Quantum Thermodynamics, Entropy of the Universe, Free Energy, and the Second Law

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Abstract

We take the view that the standard von Neumann definition, in which the entropy $S^{vN}$ of a pure state is zero, is in evident conflict with the statement of the second law that the entropy of the universe $S_{univ}$ increases in spontaneous processes, $\Delta S_{univ} > 0$. Here we seek an alternative entropy of the universe $S_{univ}$ that is in accord with the second law, in a spirit not dissimilar to von Neumann himself in lesser-known work. We perform simulations of time dependent dynamics for a previously developed [1] model quantum system becoming entangled with a quantum environment. We test the new definition of the entropy of the system-environment “universe” against the standard thermodynamic relation $\Delta F_{sys} = -T \Delta S_{univ}$, calculating system properties using the reduced density matrix and standard von Neumann entropy. Good agreement is obtained, showing the compatibility of an entropy for a pure state of a universe with the statement of the second law and the concept of free energy. Interesting deviation from microcanonical behavior within the zero order energy shell is observed in a context of effectively microcanonical behavior within the much larger total basis of the time dependent universe.

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I. INTRODUCTION

In standard thermodynamics, the second law is expressed as the statement that, except for transient fluctuations, the entropy of the universe is always increasing:

$$\Delta S_{\text{univ}} > 0$$  \hspace{1cm} (1)

A very important statement in thermodynamics relates the free energy change of the system at fixed $T, V$ to the entropy change of the universe:

$$-\frac{1}{T} \Delta F_{\text{sys}} = \Delta S_{\text{univ}}$$ \hspace{1cm} (2)

The free energy change of the system is thus a surrogate for the entropy change of the universe in the second law. This is the meaning of the statement that the free energy $F$ is a thermodynamic potential at fixed $T$ and $V$. (Other thermodynamic potentials of course pertain for different fixed conditions; in this paper we will only consider the Helmholtz free energy $F$.)

These considerations raise a problem in quantum thermodynamics. In the most common definition, introduced by von Neumann in his famous book of 1932 (the English translation was reissued in 1996), the quantum entropy is given in terms of the eigenvalues $\rho_i$ of the density matrix:

$$S^{vN} = -\sum \rho_i \ln \rho_i$$ \hspace{1cm} (3)

where the $\rho_i$ are probabilities summing to unity. By this definition, the entropy of a pure state is zero. In this view, a pure system evolves to a state with quantum entropy $S^{vN} > 0$ as a result of the system becoming entangled with an environment, as follows. The total system + environment universe $SE$ is described by a density matrix $\rho_{SE}$. The system alone is described by tracing over the environment degrees of freedom to give the reduced density matrix:

$$\rho_S = Tr_E \rho_{SE}. \hspace{1cm} (4)$$

The quantum entropy for the system $S$ is obtained by diagonalizing the reduced density matrix for the system to give eigenvalues $\lambda_i$ and then taking
\[ S_{\text{vN}}^S = -\sum \lambda_i \ln \lambda_i. \]  

(5)

But, according to the definition (3), if the combined SE universe is described by a density matrix \( \rho_{SE} \) for a pure state, then \( S_{\text{univ}}^\text{vN} = 0 \). Hence, the von Neumann definition of the quantum entropy does not encompass the idea of the entropy of the universe, i.e. the entropy of an SE total system, apart from quantum entanglement with some further exterior world. (In this paper, we use \( \text{sys} \) and \( \text{univ} \) to refer generically to system and universe; we use S, E, and SE when referring to the specific model system S, environment E, and universe SE.) The statement of the second law in standard thermodynamics, given in Eq. 1, thus ceases to have meaning, along with the foundation in the second law of the standard relation between free energy and spontaneous processes (Eq. 2). Moreover, without that connection, the basis of the theory of equilibrium in the law of van’t Hoff is lost. To be clear, this is not just a matter of settled results in thermodynamics: in modern treatments of nonequilibrium thermodynamics e.g. Kondepudi and Prigogine [3], the entropy change of the universe regarded as “irreversible entropy production” is taken as a basic working idea.

In this paper we ask, can we recover a notion of the entropy of the universe \( S_{\text{univ}} \) that does not have the problem of the von Neumann definition? And will such a definition give results in accord with Eq. 2 in numerical simulations of quantum systems? Our point of departure is a recent paper [1], following work of Gemmer et al. [4, 5] that simulated a small quantum system embedded in a quantum environment with a view toward comparison with thermodynamic behavior. The time dependent dynamics of the system were revealed through the calculation of the reduced density matrix and subsequent calculation of the von Neumann entropy, system populations, and spatial density plots. It was found that various initial states of a coupled oscillator system approach the same final distribution, which can be characterized as fluctuation about a Boltzmann distribution with a temperature \( T \). The general method gives \( \Delta S_{\text{sys}} \) for various initial states as the von Neumann entropy \( \Delta S_S^\text{vN} \), and a temperature \( T \). Accordingly, for the thermalization process, one could calculate the free energy change \( \Delta F_{\text{sys}} = \Delta E_S - T \Delta S_S^\text{vN} \). Our strategy in the present paper is to calculate \( \Delta F_{\text{sys}} \), and compare this with a separate calculation of a suitable newly defined \( -T \Delta S_{\text{univ}} \). To the extent that these two quantities are equal, we will obtain a recovery of standard thermodynamics ideas and results.

