{2} \begin{pmatrix} 1 + \tilde{\sigma} & 0 \\ 0 & 1 - \tilde{\sigma} \end{pmatrix}, \quad \tilde{\sigma} = \tanh \left(\frac{B_0}{T} \right). \quad (90)$$

and $\tilde{\sigma}$ corresponds to the parametric response of a spin-1/2 particle.

The work segment is implemented by introducing a very small field of amplitude B rotating in the xy plane with frequency ω . The work parameter is governed by the field

$$\mathbf{B} = B (\sin(\omega t), \cos(\omega t), 0). \quad (91)$$

Typically, $B_0 \approx \omega T$ and $B \approx 0.01T$, so we may approximate $B \ll B_0$. The total Hamiltonian is the combination

$$H(t) = -\frac{B_0}{2} \sigma_z - \frac{B}{2} (\sigma_z \sin(\omega t) + \sigma_y \cos(\omega t)). \quad (92)$$

The oscillating field plays the role of a perturbation which although weak may initiate transitions between the up and down spin states and will be most frequent at the resonance condition $\omega = B_0$, so the driving frequency matches the natural oscillation frequency.

The time evolution operator $U(t)$ is calculated now. To do this, define a new operator $V(t)$ by means of the equation

$$U(t) = e^{i\omega t \sigma_z / 2} V(t). \quad (93)$$

Substituting (43) into the evolution equation for $U(t)$, $i\partial_t U = H(t)U$, $U(0) = 1$. It is found that $V(t)$ obeys the Schrödinger equation:

$$i \frac{\partial V}{\partial t} = \tilde{H}(t) V, \quad V(0) = 1, \quad (94)$$

It is found that $V(t)$ satisfies

$$i \frac{\partial V}{\partial t} = \frac{1}{2} \left(\omega \sigma_z - B_0 \sigma_z - B e^{-i\omega t \sigma_z / 2} (\sigma_x \sin(\omega t) + \sigma_y \cos(\omega t)) e^{i\omega \sigma_z / 2} \right) V(t). \quad (95)$$

Using the commutation relations of the Pauli matrices and the fact that

$$e^{-i\omega \sigma_z} = \mathbf{1} \cos \left(\frac{\omega t}{2} \right) - i \sigma_z \sin \left(\frac{\omega t}{2} \right), \quad (96)$$

it is found that the terms in the evolution equation can be simplified

$$\begin{aligned} e^{-i\alpha \sigma_z} \sigma_x e^{i\alpha \sigma_z} &= (\mathbf{1} \cos \alpha - i \sigma_z \sin \alpha) \sigma_x (\mathbf{1} \cos \alpha + i \sigma_z \sin \alpha) \\ &= \sigma_x + 2 \sin \alpha \cos \alpha \sigma_y - 2i \sigma_z \sigma_y \sin^2 \alpha = \sigma_x + 2 \sin \alpha \cos \alpha \sigma_y \sin^2 \alpha, \end{aligned} \quad (97)$$

$$e^{-i\alpha\sigma_z}\sigma_y e^{i\alpha\sigma_z} = (\sigma_y \cos \alpha - i\sigma_x \sigma_y \sin \alpha)(\mathbf{1} \cos \alpha + i\sigma_z \sin \alpha) = \sigma_y - 2 \sin \alpha \cos \alpha \sigma_x + 2i\sigma_z \sigma_y \sin^2 \alpha. \quad (98)$$

By means of these results, it remains to simplify

$$\begin{aligned} & e^{-i\omega t \sigma_z/2} (\sigma_z \sin(\omega t) + \sigma_y \cos(\omega t)) e^{i\omega t \sigma_z/2} \\ = & \sigma_z (\sin \omega t - \sin \omega t + \cos \omega t \sin \omega t - \cos \omega t \sin \omega t) + \sigma_y (\sin^2 \omega t + \cos \omega t - \cos \omega t + \cos^2 \omega t) = \sigma_y. \end{aligned} \quad (98a)$$

Taking these results to (95), we arrive at

$$i \frac{\partial V}{\partial t} = H_1 V, \quad H_1 = -\frac{1}{2}(B_0 - \omega)\sigma_z - \frac{1}{2}B\sigma_y. \quad (99)$$

This means $V(t)$ evolves according to a time-dependent Hamiltonian, so the solution can be written as

$$V(t) = e^{-iH_1 t}, \quad (100)$$

and the full-time evolution operator is given by

$$U(t) = e^{i\omega t \sigma_z/2} e^{-iH_1 t}. \quad (101)$$

Since the operators σ_y and σ_z do not commute, the exponentials in (101) cannot be using the usual addition rule.

