Canonical thermalization

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Abstract. For quantum systems that are weakly coupled to a much ‘bigger’ environment, thermalization of possibly far from equilibrium initial ensembles is demonstrated: for sufficiently large times, the ensemble is for all practical purposes indistinguishable from a canonical density operator under conditions that are satisfied under many, if not all, experimentally realistic conditions.
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1. Introduction

It is commonly accepted that quantum mechanics describes the entire ‘physical world’. In particular, equilibrium statistical mechanics, and possibly also its limitations, should follow from quantum mechanics, although a really satisfying ‘derivation’ still does not seem to be available. The main objective of the present paper is such a derivation of the ‘summit’ [1] of equilibrium statistical mechanics, namely the canonical ensemble, from quantum mechanics in combination with certain, very weak assumptions regarding the preparation, the observables and the Hamiltonian of the system.

A key issue in statistical physics is the lack of knowledge about many ‘details’ of any given ‘real’ system. In particular, the initial condition of the typically $10^{23}$ particles is unknown apart from a few ‘gross’ features, for instance the (approximate) total energy and a few additional macroscopic properties in the case of a non-equilibrium initial condition. The standard way to deal with this incomplete knowledge is to consider a statistical ensemble (many repetitions of the ‘same’ experiment, formally described by a density operator) instead of one particular ‘realization’ of the experiment (formally described by either a pure or a mixed quantum mechanical state). Much less appreciated is the fact that the concrete statistical ensemble for any given ‘real’ system is also largely unknown and would be at least as hard to actually determine as the state of any single realization. It is therefore unavoidable to introduce certain postulates regarding this largely unknown statistical ensemble. Their only justification is their plausibility, an admittedly subjective concept. For instance, the present author finds it not plausible to assume for an isolated macroscopic system at equilibrium a microcanonical ensemble, be it as a postulate per se or as a consequence of some other hypothesis or principle (e.g. the Jaynes principle): its key claim is that if one were able to actually determine the ensemble averaged occupation probabilities of all energy levels, one would always find that all levels within some small energy interval are occupied with exactly equal probabilities and all other levels are not occupied at all. Since level populations are constants of motion, the same properties must apply to the possibly far from equilibrium initial ensemble. This seems indeed very unlikely to be true for any given ‘real’ system, independently of any further ‘details’ of the setup and the preparation. For instructive numerical examples, see e.g. [2].

Put differently, we find it plausible that there exists a well-defined statistical ensemble describing the initial state of any given ‘real’ system. But its details are unknown, probably very complicated, and already quite different even when the ‘same’ experiment is repeated in two different laboratories. Hence the chance that the unknown ‘true’ ensemble happens to agree with any particular ensemble we are postulating is virtually zero. Our present solution of this problem is not to assume any specific form of the ‘true’ initial ensemble, but only some very general ‘gross’ features. Namely, we will assume that the ensemble averaged occupation probabilities of the energy levels can be locally (on the energy axis) averaged in a well-defined manner. We will provide good reasons to expect that real systems satisfy the assumption by closer inspection of the preparation procedure at the origin of the initial condition.

A second important deficit of knowledge is with regard to the appropriate Hamiltonian (and Hilbert space) of the system, generating the time evolution of the initial ensemble. To begin with, we will take it for granted that the system can be treated as strictly closed (isolated, autonomous), although in real systems small remnant interactions with the rest of the world are unavoidable. The main reason is that standard quantum mechanics is only able to describe the evolution in time of closed systems. Open systems, interacting and entangled
with an environment, can be handled only ‘indirectly’, by first including the entire relevant environment of the open system into a closed supersystem, then evolving the latter by standard quantum mechanics and finally eliminating the environment again. Likewise, we assume that after including all relevant perturbations ‘from outside’ into the considered system, it must be possible to theoretically model it as strictly isolated from the rest of the world. If this were not possible, the problem could only be treated by means of a generalization of quantum mechanics. Many (often hidden) hypotheses of how small external perturbations may modify standard quantum mechanics have been proposed. We do not share the viewpoint that such extensions are a pivotal point in the foundation of statistical mechanics. Otherwise, an unavoidable consequence would be that statistical mechanics does not ‘work’ for strictly closed systems. Also numerical evidence seems to support our present viewpoint.

Taking for granted a closed system, the ‘right’ Hamiltonian (and Hilbert space) is still far from obvious, and even the existence of one particular ‘true’ Hamiltonian for any given ‘real’ system is questionable. Our present way to deal with this problem is to focus on ‘generic’ Hamiltonians while leaving any further details unspecified.

The quantum mechanical time evolution generated by the Hamiltonian will not be touched in any way, neither by heuristically modifying it to account for small remnant external perturbations (see above) nor by introducing any kind of approximation. In other words, the well-known time-inversion invariance of quantum mechanics is fully and rigorously maintained.

Within the above general framework, the main subject of our present work is the long-time evolution of a largely arbitrary and possibly far from equilibrium initial ensemble. Specifically, we address the two key claims of statistical mechanics in this context: (i) Equilibration: the ensemble approaches a stationary long-time behavior. (ii) Thermalization: provided the ensemble exhibits a sharply peaked energy distribution, the long-time steady state is captured by (i.e. is experimentally indistinguishable from) the microcanonical ensemble corresponding to the given energy peak. In particular, if the total closed system consist of a subsystem of actual interest which is weakly coupled to a much ‘bigger’ environment (canonical setup), then the steady state of the subsystem alone (after eliminating/tracing out the environment) is captured by the canonical ensemble.

A satisfactory derivation of these cornerstones of statistical mechanics from quantum mechanics is a long-standing and still unsolved fundamental problem [3]–[13], and has recently attracted considerable renewed interest in the context of (almost) integrable many-body quantum systems [2], [14]–[16].

In this work, we address the questions of how far and in what sense equilibration and thermalization can be derived within our above specified general framework with particular emphasis on the canonical setup. The main new results of our present paper are established in sections 9 and 11, demonstrating that in the long-time limit, the reduced state of the ‘small’ system is for all practical purposes indistinguishable from a canonical ensemble. More precisely, the true ensemble itself remains time-dependent forever and thus quite different from the canonical density operator, but the experimentally observable differences between the two ensembles are unresolvably small for the overwhelming majority of times. The other sections of the present paper provide the prerequisites needed in those central sections 9 and 11. They mostly collect and unify but partially also extend previously known material. The final section 12 contains the summary and outlook with a particular emphasis on closely related recent works and on the subject of (almost) integrable many-body quantum systems, which is the focus of the present focus issue.

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2. General framework

According to section 1, we consider an isolated system incorporating all relevant parts of the environment (thermal baths, reservoirs, etc) and modeled according to standard quantum mechanics by an autonomous Hamiltonian $H$ on a (separable) Hilbert space $\mathcal{H}$. Specifically, we focus on spatially finite (compact) systems with a large (macroscopic) but finite particle number, corresponding to $f$ degrees of freedom with

$$1 \ll f < \infty.$$  \hfill (1)

As a consequence, all eigenvectors of $H$ represent bound states and hence the spectrum of $H$ is discrete (quantized). As usual, $|n\rangle$ ($n = 0, 1, \ldots$) denote the (typically infinitely many) eigenvectors of $H$ and the corresponding eigenvalues $E_n$ are assumed to be ordered,

$$E_0 \leq E_1 \leq E_2 \leq \ldots$$  \hfill (2)

with a finite ground state energy $E_0 > -\infty$ [17]. In other words, the Hamiltonian can be written as

$$H := \sum_n E_n |n\rangle\langle n|,$$  \hfill (3)

where $\sum_n$ indicates a summation over all $n = 0, 1, \ldots$.

For any function $g : \mathbb{R} \to \mathbb{R}$ we adopt the common definition

$$g(H) := \sum_n g(E_n) |n\rangle\langle n|.$$  \hfill (4)

In the special case of a power series, $g(x) = \sum_k g_k x^k$, one readily sees that (4) reproduces $\sum_k g_k H^k$, as it must. But (4) also covers more general functions $g(x)$.

Degenerate energies correspond to equality signs in (2). Yet, sums like in (3) and (4) are meant to run over all $n$-values.

For any energy eigenvalue $E_n$, the projector onto the associated eigenspace of $H$ is given by

$$P_{E_n} := \sum_{m=E_n} |m\rangle\langle m|,$$  \hfill (5)

where $\sum_{E_n=E_m}$ indicates a summation over all $m$-values satisfying $E_m = E_n$. It follows that $P_{E_m} = P_{E_n}$ for degenerate energies $E_m = E_n$. Consequently, the identity operator

$$1_\mathcal{H} := \sum_n |n\rangle\langle n|$$  \hfill (6)

can be rewritten as

$$1_\mathcal{H} = \sum_{E_n} P_{E_n},$$  \hfill (7)

where $\sum_{E_n}$ indicates a summation over all mutually different $E_n$-values, i.e. degenerate energies only appear once in the sum. Likewise, the Hamiltonian from (3) can be rewritten as

$$H = \sum_{E_n} E_n P_{E_n}.$$  \hfill (8)
2.1. Level counting, entropy, temperature

In the following, we collect some ‘well-known’ results of ‘elementary level counting’. Although some details may be strictly speaking more subtle than we will say below and possibly even not yet proven rigorously in sufficient generality, our present point of view is that these unsolved issues of statistical physics are substantially less critical than those at the actual focus of our present paper (equilibration and thermalization, see section 1). Differently speaking, we will henceforth restrict ourselves to Hamiltonians $H$ that satisfy the properties given below and adopt the common opinion that they cover most cases of practical relevance.