Some readers may naturally be uneasy about defining a new entropy \( S_{\text{univ}} \) without justification in prior established principles. It may be good to remember Einstein’s injunction, stated in its
most widely quoted instance in the popular book with Infeld [6]: “Physical concepts are free creations of the human mind, and are not, however it may seem, uniquely determined by the external world.” This seems particularly apt when considering entropy, which to an unusual degree may appear to have the character of a contrivance that is nonetheless accepted because of its usefulness in describing observed behavior of the natural world. This applies to the classical entropy of thermodynamics, the statistical entropy of Boltzmann, and the von Neumann quantum entropy as well as the universe quantum entropy $S_{\text{univ}}$ defined and investigated here. The “validity” of the latter concept, like its predecessors, will depend on its usefulness in accounting for natural phenomena.

II. HISTORICAL BACKGROUND AND CONTEMPORARY CONSIDERATIONS

In this section we present further considerations on the goals of this paper, including the relation of some little-known work of von Neumann himself. The reader who is less interested in this partly historical background may wish to skip to the remaining sections.

We would like to state at the outset that in some contexts there are cogent reasons, e.g. in some aspects of quantum information theory [7], to hold to the view that the entropy of a pure quantum state is zero, and therefore that the von Neumann entropy is an appropriate definition. On the other hand, in maintaining that this point of view leads to perverse conclusions when brought into contact with ordinary laws of classical thermodynamics, we believe we are following in a line of thought of von Neumann himself, who now appears to have been very much aware of the gap left in quantum thermodynamics with the “von Neumann entropy.” In an old paper [8] that is likely to become much better known given its recent translation into English [9] along with a lucid modern commentary [10], von Neumann sought to deal with the problem of extending quantum statistical mechanics including the notion of entropy to recover results of standard thermodynamics. This line of thought however does not appear in von Neumann’s later book [2] on the mathematical foundations of quantum mechanics. We hold with von Neumann in this earlier work that more than one definition of entropy is appropriate for quantum thermodynamics. Delineating the virtues and appropriate contexts of different definitions of entropy will be one of the goals of this paper.

A few words are in order about other overarching goals in von Neumann’s work [8–10], in relation to the specifics of what we are trying to do in the present paper. In Ref. [8], von Neumann proposed and claimed to prove a “quantum ergodic theorem.” In this work von Neumann
recognizes a tension between what the commentary Ref. \[10\] characterizes as “individualist” and “ensemblist” points of view in quantum statistical mechanics. The individualist point of view starts from an individual pure quantum state. This corresponds roughly to the idea of a single classical trajectory in phase space, the point of departure for the earlier work of Boltzmann. This leads in both classical [11–16] and quantum [8, 9] statistical mechanics to the idea of a microcanonical ensemble average for a closed “universe,” and by extension to the idea in the present paper of a new quantum entropy of the universe $S_{\text{univ}}$. (To our knowledge, von Neumann did not however use the term “entropy of the universe.”) The ensemblist view focuses on mixed states, usually the system canonical ensemble, in a line running through Boltzmann [11], Gibbs [12], Einstein [13–16], and von Neumann in his book [2]. In quantum statistical mechanics, the ensemblist point of view finds expression through use of the reduced density matrix for the system, with the von Neumann entropy $S_{vN}$ the linchpin.

In classical statistical mechanics the individualist and ensemblist views can be reconciled with more or less conviction, as was in effect argued by Gibbs [12] and Einstein [13–16]. Ref. [10] asserts that a goal of von Neumann [8, 9] is to reconcile the two points of view in quantum statistical mechanics. One of our aims here is to test in simulations the compatibility of the individualist and ensemblist views, as well as the emphasis on the entropy of the universe in the second law and its compatibility with system free energy properties through Eq. 2. Furthermore, there has been significant contemporary research [1, 4, 5, 17–20] into the foundations of statistical mechanics that seeks to show that the quantum time evolution of complex systems leads naturally to ordinary thermodynamic and classical statistical mechanical behavior. It is posited that “typical” quantum states show time evolution with thermodynamic behavior, and this seems entirely consistent with the “individualist” point of view. The investigation here of a new system-environment entropy $S_{\text{univ}}$ can be regarded as fitting broadly with the goals of these contemporary endeavors, as well as the work of von Neumann, regarding the latter see especially Section III B. However, these other works have not invoked the idea of an “entropy of the universe.” The introduction here of a quantum $S_{\text{univ}}$ is intended as a distinctive approach that could lead in directions that transcend classical statistical mechanics. We note that the work of Refs. [19, 20] explicitly disavows a reliance on ergodic-type ideas in the sense of equating time and ensemble averages, in contrast to von Neumann’s notion of a quantum ergodic theorem. In the present work the entropy of the universe does not depend on such considerations, though they do enter into the analysis somewhat tangentially in Section V B.
The expression in Eq. 2 is not just a statement about total changes in thermodynamic quantities in a spontaneous process, but about time derivatives of those quantities in a nonequilibrium system undergoing change. In the language of Prigogine [3], the system expends free energy in irreversible entropy production $\sigma_i$ which is equivalent to the rate of entropy change of the universe, so Eq. 2 is expressed in differential form as

$$- \frac{1}{T} \dot{F}_{\text{sys}} = \sigma_i = \dot{S}_{\text{univ}} > 0$$ \hspace{1cm} (6)

We will test in the quantum simulations whether the above equation actually holds during the course of the spontaneous process, and not just after it has gone to completion. In particular, does the relation $\Delta S_{\text{univ}} > 0$ always hold and moreover, does equality even of the sign of the negative of the free energy always hold in a small quantum system?