To express (100) otherwise, suppose \mathbf{M} is an arbitrary matrix such that $\mathbf{M}^2 = \mathbf{1}$. When α is an arbitrary parameter, power series expansion of $e^{-i\alpha\mathbf{M}}$ yields

$$e^{-i\alpha\mathbf{M}} = \mathbf{1} \cos(\alpha) - i\mathbf{M} \sin(\alpha). \quad (102)$$

Now H_1 can be put in equivalent form

$$\begin{aligned} H_1 &= \frac{\Omega}{2} (\sigma_z \cos \vartheta + \sigma_y \sin \vartheta), \\ \Omega &= \sqrt{(B_0 - \omega)^2 + B^2}, \quad \tan \vartheta = \frac{B}{B_0 - \omega}, \end{aligned} \quad (103)$$

Since $\sigma_i^2 = \mathbf{1}$, it follows that

$$(\sigma_z \cos \vartheta + \sigma_y \sin \vartheta)^2 = \mathbf{1}. \quad (104)$$

Consequently, (100) can be used to prove that $V(t)$ is given by

$$\begin{aligned} e^{-iH_1 t} &= \mathbf{1} \cos\left(\frac{\Omega}{2}t\right) + i(\sigma_z \cos \vartheta + \sigma_y \sin \vartheta) \sin\left(\frac{\Omega}{2}t\right) \\ &= \begin{pmatrix} \cos\left(\frac{\Omega}{2}t\right) + i \cos \vartheta \sin\left(\frac{\Omega}{2}t\right) & \sin \vartheta \sin\left(\frac{\Omega}{2}t\right) \\ -\sin \vartheta \sin\left(\frac{\Omega}{2}t\right) & \cos\left(\frac{\Omega}{2}t\right) - i \cos \vartheta \sin\left(\frac{\Omega}{2}t\right) \end{pmatrix} \end{aligned} \quad (105)$$

Since

$$e^{i\omega\sigma_z t/2} = \begin{pmatrix} e^{i\omega t/2} & 0 \\ 0 & e^{-i\omega t/2} \end{pmatrix} \quad (106)$$

the evolution operator is then given by

$$U(t) = \begin{pmatrix} u(t) & v(t) \\ -v^*(t) & u^*(t) \end{pmatrix}. \quad (107)$$

The functions $u(t)$ and $v(t)$ in (107) are given as

$$u(t) = e^{i\omega t/2} \left(\cos\left(\frac{\Omega}{2}t\right) + i \sin\vartheta \sin\left(\frac{\Omega}{2}t\right) \right), \quad v(t) = e^{i\omega t/2} \cdot \sin\vartheta \cdot \sin\left(\frac{\Omega}{2}t\right). \quad (108)$$

Apart from a phase factor, the final result depends only on Ω and ϑ , and these in turn depend on B_0 , B , and ω through (108). To understand the physics of $U(t)$ a bit better, suppose the system is initially in the pure state $|+\rangle$. The probability will be found in state $|-\rangle$ after time t is

$$| \langle - | U(t) | + \rangle |^2 = |v|^2. \quad (109)$$

This expression represents the transition probability per unit time a transition will occur. Since the unitarity condition $U^\dagger U = \mathbf{1}$ implies that $|u|^2 + |v|^2 = 1$, we conclude $|u|^2$ is the probability when no transition occurs. Note v is proportional to $\sin\vartheta$, which gives a physical meaning to ϑ . It represents the transition probability and reaches a maximum when $\omega = B_0$ at resonance where $\Omega = B$, so u and v simplify to

$$u(t) = e^{i\omega t/2} \cos\left(\frac{B}{2}t\right), \quad v(t) = e^{i\omega t/2} \sin\left(\frac{B}{2}t\right). \quad (110)$$

Now that $U(t)$ is known, the evolution of any observable A can be calculated

$$\langle A \rangle_t = \text{Tr}(U^\dagger(t) A U(t) \rho). \quad (111)$$

If A is replaced by σ_z in (111), we obtain

$$\begin{aligned} \langle \sigma_z \rangle_t &= \text{Tr} \begin{pmatrix} u^*(t) & -v(t) \\ v^*(t) & u(t) \end{pmatrix} \sigma_z \begin{pmatrix} u(t) & v(t) \\ -v^*(t) & u^*(t) \end{pmatrix} \frac{1}{2} \begin{pmatrix} 1 + \tilde{\sigma} & 0 \\ 0 & 1 - \tilde{\sigma} \end{pmatrix} \\ &= \tilde{\sigma} (|u|^2 - |v|^2) = \tilde{\sigma} (1 - 2|v|^2). \end{aligned} \quad (112)$$