We emphasize that the entire present section exclusively deals with properties of the energy eigenvalues of the Hamiltonian ($3$). In other words, we do not speak about system states at all, and hence the considerations of the present section do not depend on whether the system is in or out of equilibrium, since these are specifications of the system state, not of the system per se.

To begin with, the number of energy levels below any given upper limit $E$ is defined as

$$\Omega(E) := \sum_n \Theta(E - E_n), \quad (9)$$

where $\Theta(x) := \int_{-\infty}^{x} dy \delta(y)$ is the Heaviside step function. The entropy then follows as

$$S(E) := k_B \ln \Omega(E), \quad (10)$$

where $k_B$ is Boltzmann’s constant. (The more common definition $S(E) := k_B[\ln \Omega(E) - \ln \Omega(E - \Delta E)]$ with a small but finite $\Delta E$ is well known to be equivalent to (10) but would be less convenient later on.) Focusing on the most common case, the entropy is an extensive quantity. For a system with $f$ degrees of freedom, $S(E)/k_B$ is thus very roughly speaking comparable in order of magnitude to $f$,

$$S(E)/k_B = O(f). \quad (11)$$

It follows from (9) and (11) that in macroscopic systems with $f = O(10^{23})$ degrees of freedom the energy levels are unimaginably dense on any decent energy scale: for instance, within an energy interval of $10^{-10^{20}}$ Joules there will still be of the order of $10^{10^{23}}$ levels. On these exceedingly tiny scales, the step function appearing in (9) is considered to be actually ‘washed out’, so that $\Omega(E)$ becomes a reasonably smooth function of $E$ with a well-defined derivative

$$\omega(E) := \Omega'(E) = \sum_n \delta(E - E_n), \quad (12)$$

where also the delta-function $\delta(x) = \Theta'(x)$ is considered as ‘washed out’ over many energy levels. In other words, $\omega(E)$ represents the density of states. The correspondingly washed out entropy (10) gives rise to the usual definition of temperature,

$$T(E) := 1/S'(E). \quad (13)$$

Combining (9), (10) and (12), (13) yields the useful relation

$$k_B T(E) = \Omega(E)/\omega(E). \quad (14)$$

We reiterate that in our present work, entropy and temperature are by definition given by (10) and (13), and as such are for the moment completely independent of the question of whether the considered system is at equilibrium or not. In particular, we did not establish any relation so far between the energy $E$ and the state of the system.

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The following statements can be readily verified for simple examples like the ideal gas. More detailed estimates, which we omit here, indicate that they in fact remain true quite generally: the actual dependence of the right-hand side of equation (11) on $E$ is such that the entropy approaches zero for $E \downarrow E_0$, but for the rest (i.e. for macroscopic values of $E - E_0$), the dependence on $E$ is comparably weak, essentially of logarithmic form. Likewise, (13) approaches zero for $E \downarrow E_0$. Combining all these properties of $S(E)$ with (11) we can conclude that

$$k_B T(E) = \mathcal{O}\left(\frac{E - E_0}{f}\right)$$

and hence

$$T(E + \Delta E) = T(E) \left[1 + \mathcal{O}\left(\frac{\Delta E}{E - E_0}\right)\right].$$

Note that if we did not avoid speaking about equilibrium states, then (15) could also be justified via the equipartition of energy for an extensive systems with energy $E$ at equilibrium.

Finally, we can infer from (15) and the derivative of this relation in combination with (13) that

$$-\frac{S''(E)}{k_B} = \frac{k_B T'(E)}{[k_B T(E)]^2} = \mathcal{O}\left(\frac{f}{(E - E_0)^2}\right).$$

Similarly to the first paragraph of this section, we may take the alternative point of view that we only consider model Hamiltonians $H$ that capture the following common property of real systems reasonably well: if the macroscopic system energy $E$ is changed by an amount $dE$, then the microscopic kinetic energy per degree of freedom $k_B T(E)/2$ changes by an amount that is very roughly of the order of magnitude of $dE/f$, i.e.

$$k_B T'(E) = \mathcal{O}(1/f).$$

Since $T(E_0) = 0$, integration of (18) implies (15) and (17). Similarly, the third law $S(E_0) = 0$ and (13) yield upon another integration the relation (11) and the logarithmic dependence of $S(E)$ on $E - E_0$ mentioned above (15).

It is well known that all these relations may become problematic for extremely low temperatures. Such cases are tacitly excluded from now on.

2.2. System states and dynamics

According to standard quantum mechanics, the state of the system is at any time instant $t$ given by a density operator $\rho(t)$. While we are mainly interested in statistical ensembles (mixed states) in this paper, it is nevertheless worth pointing out that formally our considerations will also cover pure states as a special case. The time evolution can be written as

$$\rho(t) = U_t \rho(0) U_t^\dagger$$

with the unitary propagator

$$U_t := \exp(-iHt/\hbar) = \sum_n \exp(-iE_n t/\hbar)|n\rangle\langle n|,$$

where we have exploited (4) in the last relation. Denoting the matrix elements of $\rho(t)$ by

$$\rho_{mn}(t) := \langle m|\rho(t)|n\rangle,$$
equations (19) and (20) yield for an arbitrary initial condition \( \rho(0) \) at time \( t_0 = 0 \) the result
\[
\rho(t) = \sum_{mn} \rho_{mn}(0) e^{-i[E_m - E_n]t/\hbar} |m\rangle \langle n|,
\]
where \( \sum_{mn} \) indicates a summation over all \( m, n = 0, 1, 2, \ldots \).

2.3. Level populations

Level populations are denoted by \( p_n \) and refer to the ensemble averaged occupation probabilities of the energy eigenstates \( |n\rangle \). In other words, \( p_n \) is the expectation value of the observable \( |n\rangle \langle n| \).

According to (21) and (22) it can be rewritten as
\[
p_n := \text{Tr}(|n\rangle \langle n| \rho(t)) = \rho_{nn}(t) = \rho_{nn}(0)
\]
independently of \( t \).

Since every density operator \( \rho(t) \) is, for any value of \( t \), non-negative and Hermitian, it follows that \((\psi, \phi) := \langle \psi | \rho(t) + \epsilon | \phi \rangle \) satisfies the scalar product axioms for any \( \epsilon > 0 \). Hence, the Cauchy–Schwarz’s inequality applies, i.e. \( |(\psi, \phi)|^2 \leq (\phi, \phi)(\psi, \psi) \). In the limit \( \epsilon \to 0 \) we thus obtain
\[
|\rho_{mn}(t)|^2 \leq \rho_{nm}(t) \rho_{nn}(t) = p_n p_m.
\]

Similarly to (23), the ensemble averaged occupation probability \( p_{E_n} \) of an energy eigenvalue \( E_n \) is given by the expectation value of the projector (5) onto the corresponding eigenspace and can be rewritten as
\[
p_{E_n} := \text{Tr}(P_{E_n} \rho(t)) = \sum_{E_m = E_n} \rho_{mm}(t) = \sum_{E_m = E_n} p_m,
\]
independently of \( t \). For convenience, the \( p_{E_n} \) will also sometimes be called level populations.

The obvious normalization conditions are
\[
1 = \text{Tr}\rho(t) = \sum_n \rho_{nn}(t) = \sum_n p_n = \sum_{E_n} p_{E_n}.
\]

Since \( P_{E_n} \rho(0) P_{E_n} \) commutes with \( H \) from (8), we can, without loss of generality, choose a basis in which both operators are simultaneously diagonal. In the following, \textit{we always work with this specific energy basis} due to its convenient property that all the non-diagonal elements of \( P_{E_n} \rho(0) P_{E_n} \) vanish,
\[
\rho_{mn}(0) = 0 \quad \text{if} \quad m \neq n \quad \text{and} \quad E_m = E_n.
\]

Given any ensemble \( \rho(t) \), let \( \mathcal{H}_+ \subset \mathcal{H} \) be the sub-Hilbert space spanned by those basis vectors \( |n\rangle \) for which \( p_{E_n} \neq 0,
\]
\[
\mathcal{H}_+ := \text{span}(|n\rangle | p_{E_n} > 0|).
\]

Exploiting (24) it follows that \( \rho_{nn}(t) = 0 \) whenever \( \rho_{nn}(t) = 0 \) or \( \rho_{mm}(t) = 0 \). Denoting by \( P_+ \) the projector onto \( \mathcal{H}_+ \), we thus can conclude that
\[
\rho(t) := P_+ \rho(t) P_+.
\]
2.4. Observables

As usual, observables are represented by Hermitian operators

\[ A = \sum_{mn} A_{mn} |m\rangle \langle n|, \tag{30} \]

\[ A_{mn} := \langle m|A|n\rangle \tag{31} \]

with expectation value

\[ \langle A \rangle(t) := \text{Tr}\{\rho(t)A\} \tag{32} \]

and, without loss of generality, are assumed not to depend explicitly on time.