Finally, it is important to be clear what we mean with the terms “system, environment, universe.” We have in mind primarily a particular small system $S$, of laboratory dimensions or less; and a corresponding environment $E$. Together, the bipartite quantum system-environment $SE$ makes up the “universe.” This certainly is not necessarily meant to imply cosmic dimensions. In fact, we see the interest of the work here in its possible significance for extremely tiny quantum “universes” that might exist in the laboratory or in nature, isolated from their larger surroundings on a sufficiently limited timescale. However, many of the same questions that motivate us apply to systems of cosmic size. It is conceivable that some of our considerations could shed light on thermodynamic problems in cosmological systems, though we will not pursue such possibilities here.

It could be argued that a focus on the “universe” entropy is misplaced, because any particular system-environment $SE$ will be embedded within a larger $SEE'$, with the smaller universe $SE$ becoming rapidly entangled with $E'$, so that $SE$ can be treated by means of its von Neumann entropy, and so on with ever-expanding layers of entanglement with the environment. On the other hand, this can be seen as simply begging the question of the entropy of the pure state of the “universe,” however narrowly or widely defined. Furthermore, it is perfectly reasonable to consider the question of timescales, as indeed already arises in Eq. 6. Small universe situations can be imagined and perhaps constructed and probed in laboratory experiments, in which $SE$ thermalizes far more rapidly than entanglement occurs with the next environment layer in $SEE'$. 
III. SPONTANEOUS PROCESS AND ENTROPY IN A QUANTUM UNIVERSE

In classical statistical mechanics (including early quantum statistical mechanics of quantized energy levels, but not quantum states undergoing entanglement) it is typically assumed that spontaneous processes occur in an SE universe when a constraint is removed. This allows a process that might be termed “ergodization” (however loosely defined) but might better be called “microcanonical spreading” (see comments shortly below) in which the universe attains the maximal entropy $S = \sum p_i \ln p_i = \ln W$ according to the Boltzmann microcanonical definition $p_i = 1/W$, where $W$ is the number of states in the microcanonical ensemble. Here we want to explore thermodynamic behavior of a spontaneous process in a system-environment quantum universe. We will focus on perhaps the most basic spontaneous process: heat flow between a quantum system and a quantum environment, with no mechanical work. In this section, we propose a definition for a quantum entropy for the SE universe, discuss the rationale for this definition, and finally specialize to the particular process for which we will perform quantum simulations.

A. Quantum Entropy of the Universe

We now propose the definition of the quantum entropy of the universe $S_{univ}$. We think of a universe described by a pure state (this last condition could be generalized, but that is not our purpose here), in general entangled, of a system S and an environment E. (Everything goes through when the universe consists of just a simple system S.) To define an entropy $S_{SE} = S_{univ}$ we choose some “reference basis” $\{|i\rangle\}$. In this reference basis a pure state is expressed as

$$|\Psi_{SE}(t)\rangle = \sum_i c_i(t) |i\rangle. \quad (7)$$

Then taking

$$p_i(t) = |c_i(t)|^2 \quad (8)$$

we define the entropy of the universe

$$S_{univ} = S^{(i)}_{univ} = - \sum_i p_i \ln p_i \quad (9)$$
with respect to the reference basis \( \{ i \} \). Henceforth we will leave out the specification \( \{ i \} \) of the reference basis. Note that the quantities \( p_i \) come from the coefficients of the pure state, not from the eigenvalues of the universe density matrix \( \rho_{SE} \), which of course would yield zero in Eq. 9.

B. Reference Basis for Heat Flow

What is the meaning of this procedure? The expression for the entropy on the right-hand side of Eq. (9) is not new. It has an evident relation to the Shannon information entropy. In the quantum context it has been discussed as the “conditional information entropy” by Stotland et al. [21]. In fact, it is a simplified form (because adapted to the special situation here of simple heat exchange with no work and no other structure either in system or environment) of an entropy proposed by von Neumann [8–10] in addition to the much more widely known “von Neumann quantum entropy”; see Eq. 34 of Refs. [8, 10] and Eq. 62 in the commentary Ref. [10]. What we are doing here is identifying this entropy with the entropy of the universe \( S_{univ} \) i.e. as an entropy related to the second law and the system-universe free energy relationship Eq. (2).

With the definition (9) the entropy depends on the choice of reference basis. In fact, it is trivial to pick a “bad” reference basis, such that the entropy \( S_{univ} \) never changes. For example, the basis of energy eigenstates of the SE universe has this property, because any time-dependent state in this basis has constant coefficients \( c_i \) in (7), hence constant entropy. We need some criterion for picking a “good” reference basis for defining the entropy. We posit that the reference basis for \( S_{univ} \) should be identifiable or compatible with some (possibly macroscopic) property that would be observed for the total SE universe. In the quantum calculations here, we will be simulating an abstract quantum system in which energy flows between a system \( S \) and an environment \( E \) – a process of heat flow. This is a process of spreading of initially localized energy and “fragmentation” of the quantum state (a term we prefer to use instead of “ergodization,” which has for us an unwarranted connotation of time averaging; we will have occasion to discuss the meaning of both these terms shortly). We take the reference basis to consist of “cells” of the relevant “macroscopic” states of the system, here, the energy. Hence, we will take the cells to be basis states of the tensor product space of the zero order energy eigenstates of the system and environment. The energy tensor product space is then our reference basis, as explicitly defined in Section IV A.