Substituting $|v|^2$, this takes the form

$$\langle \sigma_z \rangle_t = \tilde{\sigma} (\cos^2\vartheta + \sin^2\vartheta \cos(\Omega t)) = \tanh\left(\frac{B_0}{2T}\right) (\cos^2\vartheta + \sin^2\vartheta \cos(\Omega t)). \quad (113)$$

Consider the average work. Suppose $B \ll B_0$, so the unperturbed Hamiltonian H_0 can be used instead of the full Hamiltonian $H(t)$ when expectation values of

quantities are calculated which are related to the energy. Let us determine the energy of the system at any t by taking operator A to be H_0 :

$$\begin{aligned}
 \langle H_0 \rangle_t &= -\frac{B_0}{2} \langle \sigma_z \rangle_t = -\frac{1}{2} B_0 \text{Tr} U^\dagger(t) \sigma_z U(t) \rho \\
 &= -\frac{1}{2} B_0 \text{Tr} \left(\begin{pmatrix} u^* & -v \\ v^* & u \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} u & v \\ -v^* & u^* \end{pmatrix} \frac{1}{2} \begin{pmatrix} 1 + \tilde{\sigma} & 0 \\ 0 & 1 - \tilde{\sigma} \end{pmatrix} \right) \\
 &= -\frac{B_0}{4} \text{Tr} \left(\begin{pmatrix} u^* & -v \\ v^* & u \end{pmatrix} \begin{pmatrix} u & v \\ v^* & -u^* \end{pmatrix} \begin{pmatrix} 1 + \tilde{\sigma} & 0 \\ 0 & 1 - \tilde{\sigma} \end{pmatrix} \right) = -\frac{1}{4} B_0 \tilde{\sigma} (1 - 2|v|^2).
 \end{aligned} \tag{114}$$

The average work at time t is simply the difference between the energy at time t_1 and $t = 0$. Since $v(0) = 0$, this difference is

$$\begin{aligned}
 \langle W \rangle_t &= -\frac{B_0}{2} \tilde{\sigma} (1 - 2|v|^2) + \frac{B_0}{2} \tilde{\sigma} = \tilde{\sigma} B_0 |v|^2 \\
 &= \tilde{\sigma} B_0 \sin^2 \vartheta \sin^2 \left(\frac{\Omega}{2} t \right) = \tilde{\sigma} B_0 \frac{B}{\Omega^2} \sin^2 \left(\frac{\Omega}{2} t \right),
 \end{aligned} \tag{115}$$

since $\sin^2 \vartheta = 1 - \cos^2 \vartheta = B^2/\Omega^2$. The average work oscillates indefinitely with frequency $\Omega/2$. This is a consequence of the fact the time evolution is unitary. The amplitude multiplying the average work is proportional to the initial magnetization $\tilde{\sigma}$ and B^2/Ω^2 , so the ratio is a Lorentzian function.

The equilibrium free energy is $F = -T \log Z$ where $Z = 2 \cosh(B_0/2T)$. The free energy of the initial state at $t = 0$ and final state at any arbitrary time is the same yielding

$$\Delta F = 0. \tag{116}$$

This is a consequence of the fact that $B \ll B_0$. According to $\langle W \rangle \geq F$, it should be expected that

$$\langle W \rangle_t \geq \Delta F = 0. \tag{117}$$

Given the matrices for $U(t)$ and ρ that have been determined so far, the function \mathcal{G} can be computed:

$$\begin{aligned}
 \mathcal{G}(y) &= \text{Tr} (U^\dagger(y) e^{ixH_f} U(y) e^{-iyH_i} \rho) \\
 &= \text{Tr} \left(\begin{pmatrix} u^* & -v \\ v^* & u \end{pmatrix} \begin{pmatrix} e^{-iyB_0/2} & 0 \\ 0 & e^{iyB_0/2} \end{pmatrix} \begin{pmatrix} u & v \\ -v^* & u^* \end{pmatrix} \begin{pmatrix} e^{iyB_0/2} & 0 \\ 0 & e^{-iyB_0/2} \end{pmatrix} \begin{pmatrix} \frac{1}{2}(1 + \tilde{\sigma}) & 0 \\ 0 & \frac{1}{2}(1 - \tilde{\sigma}) \end{pmatrix} \right) \\
 &= |u|^2 + \frac{1}{2} \left((1 + \tilde{\sigma}) e^{iyB_0} + (1 - \tilde{\sigma}) e^{-iyB_0} \right) |v|^2.
 \end{aligned} \tag{118}$$