According to (29) it follows that

\[ \langle A \rangle(t) := \text{Tr}\{\rho(t)A_+\}, \tag{33} \]

where \( A_+ \) is the projection/restriction of \( A \) onto \( \mathcal{H}_+ \) from (28),

\[ A_+ := P_+ A P_+. \tag{34} \]

In other words, only the sub-Hilbert space \( \mathcal{H}_+ \) and the projected/restricted observables (34) actually matter. Hence, we can from now on replace \( \mathcal{H} \) and \( A \) by \( \mathcal{H}_+ \) and \( A_+ \) whenever it will be convenient.

3. The problem of equilibration

Generically, the statistical ensemble \( \rho(t) \) is not stationary right from the beginning, in particular for an initial condition \( \rho(0) \) out of equilibrium. But if the right-hand side of (22) depends on \( t \) initially, it cannot approach for large \( t \) any time-independent ‘equilibrium ensemble’ whatsoever. In fact, any mixed state \( \rho(t) \) returns arbitrarily ‘near’ its initial state \( \rho(0) \) for certain, sufficiently large time points \( t \), and similarly for the expectation values (32), as demonstrated for instance in appendix D of [18]. We emphasize that these arbitrarily close recurrences do not refer to pure states only (as in the classical Poincaré recurrences) but rather to arbitrary statistical ensembles \( \rho(t) \).

More specifically, consider any \( \rho(t) \) that is not completely independent of \( t \). Then, according to (22), there must exist at least one \( \rho_{mn}(0) \neq 0 \) with \( \omega := [E_n - E_m]/\hbar \neq 0 \). In fact, one expects that one usually finds pairs with \( \omega \)-values ranging from extremely small to extremely large values on the scale of 1 Hz, thus including any experimentally ‘reasonable’ frequency. Focusing on the specific observable

\[ A = \hat{A} + \hat{A}^\dagger, \quad \hat{A} := |m\rangle \langle n|/\rho_{mn}(0), \tag{35} \]

it readily follows from (22) that

\[ \text{Tr}\{\rho(t)A\} = 2 \cos(\omega t). \tag{36} \]

In other words, the ensemble \( \rho(t) \) exhibits permanent oscillations rather than equilibration, at least as far as the observable \( A \) is concerned.

The main implication of the two previous paragraphs is that equilibration, as specified in section 1, cannot be true and hence cannot be proven in full generality and rigor. Put differently, quantum mechanics and equilibration are strictly speaking incompatible. Equilibration can at
most approximately hold true for a restricted class of observables $A$ and initial conditions $\rho(0)$. The main objective of our present work is to show that, and in what sense, this is indeed the case under rather weak restrictions regarding observables and initial conditions. Those are the subject of the next two sections.

4. Realistic observables

The basic idea is that it is not necessary to theoretically admit any arbitrary Hermitian operator $A$ as a possible observable \[19\]–\[22\]. Rather it is sufficient to focus on experimentally realistic observables in the following sense \[23\]: any observable $A$ must represent an experimental device with a finite range of possible outcomes of a measurement:

$$
\Delta_A := \max\langle \psi | A | \psi \rangle - \min\langle \psi | A | \psi \rangle = a_{\text{max}} - a_{\text{min}},
$$

(37)

where the maximization and minimization are over all normalized vectors $|\psi\rangle \in \mathcal{H}$. Accordingly, $a_{\text{max}}$ and $a_{\text{min}}$ are the largest and smallest eigenvalues of $A$.

Moreover, we require that this working range $\Delta_A$ of the device $A$ is limited to experimentally reasonable values compared with its resolution limit $\delta A$. All measurements known to the present author yield less than 20 relevant digits, i.e. $\Delta_A/\delta A \leq 10^{20}$. Maybe some day 100 or 1000 relevant digits will become feasible, but it seems reasonable that a theory that does not go very much beyond that will do. We also remark that range and resolution are specific to the given measurement device, but are (practically) independent of the properties (e.g. the size) of the observed system.

The above specified class of admissible observables clearly includes any realistic measurement apparatus. Yet it turns out that the class of observables that will be admissible in our main results below can still be substantially extended in two steps.

First, as said at the end of section 2.4, we can replace the full Hilbert space $\mathcal{H}$ by the sub-Hilbert space $\mathcal{H}_+$ defined in (28). Accordingly, the full range $\Delta_A$ from (37) can be replaced by the reduced range

$$
\Delta'_A := \max_{\mathcal{H}_+} \langle \psi | A | \psi \rangle - \min_{\mathcal{H}_+} \langle \psi | A | \psi \rangle.
$$

(38)

According to (28), $\mathcal{H}_+$ is at most as large as $\mathcal{H}$. However, in many cases the level populations (25) may be safely negligible, e.g. beyond some finite upper energy threshold, yielding a finite-dimensional $\mathcal{H}_+$, while $\mathcal{H}$ is typically infinite dimensional. Hence, the reduced range $\Delta'_A$ from (38) will be finite even for operators $A$ with an unbound spectrum on $\mathcal{H}$, i.e. for which the full range $\Delta_A$ from (37) is infinite.

Secondly, we consider observables of the form

$$
B(b) := \sum_n b_n |n\rangle \langle n| \tag{39}
$$

with arbitrary real coefficients $b := (b_0, b_1, \ldots)$. In particular, we can conclude from (4) that arbitrary functions $g : \mathbb{R} \to \mathbb{R}$ of $H$ are of this form,

$$
g(H) = B(b) \quad \text{if } b_n := g(E_n). \tag{40}
$$

As it will turn out, it is sufficient to consider instead of $A$ in (38) any observable of the form $A - B(b)$ with arbitrary coefficients $b$. As a consequence, $\Delta'_A$ from (38) can be replaced by

$$
\Delta''_A := \min_b \{ \max_{\mathcal{H}_+} \langle \psi | A - B(b) | \psi \rangle - \min_{\mathcal{H}_+} \langle \psi | A - B(b) | \psi \rangle \}. \tag{41}
$$

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where \( \min_b \) indicates a minimization over all real coefficients \( \mathbf{b} := (b_0, b_1, \ldots) \). In particular, it follows that

\[
\Delta''_A = 0 \quad \text{if } A = B(\mathbf{b}) \quad \text{or} \quad A = g(H)
\]

for some set of coefficients \( \mathbf{b} \) or some function \( g(x) \).

From (37), (38) and (41) we see that

\[
\Delta''_A \leq \Delta'_A \leq \Delta_A.
\]

Rather than requiring that the full range-to-resolution ratio does not exceed \( 10^{20} \), as discussed below (37), it will be sufficient in our central result below to similarly limit the reduced ratio:

\[
\Delta''_A / \delta A \leq 10^{20}.
\]

5. Realistic initial conditions

5.1. Population density

Our key requirement with respect to the initial condition \( \rho(0) \) is that the concomitant ensemble averaged level populations (23) can be written in the form

\[
p_n = h(E_n) + \delta p_n
\]

with a smooth function \( h(E) \) and ‘unbiased fluctuations’ \( \delta p_n \). Physically, \( h(E) \) thus represents a locally averaged level occupation probability, henceforth abbreviated as population density.

To be more precise with respect to (45), we recall that for a system with \( f \) degrees of freedom, there are roughly \( 10^{O(f)} \) energy eigenvalues \( E_n \) per Joule, see section 2.1. Assumption (45) means that within any energy interval around some reference energy \( E > E_0 \), which contains very many levels \( E_n \), but which is still exceedingly small on any experimentally resolvable scale, the ensemble averaged level populations \( p_n \) can be split into an approximately constant ‘local’ average value \( h(E) \) and ‘unbiased fluctuations’ \( \delta p_n \), i.e. the average over all \( \delta p_n \) belonging to this interval around \( E \) is negligibly small compared to \( h(E) \) itself. The key point is that \( h(E) \) must be independent of the exact choice of the considered energy interval around \( E \).

Comparable assumptions of well-defined ‘local averages’ are tacitly taken for granted in many different physical contexts. Likewise, we find it quite plausible that the ensemble averaged level populations \( p_n \), although largely unknown (see section 1), still satisfy our present assumption under experimentally realistic conditions. Further arguments are provided in section 5.2 below.

Finally, we emphasize once more that all these considerations concern ensemble averaged level populations, i.e. mean values over many repetitions of an experiment, which the experimentalist would denote as ‘identical’ but are in fact very different on the microscopic level; see section 1.

5.2. System preparation

The key idea is that the initial condition is the result of a preparation process, during which the system was not yet isolated, admitting conclusions about the initial condition itself.