While our definition gives an \( S_{univ} \) that is manifestly basis set dependent, we believe that this is not a great problem. As just argued, it should be possible to choose a reasonable basis on physical
grounds. But it is also the case that for most basis sets, the resultant entropy will not vary greatly, a point emphasized in the work of Stotland et al. \[21\]. We believe it is fair to say, in parallel with work on thermodynamic behavior of “typical” quantum states \[5, 17–20\], that the entropy $S_{\text{univ}}$ will show very similar behavior for typical basis sets, with thermodynamic behavior of $\Delta S_{\text{univ}}$ including the relation (2) for $\Delta F_{\text{sys}}$ – and odd behavior only for a pathological choice of basis set.

C. Thermalization, Microcanonical Ensemble, and Quantum State Fragmentation

What should we expect of the quantum thermodynamics in this reference basis? We will argue by analogy to the basic ideas of classical statistical mechanics. There we expect the SE universe to be described by the microcanonical ensemble. We expect the system S embedded in E to reach a thermal distribution. This takes place through a process of microcanonical spreading or fragmentation in which the microstates of the microcanonical ensemble become, at least for practical purposes, equally likely (in the chosen reference basis, here the zero-order energy states).

Let us consider how these notions carry over to a fully quantum mechanical universe SE of a system S becoming entangled with the environment E. First consider the question of thermalization. The S and E energies are properties of S and E considered separately that one might observe or measure. When we treat entanglement of S with E in the process of heat flow, then if thermal conditions prevail, a Boltzmann distribution of zero order energy states of S should emerge in the reduced density matrix for the system. Then the zero-order energy basis of the system diagonalizes the reduced density matrix, i.e. the S energy basis is carried over to the Schmidt SE basis \[7\]. In fact, in Ref. \[1\], this is exactly the kind of behavior, subject to fluctuations, found for the system and environment that we use in the present paper. This is an indication that the system energy basis is a “good” basis for the system von Neumann entropy, and also as a component of the reference basis for the universe entropy.

The issues of how thermalization relates to microcanonical behavior in a quantum context, let alone how this might relate to a notion of “ergodic” behavior, are more subtle and problematic. Classically, microcanonical behavior is constituted by having equal probabilities $p_i = 1/W$ within a microcanonical energy shell of $W$ states of equal energy. This already assumes a division into quantum states, but not quantum dynamics. The assumption of equal probabilities is often justified by appeal to an ergodic-type hypothesis e.g. that time average is effectively equal to the ensemble average. This is problematic in our approach in which the $p_i$ values are taken as instantaneous val-
ues in Eq. 8, \( p_i = |c_i(t)|^2 \). There is no time average here, and certainly no a priori justification for assuming that all the instantaneous \( p_i \) values are equal. Furthermore, “microcanonical” behavior is an ambiguous concept in quantum thermodynamics. Conventionally, a microcanonical ensemble depends on having a narrow energy shell. However, in quantum mechanics, a time-dependent state in a spontaneous process does not have a well-defined energy. The \( W \) microcanonical states that are supposed to have equal probabilities are thus also a problematic idea. Despite these conceptual reservations, we will proceed with the definition of \( S_{univ} \) of Eq. 9, seeing to what extent Eq. 2 holds in empirical simulations, and examining the extent to which microcanonical fragmentation behavior is observed.

IV. COMPUTATIONAL QUANTUM SIMULATIONS

Our quantum simulations model a system \( S \) and environment \( E \) which become entangled in the course of the dynamics of the universe \( SE \). Here we outline the features of the model. More details are presented in Ref. [1] where we found that the model universe evolves toward a thermal distribution with a temperature \( T \). The system consists of two linearly coupled harmonic oscillators; the environment \( E \) consists of a bath of levels with a degeneracy pattern devised to have a statistical mechanical temperature. We choose a random coupling scheme between \( S \) and \( E \). For the system \( S \), we calculate the reduced density matrix from the time-evolving pure state of the \( SE \) universe. From these we obtain the free energy change \( \Delta F_{sys} \) of the system and the entropy change \( \Delta S_{univ} \) of the universe.

A. System, Environment, Model Hamiltonian, and Temperature

The total Hamiltonian operator is a sum of three parts

\[
\hat{H} = \hat{H}_S + \hat{H}_E + \hat{H}_{SE}
\]

for system, environment, and system-environment interaction. We work in the basis of the energy eigenrepresentation of both the system and environment which means that both \( \hat{H}_S \) and \( \hat{H}_E \) are represented in diagonal form. The system basis will consist of states \( \{|n\} \); the environment basis of states \( \{|m,l\} \) with quantum numbers \( n, m, l \) to be defined shortly. The product basis is then \( \{|n\} \otimes |m,l\} \equiv |n,m,l\} \).
1. Isolated System Hamiltonian

For the system we take two linearly coupled oscillators, labeled 1 and 2, with Hamiltonian

$$\hat{H}_S = (n_1 + n_2)\omega_0 + \kappa(a_1^\dagger a_2 + a_1 a_2^\dagger)$$

(11)

where $n_1, n_2$ are the numbers of quanta in modes 1, 2 and $\omega_0, \kappa$ are parameters that we take to be 34.64 and 1.0 in reduced units (the rationale for various parameter choices is detailed below). The coupled system yields normal mode eigenstates that can be labeled by quantum numbers $n_s, n_a$ for the number of quanta in the symmetric and antisymmetric modes. The Hamiltonian in this normal mode representation is

$$\hat{H}_S = n_s \omega_s + n_a \omega_a = n_s(\omega_0 - \frac{1}{2}\kappa) + n_a(\omega_0 + \frac{1}{2}\kappa)$$