Set $x = i\beta$ and recall use definition (42) for $\tilde{\sigma}$ in the second term of (118) to give

$$\begin{aligned}
 &\left(1 + \tanh \left(\frac{\beta}{2} B_0 \right) \right) e^{-\beta B_0} + \left(1 - \tanh \left(\frac{\beta}{2} B_0 \right) \right) e^{\beta B_0} \\
 &= 2 \cosh(\beta B_0) - 2 \tanh \left(\frac{\beta}{2} B_0 \right) \sinh(\beta B_0) = 1.
 \end{aligned} \tag{119}$$

Substituting (119) into (118), we can conclude

$$\langle e^{-\beta W} \rangle = \mathcal{G}(i\beta) = |u|^2 + |v|^2 = 1. \quad (120)$$

This is the Jarzynski inequality, since it is the case that $\Delta F = 0$ here. The statistical moments of the work can be obtained by writing an expression for \mathcal{G} into a power series

$$\mathcal{G}(y) = |u|^2 + |v|^2 \left(1 + i\tilde{\sigma}B_0y - \frac{1}{2}B_0^2y^2 + \dots \right). \quad (121)$$

From (121), the first and second moments can be obtained; for example

$$\langle W \rangle = \tilde{\sigma}B_0|v|^2, \quad \langle W^2 \rangle = B_0^2|v|^2. \quad (122)$$

As a consequence, the variance of the work can be determined

$$\text{var}(W) = \langle W^2 \rangle - \langle W \rangle^2 = B_0^2|v|^2 - \tilde{\sigma}^2B_0^2|v|^4 - B_0^2|v|^2(1 - \tilde{\sigma}^2|v|^2). \quad (123)$$

A final calculation that may be considered is the full distribution of work $\mathcal{P}(W)$. Now $\mathcal{P}(W)$ is the inverse Fourier transform of $\mathcal{G}(y)$:

$$\mathcal{P}(W) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dy \mathcal{G}(y) e^{-iyW}. \quad (124)$$

Using the Fourier integral form of the delta function, (124) can be written as

$$\begin{aligned} \mathcal{P}(W) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dy \mathcal{G}(y) e^{-iyW} \\ &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dy \left(|u(t)|^2 + |v(t)|^2 \left[\frac{1}{2}(1 + \tilde{\sigma})e^{iB_0y} + \frac{1}{2}(1 - \tilde{\sigma})e^{-iB_0y} \right] \right) e^{-iyW}. \quad (125) \\ &= |u|^2 \delta(W) + \frac{1}{2} |v(t)|^2 \delta(W - B_0) + \frac{1}{2} |v(t)|^2 (1 + \tilde{\sigma}) \delta(W + B_0). \end{aligned}$$

Work taken as a random variable can take three values $W = 0, +B_0, -B_0$ where B_0 is the energy spacing between the up and down states. The event $W = B_0$ corresponds to the case where the spin was originally up and then reversed, so an up-down transition. The energy change is $(B_0/2) - (-B_0/2) = B_0$. Similarly, $W = -B_0$ is the opposite flip from this one, and $W = 0$ is the case with no spin flip.

The second law would have us think that $W > 0$, but a down-up flip should have $W = -B_0$, so $\mathcal{P}(W = -B_0)$ is the probability of observing a local violation of the second law. However, since $\mathcal{P}(W = \pm B_0)$ is proportional to $1 \pm \tilde{\sigma}$, up-down flips are always more likely than down-up. This ensures that $\langle W \rangle \geq 0$, so violations of the second law are always exceptions to the rule and never dominate.

The work performed by an external magnetic field on a single spin-1/2 particle has been studied so far. The energy differences mentioned correspond to the work. For noninteracting particles, energy is additive. Hence the total work $\langle \mathcal{W} \rangle$ which is performed during a certain process is the sum of works performed on each individual particle $\mathcal{W} = W_1 + \dots + W_N$. Since the spins are all independent and energy is an extensive variable, it follows that $\langle \mathcal{W} \rangle = N\langle W \rangle$, where $\langle W \rangle$ is the average work from (115).

6. Conclusions

We have tried to give an introduction to this frontier area that lies in between that of thermodynamics and quantum mechanics in such a way as to be comprehensible. There are many other areas of investigation presently which have had interesting repercussions for this area as well. There is a growing awareness that entanglement facilitates reaching equilibrium [21–23]. It is then worth mentioning that the ideas of einselection and entanglement with the environment can lead to a time-independent equilibrium in an individual quantum system and statistical mechanics can be done without ensembles. However, there is really a lot of work yet to be done in these blossoming areas and will be left for possible future expositions.


Author details

Paul Bracken

Department of Mathematics, University of Texas, Edinburg, TX, USA

*Address all correspondence to: paul.bracken@utrgv.edu

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