The simplest case consists of a time-dependent parametric change of the Hamiltonian during the preparation phase. More complex, but ultimately applying to every real experiment, is some type of contact with the ‘rest of the world’ prior to the actual isolation of the system.
The first consequence is an entanglement with the rest of the world during the preparation phase \((t < 0)\), implying that the reduced initial state (at \(t = 0\)) of the system (after tracing out the rest of the world) will be a mixed state even for a single realization of the experiment. Already this reduction step brings along a certain ‘randomization’ of the system level populations. More importantly, there will unavoidably arise some kind of time dependences of the system Hamiltonian during the preparatory period \(t < 0\), the last of them being caused by the actual shutting down of all connections with the rest of the world. Such a time dependence of the system Hamiltonian is known to generically entail an approximately diffusive ‘spreading’ of occupation probabilities \([25]\). Since the levels are so exceedingly dense, the diffusion will—already during a very short time span and even for a very weak time dependence of the Hamiltonian—effectively lead to a diffusive randomization of the \(p_n\)’s in accordance with \((45)\).

In theoretical studies, it is quite common to generate the out of equilibrium initial condition by means of a ‘sudden’ (discontinuous) parametric change of the Hamiltonian \([2, 15, 16]\), called ‘quantum quench’. Such a procedure thus misses the above-mentioned diffusive ‘spreading’ of the occupation probabilities.

5.3. Energy density

The energy probability density, or energy density for short, is defined as

\[
\rho(E) := \langle \delta(E - H) \rangle. \tag{46}
\]

Accordingly, \(\rho(E) \, dE\) quantifies the ensemble averaged probability to find a value between \(E\) and \(E + dE\) when measuring the energy of the system.

With \((4), (22), (23)\) and \((32)\) it follows that

\[
\rho(E) = \sum_n p_n \delta(E - E_n) \tag{47}
\]

independently of \(t\). In the same spirit as around \((12)\) and in the discussion of \(h(E)\) below \((45)\), the delta-functions in \((46)\) and \((47)\) are understood to be ‘washed out’ over many energy levels in order to give rise to a well-defined, smooth energy density. As a consequence one finds that \([24]\)

\[
\rho(E) = h(E) \omega(E). \tag{48}
\]

While a detailed derivation of this relation is provided in appendix C, it is intuitively quite obvious: the probability \(\rho(E) \, dE\) to encounter an energy between \(E\) and \(E + dE\) is equal to the locally averaged population \(h(E)\) of the energy levels multiplied by the local level density \(\omega(E)\) times the interval length \(dE\).

5.4. Maximal level population

To get an idea of the exotic orders of magnitudes arising in the context of \((45)\), let us assume that there are exactly \(10^{10^{25}}\) equally spaced energy levels \(E_n\) per Joule and that our energy interval around \(E\) has a length between \(10^{-(10^{25})}\) J and a few J. Then, our interval contains at least roughly \(10^{25(10^{25})}\) energy levels. Assuming that \(h(E)\) is approximately constant within the interval and is zero outside, the normalization \((26)\) implies that \(h(E) = 10^{-O(10^{25})}\) within the interval. Recalling that this is the local average value of \(p_n\), it seems quite reasonable to assume that all the individual \(p_n\) values do not exceed the range between zero and \(10^{10^{25}}\) times.
the average value $h(E)$. Otherwise, the average over the $\delta p_n$'s would not be negligible compared
with $h(E) = 10^{-O(10^3)}$ for every possible choice of the interval.

Returning to the general case, we can conclude that even if $h(E)$ varies very fast on any
experimentally realistic scale and even if the energy levels are populated extremely unequally,
we still expect that $\max_n p_n$ will be extremely small, typically

$$\max_n p_n = 10^{-O(f)}.$$  \hfill (49)

On this rather heuristic level, $(45)$ thus implies $(49)$. Intuitively it even seems plausible that the
two conditions are more or less equivalent.

Next we remark that the mere existence of the level density $(12)$ implicitly takes for
granted that the multiplicities of degenerate energies are not exceedingly large, i.e. very much
smaller than $10^{O(f)}$. There can be little doubt that this assumption will be fulfilled under all
experimentally realistic conditions. Under the very same assumption, we can infer from $(25)$
and $(49)$ the very rough estimate

$$\max_{E_n} p_{E_n} = 10^{-O(f)}.$$  \hfill (50)

Note that $p_{E_n}$ is the occupation probability of $E_n$ from $(25)$ and as such does not refer to
any specific energy basis. In contrast, $(49)$ is implicitly understood with respect to the specific
basis introduced above $(27)$. This is the main advantage of $(50)$ compared to $(49)$.

5.5. Physical arguments

Besides those already discussed in section 5.2, there are the following additional physical
reasons to expect that $(49)$ and $(50)$ are fulfilled under experimentally realistic circumstances.

Firstly, the time–energy uncertainty relation seems to prohibit for all practical purposes the
determination of the system energy with a precision that would be necessary to populate only
a relatively small number of levels with appreciable probability so that $(49)$ and $(50)$ would be
violated.

Secondly, while an ideal energy measurement would, in principle, allow us to prepare the
system at one specific energy eigenvalue, every real (finite resolution) measurement will result
in appreciable probabilities of very many levels.

5.6. Example $(35)$

It is instructive to reconsider our example from $(35)$ and $(36)$ and see what happens to the
concomitant incompatibility with equilibration in the case that we restrict ourselves to realistic
observables and initial conditions, satisfying $(44)$ and $(49)$, respectively. To begin with, one
readily sees that the spectrum of $A$ from $(35)$ (within $\mathcal{H}_+ = \dim \mathcal{H}_+$) consists of two eigenvalues
$a_{\pm} = \pm |\rho_{nm}(0)|^{-1}$ and, in the case $\dim \mathcal{H}_+ > 2$, of one further eigenvalue $a_0 = 0$. With $(24)$,
$(37)$ and $(38)$ we can conclude that

$$\Delta A = \Delta'A = 2|a_{\pm}| \geq 2/\max_n p_n.$$  \hfill (51)

A somewhat more tedious calculation shows that also $\Delta''A$ from $(41)$ coincides with $\Delta A$
in our present example. For experimentally realistic initial conditions we can infer with $(49)$ that
$\Delta A \geq O(10^f)$. For macroscopic systems ($f \gg 1$) it follows that the oscillations from $(36)$
are beyond any realistic experimental resolution limit $\delta A$ according to $(44)$. The same thing may,
alternatively, also be viewed as follows: any single (ideal) measurement process always results
in one of the three outcomes $a_+$, $a_-$ or $a_0$. Hence an infeasible number of repetitions is needed to resolve the order-one variations of the ensemble average (36).

In short, while mathematically speaking the observable (35) indeed leads to perpetual oscillations (36), such oscillations cannot be resolved in practice for experimentally realistic observables and initial conditions.

The above example also suggests that our assumptions of experimentally realistic observables and initial conditions (or some similar restrictions) are almost unavoidable for taming the oscillations in (22) and thus overcoming the concomitant incompatibility with the basic statistical mechanical claim of equilibration; see section 3.

6. Generic Hamiltonians

As detailed in section 1, the ‘true’ Hamiltonian $H$ of a given system is usually not known in detail. Therefore, we assume that these details are of ‘generic’ character in so far as the level counting properties from section 2.1 are satisfied and energy differences $E_j - E_k$ and $E_n - E_m$ are never exactly equal apart from trivial cases. More precisely, we require that

$$\text{If } E_j \neq E_k \text{ and } E_m \neq E_n,$$

then

$$E_j - E_k = E_n - E_m$$

implies

$$E_j = E_n \text{ and } E_k = E_m.$$  \hspace{1cm} (52)

A condition similar to (52) is well known under the names ‘non-resonance condition’ or ‘non-degenerate energy gap condition’ and is considered to be satisfied by generic Hamiltonians; see e.g. [6, 9, 10, 13] and, in particular, section 3.2.1 in [26] and references therein. The essential intuitive argument is as follows: consider an arbitrary ‘path’ $H(\lambda)$ in the ‘space of all Hamiltonians’, parameterized by $\lambda$. In the absence of any special reasons like symmetries, it is quite plausible that every gap $E_n - E_m$ evolves as a function of $\lambda$ somewhat differently from all the other gaps. While we cannot exclude that two gaps may happen to coincide for specific $\lambda$-values, these special points are of measure zero. In other words, Hamiltonians with degenerate energy gaps are of measure zero compared to ‘all’ Hamiltonians.

We remark that our present condition is weaker than the usual non-resonance condition [6, 9, 10, 13, 26] in so far as (52) still admits the possibility of degenerate energy eigenvalues.

7. Equilibration for isolated systems

Being confident that the above-discussed conditions (44), (50) and (52) are fulfilled under many, if not all, experimentally realistic conditions, we henceforth take them for granted and turn to the question of how far they are sufficient to yield equilibration, i.e. a stationary long time behavior of the statistical ensemble (cf section 1).