(12)

The coupling in Eq. 11 preserves the total quantum number $N = n_1 + n_2 = n_s + n_a$, often referred to as the polyad number. Associated with a given $N$ are a set of $N + 1$ normal mode states, referred to as a polyad of states. Each distinct polyad constitutes an isolated system since the Hamiltonian preserves the polyad number (i.e. distinct polyads are not coupled). The normal mode energies are equally spaced within a polyad. In reduced units we define the value of the spacing between states within the $N = 5$ polyad as 1. Although the calculations are performed in reduced units, we present final results in wavenumbers and picoseconds based on the absolute spacing of 111.77 cm$^{-1}$ between these polyad states. This value corresponds to the parameter $\kappa$ in Eq. 11 in absolute units and was adapted from a fit to the water stretching mode spectrum in Ref. [22, 23]. For convenience we will label each energy eigenvalue of the normal mode system using the quantum number $n = 0 \cdots 5$.

2. Isolated Environment Hamiltonian

We take the quantum environment $E$ as a set of evenly spaced harmonic levels that can be completely defined using an energy quantum number $m$ and a degeneracy quantum number $l$. These quantum numbers together specify each zero order $E$ state as $|m, l\rangle$. The zero order $E$ Hamiltonian is taken as
where $\omega_E$ is a parameter of the model, taken to be 1. We choose to make the zero order harmonic spacing of $E$ equal to that of the system. The degeneracy of each level is given by $g(m) = A b^{\omega_E}$ where $A$ and $b$ are parameters of the model. The rationale for this degeneracy behavior has to do with temperature, as explained shortly.

3. Temperature

The thermodynamic definition of temperature is given by

$$\frac{1}{T} = \frac{\partial S}{\partial U}. \quad (14)$$

The connection with statistical mechanics is made through the relation $S = k_b \ln W$, and then related to our construction by using the degeneracy formula $S = k_b \ln (A b^U)$ where $k_b$ is the Boltzmann factor. This yields

$$T = \frac{1}{k_b \ln (b)} \quad (15)$$

which shows that the base of the exponential scaling of the degeneracy in fact defines the temperature. In this work we take $b = 2$ which leads to a temperature of 230.41 degrees Kelvin. We assume that we work in a sufficiently narrow energy range of the bath that $T$ is energy independent.

4. System-Environment Interaction

The SE interaction will be taken to be a random coupling. The SE interaction disrupts the perfect degeneracy pattern defined above. We include the diagonal portion of the SE interaction directly in the $E$ Hamiltonian and represent it as

$$\hat{H}_E^{shift}|m,l\rangle = X(m,l)|m,l\rangle \quad (16)$$

$$\hat{H}_E = \hat{H}_E^0 + \hat{H}_E^{shift} \quad (17)$$
where \( X(m,l) \) is a random variate selected from a gaussian distribution with zero mean and standard deviation, \( \sigma = \alpha \omega E \sqrt{2} \). The eigenvalue equation for the final E Hamiltonian is given by

\[
\hat{H}_E |m,l\rangle = \left[ n \omega_E + X(m,l) \right] |m,l\rangle
\]

This spreading of the degenerate environment eigenvalues is shown in Figure 1 by the gaussians centered on each level.

The composite SE zero-order states \(|n \rangle \otimes |m,l\rangle \equiv |n,m,l\rangle\) have off-diagonal elements

\[
\langle n,m,l| \hat{H}_{SE} |n',m',l'\rangle = Y(n,m,l)
\]

where \( Y(n,m,l) \) is a random variate selected from a gaussian distribution with zero mean and standard deviation \( \sigma = \alpha \omega_E \). (Note that although \( \alpha \) is the same, this is a different standard deviation than above.) To maintain a Hermitian matrix, we generate random variates only for the upper triangle and map these to the lower triangle. The resulting Hamiltonian is diagonalized to yield the energy eigenvalues and vectors of SE, which allows for analytic time propagation of the initially selected states.

5. Simulation Basis and “Microcanonical Shell”

The system basis \( \{|n\rangle\} \) consists of \( N_S = 6 \) states with \( n = 0 \cdots 5 \). Our environment basis has zero-order quantum numbers \( m = 0 \cdots 7 \) with a degeneracy pattern \( 6 \times \{1,2,4 \cdots 128\} \) (see discussion above of environment energy pattern and temperature) or \( N_E = \{6 + 12 + 24 + \cdots + 768\} = 1530 \) states, for a total of \( N_{SE} = N_S \times N_E = 9180 \) SE basis states.

We will work with initial SE states that have a zero-order energy \( \sim 5 \), thus SE energy quantum numbers with \( n + m = 5 \). Since the S states are singly degenerate with energy \( = 0 \cdot 5 \) and the first six E levels have energy \( \leq 5 \), there are a total of 378 SE zero-order states with energy \( \sim 5 \). These comprise a “microcanonical shell” with energy \( E \sim 5 \). This scheme is illustrated in Fig. 1.