7.1. Equilibrium ensemble

Given an arbitrary but fixed $\rho(0)$ evolving according to (22), we will see below that the pertinent equilibrium ensemble is given by the density operator (sometimes called the generalized Gibbs ensemble)

$$\rho_{eq} := \rho(t),$$  \hspace{1cm} (53)

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where the time average of an arbitrary function or operator \( h(t) \) is defined as
\[
\overline{h(t)} := \lim_{T \to \infty} \frac{1}{T} \int_0^T dt \ h(t).
\]
(54)

In other words, the equilibrium ensemble \( \rho_{eq} \) is the time averaged ‘true’ ensemble \( \rho(t) \). As such, it is time independent and, moreover, inherits all the defining properties of a genuine density operator from \( \rho(t) \). Namely, one readily sees that \( \rho_{eq} \) is a non-negative, Hermitian operator of unit trace and satisfies the dynamics (22).

Making use of the specific basis introduced above (27), one can conclude— as detailed in appendix D—from (23) and (53) that
\[
\rho_{eq} = \sum_n \rho_{nn}(0) \ |n\rangle \langle n| = \sum_n p_n \ |n\rangle \langle n|.
\]
(55)
i.e. \( \rho_{eq} \) amounts to the (time-independent) diagonal part of \( \rho(t) \) from (22).

Focusing on observables of the specific form (39), it follows with (22) and (55) that
\[
\text{Tr}\{\rho(t) \ B(b)\} = \text{Tr}\{\rho_{eq} \ B(b)\}.
\]
(56)

In particular, we can conclude with (40) that
\[
\text{Tr}\{\rho(t) \ g(H)\} = \text{Tr}\{\rho_{eq} \ g(H)\}
\]
(57)
for arbitrary functions \( g: \mathbb{R} \to \mathbb{R} \).

7.2. Main result

It readily follows from (32), (53) and (54) that
\[
\langle A \rangle(t) = \text{Tr}\{\rho_{eq} \ A\}.
\]
(58)

In other words, on the average over all times \( t \geq 0 \), the ‘true’ statistical ensemble \( \rho(t) \) is indistinguishable from the equilibrium ensemble \( \rho_{eq} \).

The natural next step is to consider the mean square deviation
\[
\sigma^2_A := [\langle A \rangle(t) - \langle A \rangle(t)]^2.
\]
(59)

The following relation is derived in appendix D:
\[
\sigma^2_A \leq (\Delta_A^\prime\prime)^2 \text{Tr}\{\rho_{eq}^2\},
\]
(60)
where \( \Delta_A^\prime\prime \) is defined in (41). The last factor \( \text{Tr}\{\rho_{eq}^2\} \) in (60) is the so-called purity of \( \rho_{eq} \), i.e. the purity of the time-independent part of \( \rho(t) \), but not the purity of \( \rho(t) \) itself. In principle, \( \rho(t) \) may even be a pure state (see above (19)) with a purity of one, while the purity of the concomitant \( \rho_{eq} \) may still be as small as \( 10^{-O(1)} \) according to (50) and the relation (B.1) in appendix B.

Observing that \( \text{Tr}\{\rho_{eq}^2\} = \sum_n \rho_{nn}^2(0) \) according to (55) and introducing relation (B.1) from appendix B into (60) we finally obtain
\[
\sigma^2_A \leq (\Delta_A^\prime\prime)^2 \max_n p_{E_n},
\]
(61)
where \( p_{E_n} \) is the occupation probability of \( E_n \); see (25).

Considering \( \text{Tr}\{\rho(t) \ A\} \) as a random variable, generated by randomly sampling time points \( t \) according to a uniform distribution on \([0, \infty)\), the corresponding mean value and variance are
given by (58) and (59). The next step is to invoke Chebyshev’s inequality [18, 27], stating that for any random variable $x$ with average $\mu$ and variance $\sigma^2$ and any given $\kappa > 0$, the probability $\text{Prob}(|x - \mu| > \kappa)$ that $x$ deviates from $\mu$ by more than $\kappa$ satisfies $\text{Prob}(|x - \mu| > \kappa) < (\sigma/\kappa)^2$.

In our present case, we can thus conclude that

$$\text{Prob} \left( |\text{Tr}\{\rho(t)A\} - \text{Tr}\{\rho_{eq}A\}| \geq \delta A \right) \leq \left( \frac{\sigma_A}{\delta A} \right)^2,$$

(62)

where $\delta A$ is the resolution limit of $A$; see section 4. With (61) we arrive at the first main result of our present paper:

$$\text{Prob} \left( |\text{Tr}\{\rho(t)A\} - \text{Tr}\{\rho_{eq}A\}| \geq \delta A \right) \leq \left( \frac{\Delta A}{\delta A} \right)^2 \max_n p_{E_n},$$

(63)

where $p_{E_n}$ is the ensemble averaged occupation probability of the (possibly degenerate) energy eigenvalue $E_n$; see (25). We recall that the only ingredients in deriving this result were the (generalized) non-resonance condition (52) and the assumption that the measurement range $\Delta A$ from (41) is finite, cf section 4. For the rest, (63) is a completely general and rigorous relation, formally valid for any choice of $\delta A > 0$. It generalizes the previously known result from [12], which did not admit degenerate energy eigenvalues, nor the minimization over arbitrary $B(b)$ in (41).

7.3. Discussion

For realistic initial conditions and generic Hamiltonians we can take for granted the rough estimate (50), yielding with (63) the result

$$\text{Prob} \left( |\text{Tr}\{\rho(t)A\} - \text{Tr}\{\rho_{eq}A\}| \geq \delta A \right) \leq \left( \frac{\Delta A}{\delta A} \right)^2 O(1).$$

(64)

Focusing on large systems (1) we can conclude that for the overwhelming majority of times $t \geq 0$ the difference between $\text{Tr}\{\rho(t)A\}$ and $\text{Tr}\{\rho_{eq}A\}$ is way below the instrumental resolution limit $\delta A$ for any experimentally realistic observable according to (44). In other words, the system looks exactly as if it were in the steady state ensemble $\rho_{eq}$ for the overwhelming majority of times $t \geq 0$, although the ‘true’ density operator $\rho(t)$ is actually quite different; see section 3. This is the main result of our present paper regarding the question of equilibration, see section 1.

Note that these conclusions do not really require a macroscopic number $f$ of degrees of freedom. Put differently, our result also explains the common numerical observation that already quite small particle numbers often equilibrate and thermalize surprisingly well.

As promised in the introduction, the derivation of (61)–(64) is based on the exact quantum mechanical time evolution (19)–(22) without any modification or approximation. In other words, the full quantum mechanical time-inversion invariance is still contained in (64). In particular, (64) is compatible with the recurrence property of $\text{Tr}\{\rho(t)A\}$ mentioned below (34), but implies that such excursions from the ‘apparent equilibrium state’ $\rho_{eq}$ must be exceedingly rare events.

Exactly the same ‘apparent equilibration’ towards $\rho_{eq}$ emerges if one propagates $\rho(0)$ backward in time (keeping the system isolated also for $t < 0$). Along the entire real $t$-axis, an initial condition $\rho(0)$ far from equilibrium thus closely resembles one of the above-mentioned rare excursions, except that the location of this excursion is on purpose chosen as the time origin.
In other words, quantum mechanical time inversion invariance is maintained, but when starting out of equilibrium, an ‘apparent time arrow’ emerges with extremely high fidelity.

Note that any single excursion of $\text{Tr}[\rho(t)A]$ from the ‘apparent equilibrium value’ $\text{Tr}[\rho_{\text{eq}}A]$ is a priori not expected to exhibit any special symmetry with respect to time inversion. Only the probabilistic properties of an ensemble of such excursions are, in the absence of magnetic fields, expected to satisfy a microreversibility or detailed balance type of symmetry with respect to time inversion. Note that these considerations apply both to ‘small’ and ‘large’ excursions.

While (64) provides a bound for the relative amount of time the system exhibits notable deviations from equilibrium, the typical duration of one given excursion, or equivalently, the characteristic relaxation time of an out of equilibrium initial condition $\rho(0)$ remains unspecified. Note that statistical mechanics itself also makes no statements in this respect. Hence, it is justified to omit them within a foundation of statistical mechanics. However, we remark that since our assumptions on the initial condition and Hamiltonian were very weak and we kept the exact quantum mechanical time evolution (19)–(22), we expect that the actual relaxation time will be close to that of the real system we are modeling, provided this modeling is not too bad. Since one can easily imagine real systems with arbitrarily large or small relaxation times, any further quantification of the relaxation process inevitably would require a considerably more detailed specification of the Hamiltonian $H$, the initial state $\rho(0)$ and the observable $A$. Thus, our main result (64) may well be already quite close to ‘the maximum one can say in full generality’.

As mentioned above (19) and below (60), in principle $\rho(t)$ may even be a pure state of the form $|\psi(t)\rangle\langle\psi(t)|$. In this case, the occupation probabilities $p_{E_n}$ of the energy eigenvalues $E_n$ appearing in (63) can be rewritten according to (25) as

$$p_{E_n} = \sum_{E_n=E_n} |\langle\psi(t)|m\rangle|^2.$$  

As long as all these occupation probabilities are small, e.g. satisfying the rough estimate (50), the above relation (64) and the subsequent discussion still remain valid for pure states $\rho(t) = |\psi(t)\rangle\langle\psi(t)|$.

If the system is prepared in a pure energy eigenstate, i.e. $\rho(t) = \rho(0) = |n\rangle\langle n|$, then $\Delta_A'' = 0$ for arbitrary $A$ according to (28) and (41). In other words, (64) still represents a tight upper estimate in this case, which in fact represents ‘the opposite extreme’ compared to the property (49) or (50) of experimentally realistic initial conditions.

Likewise, for observables of the form (39) or of the form $g(H)$ with arbitrary $g$, we have $\Delta_A'' = 0$ in (64) according to (42).

We close with the following conceptual remarks regarding the notion of ‘experimentally realistic observables and initial conditions’. In sections 4 and 5, we have specified certain properties that we propose to be necessary for observables or initial conditions to be considered as ‘experimentally realistic’. But these properties are not meant to be sufficient. While establishing such exact (necessary and sufficient) conditions is not the subject of our present work, we provide some simple examples to illustrate our point: for any $A$ and any fixed $\tau$, the observable $B := U_{\tau}A U_{\tau}^\dagger$ satisfies $\text{Tr}[\rho(t)B] = \text{Tr}[\rho(t-\tau)A]$ according to (19). Whenever $A$ was realistic according to the criterion from section 4, the same applies to $B$ ($\Delta_B = \Delta_A$). According to (32), $B$ imitates (for any $\rho(t)$) the behavior of $A$ with a time delay of $\tau$. If $\rho(0)$ is a far from equilibrium initial condition and $\tau$ exceeds the relaxation time for the time inverted
dynamics, the observable $B$ thus initially behaves as if the system were already equilibrated but then all of a sudden undergoes an excursion as if the system transiently moved very far from equilibrium. Turning to negative $\tau$ values, $B$ would represent a device that can ‘look’—in principle arbitrarily far—into the future. There can be little doubt that such observables are not ‘realistic’. Likewise, for any given $\rho(t)$ satisfying the quantum mechanical time evolution (19), a hypothetical initial condition of the form $\tilde{\rho}_\tau(0) := \rho(-\tau)$ produces analogous ‘unrealistic’ phenomena while being ‘experimentally realistic’ according to section 5 whenever $\rho(0)$ was so (the level populations of $\rho(0)$ and of $\tilde{\rho}_\tau(0)$ are equal). To identify suitable criteria for sorting out such pathologies is a very subtle task, especially in view of the fact that the so-called spin-echo experiments seem indeed to be able to realize such initial conditions $\tilde{\rho}_\tau(0)$ to some extent [28].

8. The problem of thermalization

According to (55) and the discussion below (64), expectation values (32) become practically indistinguishable from

$$\text{Tr}\{\rho_{eq}A\} = \sum p_n A_{nn}$$  \hspace{1cm} (66)

after initial transients have died out. In this respect, the problem of equilibration raised in section 1 can be considered as settled and we can henceforth focus on (66).

Turning to the issue of thermalization, the key question is, thus, how far the equilibrium expectation value of $A$ from (66) is in agreement with that predicted by the microcanonical ensemble, namely

$$\text{Tr}\{\rho^{\text{mic}}A\} = \sum p_n^{\text{mic}} A_{nn},$$  \hspace{1cm} (67)

where the level populations $p_n^{\text{mic}}$ are equal to a normalization constant if $E_n$ is contained within a small energy interval

$$I := [E - \Delta E, E]$$  \hspace{1cm} (68)

and zero otherwise [29].

In the case (66) and (67) yield measurable differences for experimentally realistic $\rho(0)$ and $A$, the ‘purely quantum mechanical’ prediction (66) is commonly considered as ‘more fundamental’ [2, 15, 16]. From this point of view, our derivation of equilibrium statistical mechanics is complete, provided the latter is valid itself.

What are these validity conditions, beyond which the microcanonical formalism of equilibrium statistical mechanics may break down?

A first well-known validity condition for the microcanonical formalism is, as said below (67), that only $E_n$ within a small energy interval (68) have a non-vanishing occupation probability. More generally, as already mentioned in section 1, in equilibrium statistical mechanics it is taken for granted that the system energy is fixed up to unavoidable experimental uncertainties. On the other hand, realistic initial conditions according to section 5 in particular require that this energy uncertainty is much larger than $10^{-0.f}$ Joules, which is obviously always fulfilled in practice, but we have never introduced or exploited any type of upper limit for this uncertainty so far, i.e. the energy uncertainty may still be arbitrarily large in (64) and (66). In other words, for large energy uncertainties, our key relation (66) remains valid, while equilibrium statistical mechanics is likely to become invalid. This is clearly a not at all surprising case of disagreement between (66) and (67).
To avoid such ‘almost trivial’ cases, we henceforth take for granted that the system energy is known up to an uncertainty $\Delta E$ that is as small as possible, but still experimentally realistic, cf section 5.

A second (often tacit) validity condition of the microcanonical formalism is that the expectation values (67) are required/assumed to be (practically) independent of the exact choice of the interval $I$ in (68), i.e. of its upper limit $E$ and its width $\Delta E$. But essentially this means nothing else than:

\[
\text{In (66) the details of } p_n \text{ are largely irrelevant.}
\] (69)

The same conclusion (69) follows from the equivalence of the microcanonical and canonical ensembles (for all energies $E$), considered as a self-consistency condition for equilibrium statistical mechanics [20, 21].

Clearly, given property (69) holds, the expectation values (66) and (67) are indeed practically indistinguishable.

Our first remark regarding property (69) itself is that no experimentalist can control the populations $p_n$ of the unimaginably dense energy levels $E_n$, apart from the very gross fact that they are ‘mainly concentrated within the interval $I$ from (68)’. If the details mattered, not only would equilibrium statistical mechanics break down, but also reproducing measurements, in particular in different laboratories, would be largely impossible; see also the discussion in sections 1 and 5. Secondly, one can readily construct observables and initial conditions, being experimentally realistic according to our definitions in sections 4 and 5 but still violating (69). The fact that equilibrium statistical mechanics is known to have an extremely wide experimental applicability implies that our notion so far of ‘experimentally realistic’ is still too general (see also at the end of section 7.3).

The simplest way to guarantee property (69) seems to require/assume that the expectation values $A_{nn} = \langle n | A | n \rangle$ hardly vary within any small energy interval of the form (68). This is similar in spirit to classical coarse graining and, in fact, is part of a common conjecture about the semiclassical behavior of fully chaotic classical systems (see [9, 30] and references therein). In particular, negligible variations of $A_{nn}$ for close by $n$-values imply Serdicki’s ‘eigenstate thermalization hypothesis’ [31] (anticipated in [7] and revisited in [2]), implying that each individual energy eigenstate $|n\rangle$ behaves like the equilibrium ensemble.

An alternative way to guarantee property (69) follows from the argument by Peres [6] that even if the $A_{nn}$ may notably vary with $n$, the immense number of relevant summands in (66) may—for ‘typical’ $A$ and $\rho(0)$—lead to a kind of statistical averaging effect and thus a largely $\rho(0)$-independent overall value of the sum.

Numerically, the validity and possible failure of such conjectures and of property (69) itself have been exemplified e.g. in [2, 7, 15, 32]. While the details—in particular the role of ‘more basic’ system properties like ‘ergodicity’ and ‘(non)integrability’—are still not very well understood [2, 5, 6, 30, 33, 34], ‘equilibration’ in agreement with (66) was seen numerically in all known cases.

9. Canonical setup

The objective in the remainder of the paper is to establish thermalization without making use of the unproven property (69). While the general case seems extremely difficult to tackle, as discussed above, we focus on the most important special case, namely the so-called canonical
setup: an isolated compound system, consisting of a (sub-)system that is weakly coupled to a ‘heat bath’.

In analogy to section 2, the starting point is a system (subsystem, central system, system of actual interest, index ‘S’) with \( f_S \) degrees of freedom, Hamiltonian \( H_S \), and Hilbert space \( \mathcal{H}_S \) together with an environment (e.g. a heat bath, index ‘B’) with \( f_B \) degrees of freedom, Hamiltonian \( H_B \), and Hilbert space \( \mathcal{H}_B \). As usual, the environment is assumed to be macroscopic and much ‘bigger’ than the system, i.e.

\[
f_B \gg f_S.
\]  

(70)

The system \( S \) may or may not be macroscopic, i.e. \( f_S \) may but need not be a large number (in the range of \( 10^{23} \)). On the other hand, \( f_B \) is of the order of \( 10^{23} \) or even larger (e.g. if \( f_S \) is already of this order). The system-plus-environment compound (total system, supersystem, no index) thus has

\[
f = f_S + f_B
\]  

(71)

degrees of freedom and ‘lives’ in the product space

\[
\mathcal{H} := \mathcal{H}_S \otimes \mathcal{H}_B.
\]  

(72)

The contact (coupling) between the system and the environment is described by an interaction Hamiltonian \( H_{\text{int}}: \mathcal{H} \rightarrow \mathcal{H} \) and a ‘coupling strength’ \( \lambda \), resulting in a total Hamiltonian of the form

\[
H(\lambda) = H_S \otimes 1_{\mathcal{H}_B} + 1_{\mathcal{H}_S} \otimes H_B + \lambda H_{\text{int}}.
\]  

(73)

where \( 1_{\mathcal{H}_S} \) indicates the identity on \( \mathcal{H}_S \), and similarly for \( 1_{\mathcal{H}_B} \).