6. Initial State Selection

We choose the initial state of SE to be a pure superposition state of the \(|n,m,l\rangle\) basis states, with equal coefficients for each E basis state. We do this not because this particular initial state is
FIG. 1: Energy level diagram and “microcanonical shell” scheme for the system + environment universe SE, from Ref. [1]. There are 6 system eigenlevels and 8 environment energy levels. The degeneracy scheme for the environment is shown along with a small gaussian spread for the environment levels. We select initial states of the system and environment making use of the notion of a constant total universe energy $E \sim 5$ (dotted red line) with the initial system state thought of as a fluctuation within the SE universe, enabled by the environment bath. For a given fluctuated system state (colored dot on system level) the corresponding environment state (matching colored dot on environment level) is chosen in order to conserve the total universe energy. The set of all zero order levels with total energy $E \sim 5$ constitutes the microcanonical shell.

necessarily more likely than others, but simply as a reflection of our ignorance about the condition of the environment in the initial state. The equal coefficient assumption may be said to correspond to “microcanonical” conditions of the environment in the initial fluctuated system state. We illustrate the balance between the total universe energy with the portion placed in $S$ and $E$ in Figure 1. For example, if we have a total universe energy of 5 and we wish to place the system initially in the third $S$ energy level ($n = 2$, dark blue dot), then in order to maintain the total energy of the universe $E$ must occupy the fourth environment energy level ($m = 3$, dark blue dot). All of the quasi-degenerate levels for the fourth $E$ have equal initial probability, which is equivalent to supposing that we are starting our state on a particular energy “micro-shell” given our fluctuated $S$ state. The choice of the total energy in the universe is arbitrary; by picking 5 we are able to excite all levels within $S$ as illustrated by the series of colored circles in Figure 1. In this work we made use of 6 $S$ eigenlevels and 8 $E$ eigenlevels with the degeneracy scheme in Figure 1. We note that more $E$ levels than $S$ levels are included (8 vs. 6, neglecting degeneracy). This choice yielded more consistent results for the fitted temperature obtained for each initial state. One way of thinking about this result is that the “extra” $E$ energy levels are needed to converge the calculation.
B. Dynamical Analysis

1. Reduced Density Matrix and Entropy

We perform analytic time propagation of the initial states, using an expansion in terms of the eigenstates of the SE universe, to obtain the time dependent SE state $|\Psi(t)\rangle$ and from it the reduced density matrix. We begin with the universe density operator $\rho_{SE}$ and calculate the RDM $\rho_S = Tr_E \rho_{SE}$ with matrix elements

$$\rho_S^{n,n'} = \sum_{m,l} \langle n,m,l|\Psi(t)\rangle \langle \Psi(t)|n',m,l \rangle$$

where the summation gives the trace over E.

C. Free Energy Calculation

The calculation of the change in the free energy of the system is based on system properties including the von Neumann entropy, calculated entirely from the RDM of the system $\rho_S$:

$$\Delta F_{sys} = \Delta U_s - T \Delta S^N_s$$

$$U_s = \langle E \rangle_S$$

(Here $sys$ refers to the generic system as in Eq. 2, and $S$ refers to the model system as in Eq. 10.) We use the temperature $T = 230.41$ from the analytic degeneracy formula in Ref. [1]. Another possibility would be to use the temperature obtained from fitting the reduced system density to a Boltzmann distribution, a procedure we compared to $T$ in Ref. [1]. This gave a fluctuating $T_{fit}$ in reasonably good agreement with $T = 230.41$, but using $T_{fit}$ here in the present application gives decidedly inferior results (which we do not report here) to the analytic $T = 230.41$. 

15
FIG. 2: Total entropy of the universe calculated using $\sum_i p_i \ln(p_i)$ where the $p_i$'s are the populations in the zero order basis of the universe. The total universe basis has a size of 9180 (6 system levels times 1530 environment levels).

V. RESULTS

A. Universe Entropy and System Free Energy

Figure 2 shows the calculations of irreversible entropy production $\Delta S_{univ}$ as a function of time for each initial state. Figure 3 shows comparison of the $\Delta S_{univ}$ with the $\Delta F_{sys}$ calculations. In general, they compare well, with some interesting differences along the way evolving in time. We will briefly consider these anomalies after first discussing the generally good agreement with Eq. 2 and its connection to the general principles enunciated earlier.

B. Microcanonical spreading and state fragmentation

Earlier we framed our expectations of the quantum thermodynamic procedure by appeal to the idea of the microcanonical ensemble of classical statistical mechanics. Here we examine to what extent a notion of and microcanonical behavior is observed in the quantum simulations. Micro-
FIG. 3: A comparison of two methods of calculating the free energy change. The solid lines represent $\Delta U_S - T \Delta S_S$ with $T = 230$ Kelvin. The dashed lines represent $-T \Delta S_{\text{univ}}$ also with $T = 230$ Kelvin.

canonical behavior would be observed if through a process of equal “fragmentation,” all of the $p_i$ in Eq. 7 turned out to be equal $p_i = 1/W$ for the “microcanonical shell” of $W$ energetically accessible states, and all other $p_i$ were zero for basis states outside the shell. However, this seems a problematic notion. As discussed in Section III C, there is no reason whatsoever to expect a priori that the instantaneous values $p_i = |c_i(t)|^2$ should all be equal to a single value $1/W$. Our definitions do not involve even implicitly a notion of time averages or “ergodic” behavior. Furthermore, as noted already, there is no exact notion of a microcanonical shell because the states considered are time-dependent, with no exactly defined energy. There would be no point in using the entire SE basis in the simulations if the dynamics were expected to be confined to the basis of the microcanonical shell! On the other hand, complete “fragmentation” within the entire SE product basis of dimension $N_{SE} = N_S \times N_E$ seems out of the question at less than infinite temperature, and in any case would not correspond to a sensible idea of microcanonical behavior at fixed energy.