We will mainly be interested in observables that only concern system properties, i.e. observables that are of the form

\[
A = A^S \otimes 1_{\mathcal{H}_B}.
\]  

(74)

Within this general framework, we take for granted that all conditions for equilibration of the isolated system-plus-bath compound in the sense of section 7 are fulfilled, i.e. the observables (74) satisfy (44), the ensemble averaged energy level populations satisfy (50), and the Hamiltonian (73) satisfies the generalized non-resonance condition (52). As expected and demonstrated in detail later, these requirements in particular rule out \( \lambda = 0 \). A further requirement is the subject of the next subsection.

9.1. Weak coupling condition

Some kind of weak coupling assumption is an indispensable (although often tacit) prerequisite of the canonical formalism. The simplest possibility would be to require that \( \lambda \) in (73) is so small that the eigenvectors \( |n\rangle \) and eigenvalues \( E_n \) of \( H(\lambda) \) deviate only very little from those of \( H(0) \). However, according to ordinary perturbation theory, these deviations will be governed by terms of the form \( \lambda \langle m|H_{\text{int}}|n\rangle/[E_m - E_n] \). Since some \( E_m - E_n \) are of the order of \( 10^{-O(f)} \) Joules (see below (11)), the admissible \( \lambda \)-values would be so small that no realistic model would satisfy the condition.

For this reason, we henceforth focus on system-plus-bath compounds (73) that satisfy the following ‘operational’ weak coupling condition: after equilibration of the system-plus-bath compound, a reversible (adiabatically slow) decoupling of the system from the bath does not lead to any experimentally resolvable changes.
As far as expectation values of system observables $A$ are concerned, we recall that the ‘true’, time-dependent expectation values $\langle A \rangle(t)$ may, even after equilibration, still exhibit quite notable ‘excursions’ at exceedingly rare time points $t$ (cf section 7). In this case, the above weak coupling condition tacitly refers to time-averaged expectation values.

The quantities, for which the weak coupling condition will actually be taken for granted later on, are observables of the form (74) and the energy density (46) of the total system-plus-bath compound.

Physically, there can be little doubt that most real systems in contact with a heat bath satisfy the above weak coupling condition. Hence, the same is expected for ‘realistic models’ of such systems. Yet, in view of the perturbation theoretical considerations above, a mathematical proof for any given model seems extremely difficult. In fact, the condition concerns not only the Hamiltonian (73) but simultaneously the observables (74) and initial conditions $\rho(0)$ (cf section 5) of the system-plus-bath compound. The nature and difficulty of the problem may become more evident by considering a particularly ‘simple’ special case, namely observables of the form (74) and canonical density operators. In this special case, we may consider the relation
\[
\text{Tr} \left\{ \frac{e^{-H(\lambda)/k_B T}}{Z(\lambda)} A \right\} = \text{Tr}_S \left\{ \frac{e^{-H_S/k_B T}}{Z_S} A^S \right\},
\]
(75)
with $A$ from (74), $H(\lambda)$ from (73), Tr and Tr$_S$ indicating the traces over the Hilbert spaces $\mathcal{H}$ and $\mathcal{H}_S$ in (72), respectively, and $Z(\lambda)$ and $Z_S$ representing standard partition sums, normalizing the respective density operators. This relation (75) is an elementary identity for $\lambda = 0$, is usually considered as ‘obvious’ for ‘weak coupling’, but to the best of the present author’s knowledge is unproven (and probably wrong and thus unprovable without strong extra assumptions on $A^S$) for small but still experimentally realistic coupling strengths $\lambda$.

Since the solution of these long-standing and very subtle problems is not the actual main theme of our present work, we adopt the standpoint that the above weak coupling condition is an implicit additional requirement regarding experimentally realistic Hamiltonians, observables and initial conditions on top of the previous requirements (44), (50) and (52). In all of what follows, we focus on systems that satisfy all those requirements, being confident that they include the majority of experimentally realistic models.

9.2. Main implications of weak coupling

The ‘true’ time-averaged expectation values are, according to (58), given by
\[
\langle A \rangle(t) = \text{Tr}\{\rho_{\text{eq}}(\lambda) A\},
\]
(76)
where the argument $\lambda$ of $\rho_{\text{eq}}$ has been added to remind us of the fact that we are dealing with the given, ‘true’ Hamiltonian (73) with a ‘small’ but non-vanishing coupling strength $\lambda$. Likewise, the ‘true’ density operator from (22) is now rewritten in the form
\[
\rho(t) = \sum_{mn} \rho_{mn}(0) e^{-i\omega_{mn}(\lambda)t} D_{mn}(\lambda)
\]
(77)
where $\omega_{mn}(\lambda) := [E_m(\lambda) - E_n(\lambda)]/\hbar$, $D_{mn}(\lambda) := |m(\lambda)\rangle \langle n(\lambda)|$, and where $|n(\lambda)\rangle$ and $E_n(\lambda)$ refer to the eigenvectors and eigenvalues of the Hamiltonian (73) for an arbitrary but fixed $\lambda$-value.
As soon as $\lambda$ in (73) starts to change in the course of time, the density operator is no longer given by (22) but rather follows from the Liouville–von Neumann equation

$$i\hbar\dot{\rho}(t) = [H(\lambda(t)), \rho(t)].$$

(78)

While an explicit solution for general protocols $\lambda(t)$ is hopeless, in the special case of adiabatically slow (quasi-static) parameter changes, the Adiabatic Theorem can be invoked to yield

$$\rho(t) = \sum_{mn} \rho_{mn}(0) e^{-i\int_0^t \omega_{mn}(\lambda(s))\,ds} D_{mn}(\lambda(t)),
$$

(79)

where we have tacitly restricted ourselves to the simplest and most relevant case of non-degenerate energy levels, see also appendix E.

The adiabatically slow decoupling process appearing in the weak coupling condition (section 9.1) means that $\lambda(t)$ in (79) is given during a large but finite initial time span by the ‘true’, finite coupling strength, then adiabatically slowly changes to the value zero and afterwards remains zero for all later times $t$ until infinity. Consequently, the time average of the density operator in (79) is governed by the infinitely long time period with $\lambda(t) = 0$, i.e.

$$\langle \rho(t) \rangle = \sum_{n} \rho_{nn}(0) |n(0)\rangle \langle n(0)|.$$

(80)

Invoking the weak coupling condition from section 9.1, it follows that the ‘true’ time-averaged expectation values (76) are practically indistinguishable from those obtained with the help of (80), i.e.

$$\langle A(t) \rangle = \sum_{n} p_{n} \langle n(0) | A | n(0) \rangle,$$

(81)

where $p_{n} := \rho_{nn}(0) = \langle n(\lambda(0)) | \rho(0) | n(\lambda(0)) \rangle$ are the level populations of the ‘true’ system at time $t = 0$, cf (23). In other words, although the true system–bath coupling strength $\lambda$ is finite, we can formally work in the zero coupling limit as far as time-averaged expectation values are concerned.

A well-known further consequence of the Adiabatic Theorem (79) is the time independence of the level populations $\langle n(\lambda(t)) | \rho(t) | n(\lambda(t)) \rangle$, which can thus be identified with $p_{n} = \rho_{nn}(0)$ for all times $t$. Considering $\lambda$ rather than $t$ as an independent variable, we may equivalently say that the $p_{n}$ are $\lambda$ independent. It follows that in the relation $p_{n} = h(E_{n}(\lambda)) + \delta p_{n}$ from (45), the right-hand side must be $\lambda$ independent in the same sense. By locally averaging over many $n$-values (see below (45))\(^1\), we can conclude that also $h(E_{n}(\lambda))$ must be $\lambda$-independent.

In view of the $\lambda$-dependence of $E_{n}(\lambda)$ it follows that also the function $h(E)$ generally must acquire a dependence on $\lambda$. Indicating this fact by adding an index $\lambda$ to $h(E)$, we can conclude that

$$h_{\lambda}(E_{n}(\lambda)) = h_{0}(E_{n}(0))$$

(82)

for all $n$ and that relation (45) now takes the form

$$p_{n} = h_{\lambda}(E_{n}(\lambda)) + \delta p_{n}$$

(83)

\(^1\) In doing so, we have without loss of generality assumed a labeling of the $E_{n}(\lambda)$ so that $E_{n+1}(\lambda) \geq E_{n}(\lambda)$ for all $n$ (cf (2)) independently of $\lambda$ and thus local averages always involve the same subsets of levels in the vicinity of a given $E_{n}(\lambda)$, independently of $\lambda$; see also appendix E.
with $\lambda$-independent $p_\sigma$ and $\delta p_\sigma$. Likewise, the density of states (12) and the energy density (47) acquire a $\lambda$ dependence and, thus, are now denoted by $\omega_\lambda(E)$ and $\rho_\lambda(E)$, respectively. Similarly to (48), one can conclude (see footnote 1) that

$$\rho_0(E) = h_0(E) \omega_0(E).$$

Finally, the weak coupling condition as discussed in section 9.1 includes the practical indistinguishability of the ‘true’ energy density from the energy density after decoupling the system from the bath, i.e.

$$\rho_\lambda(E) = \rho_0(E).$$

9.3. Zero coupling limit

We consider the Hamiltonian (73) in the limit of vanishing coupling strength $\lambda$. Denoting by $|n\rangle_S$ and $E^S_n$ the eigenvectors and eigenvalues of $H_S$ and by $|m\rangle_B$ and $E^B_m$ those of $H_B$, those of (73) with $\lambda = 0$ follow as

$$|nm\rangle := |n\rangle_S|m\rangle_B,$$

$$E_{nm} := E^S_n + E^B_m.$$  

9.3.1. Violation of the non-resonance condition. The fact that systems consisting of non-interacting sub-systems require special attention with respect to the generalized non-resonance condition (52) was first noted in [13].