The actual behavior in the simulations tells a story that weaves an interesting pathway amidst
these conflicting considerations. As noted above, we can define a kind of microcanonical shell of zero order SE states with zero order energies $E \sim 5$. We determined above that there are 378 such zero order states, out of a total of 7180 states in our full zero order SE basis. It is very interesting that in the simulations of Fig. 2, we find in all cases a final $S_{univ} \sim 6$. Exponentiating to get an effective number of states, we find $e^6 \sim 403$, a pretty good match to a microensemble with 378 states. (The actual range observed for all initial states is $S_{univ} = 5.97 - 6.02$.)

![FIG. 4: A plot of $p_i$ versus the zero order energy for the states with $E \sim 5.0$ for the $n = 0$ initial state. The three panels show various levels of detail discussed in the text.](image)
We explore this observation further by examining the $p_i$ of the states of the zero order basis in the expansion (4) for $|\Psi(t)\rangle$. With exact equal fragmentation confined within the $E = 5$ microcanonical shell, 378 of the zero order states would have $p_i = 1/378$ and all the remaining states of the 7180 member basis would have $p_i = 0$. What is actually obtained in the simulations is shown in Fig. 4. These are a set of stick diagrams for the entire SE basis for the late-time SE state $|\Psi(t)\rangle$ obtained by time evolving the initial $n = 0$ state in interaction with the environment. (The diagrams for all the initial states $n = 0 - 5$ are qualitatively very similar). The stick diagram shows the magnitudes $p_i$ of the zero order SE states in the final equilibrated state pure SE state $|\Psi(t)\rangle$ (at a single moment in time – the data are fluctuating). In this “fragmentation” of the final state it can be seen that all the most significant magnitudes are grouped in a narrow band about $E = 5.0$. These are the states with zero order energy around $E = 5$, the notional energy of our microcanonical shell. (Recall that these zero order states have a spread in zero order energy due to the small spread assumed for the environment states). Outside of this band of states around $E = 5.0$, all the $p_i$ are small, but visible in the stick diagram for zero order states of zero order energy $E \neq 5.0$, especially 4.0 and 6.0. As we shall see, these small contributions from the other energy microshells are and important.

The magnitude of the sticks in the $E = 5.0$ band show considerable variation. These are far from being all equal and hence are not very close to “microcanonical” behavior within the energy shell. This is shown in fine detail in the bottom panel of Fig. 4. It is most interesting that the entropy calculated from the $p_i$ from the $E = 5.0$ microcanonical shell according to

$$\sum_{i,E=5.0} p_i \ln p_i$$  \hspace{1cm} (22)

is not especially close to the observed final $S_{univ} \sim 6$; instead, it is typically $\sim 5$. This means the remainder of the entropy $\sim 1$ comes from contributions from the other bands, mainly $E = 4.0$ and 6.0. Table 1 shows this for all of the initial oscillator energy eigenstates. The entropy contribution from the $E = 5.0$ microcanonical shell corresponds to an effective number of states $e^5 \sim 148$, while the total effective number of states is much larger at $e^6 \sim 403$. Interestingly, this effective number of states is slightly larger than the 378 of the microcanonical shell. This can perhaps be understood as an effect of having a time-dependent quantum state. This is associated with an energy uncertainty, which in turn is associated with an “off-shell” effect on the entropy, making it slightly larger than “microcanonical.” The effect here is consistent with the small energy uncertainty in
TABLE I: The first column is the total entropy $S_{\text{univ}}$ attained for each initial state. The second column if the partial entropy obtained from the subset of states with the microcanonical energy $E = 5$.

| $n$ | $S_{\text{univ}}$ | $S_{\text{partial}}$ |
|-----|-------------------|----------------------|
| 0   | 6.00              | 5.14                 |
| 1   | 6.02              | 5.16                 |
| 2   | 5.97              | 5.08                 |
| 3   | 5.98              | 5.10                 |
| 4   | 5.97              | 5.11                 |
| 5   | 6.00              | 5.14                 |

our simulations. If the explanation of the $S_{\text{univ}}$ “entropy excess” offered here is correct, it is an interesting aspect of quantum thermodynamics of time dependent systems that merits further exploration in future work, especially in systems with much stronger time dependence and quantum energy uncertainty.

To summarize: the $p_i$ for the SE basis states with the microcanonical zero order $E = 5$ are certainly not all equal. The sub-entropy from the microcanonical shell does not nearly equal the actual $S_{\text{univ}}$. However, there are small but significant entropy contributions from other microcanonical shells. Together, all the contributions give a final $S_{\text{univ}} \sim 6$ which is close to the “microcanonical” value of $\ln 378$ for the $E = 5$ shell alone. This means that we are obtaining an effective number of microcanonical states that is close to the microcanonical answer from counting the relevant zero order states. We can say that while complete equal fragmentation is not obtained within either the microcanonical shell or the complete SE basis, a kind of microcanonical fragmentation occurs within an effective basis, mimicking microcanonical behavior in the numerical value of $S_{\text{univ}}$. In fact, there is a slight excess in entropy which has an explanation in terms of the energy uncertainty associated with time-dependent behavior.

C. Anomalies

In Fig. 2 all the initial states evolve to nearly the same final $\Delta S_{\text{univ}}$ with the desired agreement at long times between the free energy and entropy measures, the key relation of Eq. 2. However, along the way there are some anomalies that are worth noting. These have to do in part with whether the differential version Eq. 6 of the fundamental relation Eq. 2 holds at all times. Especially in the bottom panel of Fig. 2 There is a pronounced dip in which the entropy production
\( \dot{S}_{\text{univ}} \) becomes negative for a time. This occurs for all the initial states, at about the same time. The comparison is also interesting in Fig. 3 of the free energy change \( T \Delta F_{\text{sys}} \) with \(-\Delta S_{\text{univ}}\), the key relation in Eq. 2. Though generally they match reasonably well, especially in the long-time equilibrium limit, for shorter times, there are significant differences, especially evident in the bottom panel of Fig. 3. \( S_{\text{univ}} \) (which is shown with a minus sign) increases much more rapidly than the free energy \(-T \Delta F_{\text{sys}}\) at short times, before the dip in \( S_{\text{univ}} \). There is no dip in the free energy, only a point of inflection. It is as if the system is encountering a bottleneck of some kind on the way to equilibrium, reflected as the bump in \(-S_{\text{univ}}\). After surmounting the bottleneck, the free energy declines much more rapidly, before finally flattening out as equilibrium is approached. These anomalies could be truly interesting, but they might also be mere artifacts, related to the harmonic nature of the energy level pattern of both the system and bath. These questions merit further exploration in future work on anharmonic systems.

VI. DISCUSSION: FUNDAMENTAL ISSUES OF QUANTUM THERMODYNAMICS AND STATISTICAL MECHANICS

We have found good correspondence in the quantum simulations between the two sides of Eq. 2 for the system free energy and the entropy of the universe, parallel and consistent with fundamental principles of classical thermodynamics. This has been attained using two very different notions: an entropy of the universe \( S_{\text{univ}} \) defined for the pure state of the system-environment universe; and the free energy of the system using the reduced density operator to get the standard von Neumann entropy of the system \( S^{\text{vN}} \) and the system energy \( \langle E \rangle \). A way to think about this is that the use of the two different entropies \( S^{\text{vN}} \) for the system and \( S_{\text{univ}} \) for the SE universe represents different informational transformations of S and SE in the spontaneous process. The system entropy \( S^{\text{vN}} \) is a measure of loss of information of the system brought about by entanglement, after the process of tracing over the environment in obtaining the reduced density operator. The universe entropy by contrast is a measure of the information content of the pure state of the universe. The change in the universe entropy \( \Delta S_{\text{univ}} \) represents the increase of the complexity of the universe state needed to bring about a given change in energy and information (represented by the von Neumann entropy) of the system. This information about the universe is not actually known or available without going to great trouble to measure it. In this sense, \( \Delta S_{\text{univ}} \) also represents an increase in “unknown information” in a spontaneous process. The two entropies \( S_{\text{univ}} \) and \( S^{\text{vN}} \) can thus be regarded as
having complementary meanings and uses.

We believe our methods and results are broadly consistent with the program of reconciling the “ensemblist” and “individualist” points of view in quantum thermodynamics and statistical mechanics [10]. This program has a venerable line of descent, through Boltzmann, Gibbs, and Einstein [11–16] von Neumann himself [8, 9]; and forward through the modern commentary on von Neumann of Lebowitz et al. [10] and arguably in other contemporary work [17–20] in the foundations of statistical mechanics. The terms “ensemblist” and “individualist” correspond roughly to an ensemble from the reduced density matrix, e.g., the canonical ensemble; and dynamics and entropy of a single pure state of an SE universe. In previous work [1, 4] the compatibility of these approaches was demonstrated in quantum simulations insofar as a thermal distribution is obtained in the process of quantum entanglement of system and environment for a single pure state. It can be said that the quantum canonical ensemble is “embedded” in the microcanonical ensemble. In this paper we have now demonstrated, in simulations, the compatibility of the system property of quantum free energy $F_{sys}$ with the universe pure state property $S_{univ}$. We consider these to be essential steps in the program of reconciling the ensemblist and individualist points of view in the quantum domain.

An unexpected aspect of this is the extent to which the simulations depart from a reasonably strict definition of microcanonical behavior within an energy microshell. It is surprising how much “off-shell” basis states contribute to the entropy $S_{univ}$, though understandable as an essential aspect of quantum time-dependence. On the other hand, the entropies obtained agree rather well with the entropy one would predict simply by counting the number of states in the energy microshell, and making microcanonical “fragmentation” assumptions. Effectively, the SE universe mimics microcanonical behavior while playing a bit fast and loose with the rules and definitions.

In summary, we have found compatibility of the notion of the quantum entropy and free energy of the system with the notion of an entropy of the universe that is defined differently than the von Neumann entropy. This is in accord with the classical statement of the second law of thermodynamics that the entropy of the universe increases in spontaneous processes. Whatever the conceptual virtues or shortcomings of our approach to quantum entropy, it gives impressive numerical results. By this route, it should be possible to use relationships among appropriately defined quantum entropies that mirror and preserve the conventional relationships of standard thermodynamics. At the same time, this may open up the exploration of novel quantum thermodynamic effects, for example, in exploration of the interplay of quantum thermal effects with the
emergence of the classical from the quantum world in quantum entanglement.

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