Taking into account that the original indices in (52) now become double indices according to (87), condition (52) takes the modified form

If $E_{j_1j_2} \neq E_{k_1k_2}$ and $E_{m_1m_2} \neq E_{n_1n_2}$,

then $E_{j_1j_2} - E_{k_1k_2} = E_{n_1n_2} - E_{m_1m_2}$

implies $E_{j_1j_2} = E_{n_1n_2}$ and $E_{k_1k_2} = E_{m_1m_2}$.  

One readily sees that this condition is violated by considering the following specific choice [13]: $j_1 = k_1 = n_2 =: n$ and $k_2 = m_1 = m_2 = n_1 =: m$. In the generic case, it will be possible to find indices $n$ and $m$ so that all four energies $E_{nn}$, $E_{nm}$, $E_{nn}$ and $E_{nm}$ appearing in (88) are different. With (87) it follows that $E_{nn} - E_{nm} = E_{nn} - E_{nm}$. In other words, condition (88) is violated.

9.3.2. Exploiting the product basis. The purpose of this subsection is to rewrite the pertinent relations from section 9.2 in terms of the product energy basis (86) and the corresponding energy eigenvalues (87) in the zero coupling limit.

Essentially, we are just relabeling all eigenvectors and eigenvalues in a way that will turn out particularly convenient later on. Namely, all the single labels $n(\lambda)$ are now replaced by double labels $nm(\lambda)$ with the additional convention that the argument $\lambda$ will be omitted in the case $\lambda = 0$, in agreement with the notation in section 9.3.1. Note that only in the zero coupling limit does the first of the two indices in $nm$ refer to the system and the second to the bath, but not any more for $\lambda \neq 0$.

Specifically, $|n(0)\rangle$ and $E_n(0)$ from section 9.2 are now denoted as $|nm\rangle$ and $E_{nm}$ and satisfy (86) and (87). Likewise, $|n(\lambda)\rangle$ and $E_n(\lambda)$ are now denoted as $|nm(\lambda)\rangle$ and $E_{nm}(\lambda)$. Finally, the $\lambda$-independent level populations $p_\sigma$ now become $p_{nm}$. 

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For observables of the form (74), the time-averaged expectation value (81) can thus be rewritten as

\[
\langle A \rangle(t) = \sum_{mn} p_{nm} s \langle n | A^s | n \rangle_s
\]

\[
= \sum_n p^s_n s \langle n | A^s | n \rangle_s, \tag{89}
\]

\[
P^s_n := \sum_m p_{nm}, \tag{90}
\]

Next, we rewrite the \( p_{nm} \) according to (83) as

\[
p_{nm} = h_\lambda(E_{nm}(\lambda)) + \delta p_{nm}. \tag{91}
\]

Regarding the ‘unbiased fluctuation’ \( \delta p_{nm} \) (cf section 5.1) one can conclude that for any fixed index \( n \), the sub-set \( \delta p_{nm} \) with variable indices \( m = 0, 1, 2, \ldots \) is unbiased as well, i.e.

\[
\sum_m p_{nm} = \sum_m h_\lambda(E_{nm}(\lambda)). \tag{92}
\]

More precisely, the energies \( E_{nm} \) from (87), with \( n \) arbitrary but fixed and \( m \) variable, are still unimaginably dense, and the same property is inherited by \( E_{nm}(\lambda) \). Further, there is no reason to expect the emergence of any special ‘correlations’ between the ensemble averaged fluctuations \( \delta p_{nm} \) by selecting any sub-set with a fixed \( n \) in (91).

Note that during the preparation phase (cf section 5.2), there may exist an indirect, non-weak coupling between system and bath in the canonical setup, namely when both parts are interacting simultaneously with the rest of the world. Then, it is even more obvious to expect that (92) will be canonically fulfilled.

Rewriting (82) as \( h_\lambda(E_{nm}(\lambda)) = h_0(E_{nm}) \) it follows with (90) and (92) that \( p^s_n = \sum_m h_0(E_{nm}) \) and with (84) and (85) that \( p^s_n = \sum_m \rho_\lambda(E_{nm})/\omega_0(E_{nm}) \). Dropping indices ‘0’ corresponding to \( \lambda = 0 \) as usual, we finally arrive at

\[
P^s_n = \sum_m \frac{\rho(E_{nm})}{\omega(E_{nm})}, \tag{93}
\]

where \( \rho(E) \) stands for the ‘true’ energy density \( \rho_\lambda(E) \) of the system-plus-bath compound at finite coupling \( \lambda \).

9.3.3. Additivity of entropy. Here, we revisit the issues of level counting, entropy and temperatures from section 2.1 for the special Hamiltonian (73) with \( \lambda = 0 \).

The definitions and relations (9)–(17) can be taken over without any change to our present special case, except that all single indices \( n \) now become double indices \( nm \) (see (86) and (87)). We reiterate that all those definitions and relations remain for the moment on a purely formal level without any reference to the actual system state. Their only purpose at this stage is to count levels in a convenient way.

Since \( \lambda = 0 \) in (73), we are dealing with two individual isolated systems and hence analogous definitions and equations as in (9)–(17), but now with indices ‘S’ and ‘B’, apply separately to the system and to the bath. As detailed in appendix A, the following relations between those separate system and bath quantities and the original quantities for the system-plus-bath compound (73) with \( \lambda = 0 \) can be established: focusing on \( E > E_0 \), we denote by
In the generic case this maximum is unique and is contained in the interval \((E_0, E)\). Adopting the definition

\[
E_S(E) := E - E_B(E),
\]

the following results are established in appendix A:

\[
S(E) = S_B(E_B(E)) + S_S(E_S(E)),
\]

\[
T(E) = T_B(E_B(E)) = T_S(E_S(E)).
\]

More precisely, these relations are asymptotically exact approximations for \(f_B \to \infty\). But since \(f_B\) is at least of the order of \(10^{23}\) (see below (70)) they are satisfied with extremely high accuracy.

In other words, in the zero coupling limit the entropies of the systems-plus-bath compound exhibit additive behavior provided the total energy \(E\) is distributed among the system and the bath such that \(S_B(E') + S_S(E - E')\) is maximized, which in turn has the consequence that all temperatures are identical, i.e. the so-called equilibrium condition (or zeroth law of thermodynamics) is fulfilled.

10. Outlook on general non-interacting systems

Systems consisting of non-interacting particles or other types of non-interacting sub-systems are popular models in many different contexts. Also the canonical system-plus-bath setup from the previous section is of this structure. Strictly speaking, every single sub-system would thus be isolated and its energy would be a conserved quantity, thus prohibiting any kind of equilibration or thermalization process between different sub-systems. To each of them, the discussion of thermalization and the concomitant open questions from section 8 apply. In particular, individual sub-systems that are ‘small’ (e.g. single particles) may not even exhibit equilibration (cf section 1). Accordingly, the term ‘non-interacting’ actually means an interaction that is strictly speaking finite, thus giving rise to ‘normal’ equilibration and thermalization, but in certain other respects still ‘negligibly small’. A more precise formulation of such a weak coupling condition and its implications analogous to section 9 is straightforward.

Similarly to section 9.3.1, one finds that the generalized non-resonance condition (52) is violated at zero coupling [13] but is generically restored as soon as the slightest interaction between the sub-systems is included. Note that in section 9.3.1 it is tacitly assumed that the two non-interacting sub-systems are distinguishable. In the opposite case of indistinguishable sub-systems (e.g. indistinguishable particles), all admitted states of the compound system must be symmetric (bosonic sub-systems) or anti-symmetric (fermionic sub-systems) against exchanging the indices of the two sub-systems, i.e. the pair \((n, m)\) has to be identified with (is indistinguishable from) \((m, n)\) for all \(n, m\) in (86) and (87). Accordingly, in the identity \(E_{nn} - E_{nm} = E_{mn} - E_{mm}\) discussed below (88), the two energies \(E_{nm}\) and \(E_{mn}\) must be identified. Yet, condition (88) is still violated.

These considerations demonstrate that the generalized non-resonance condition (52) is quite a sensitive criterion in the context of equilibration and thermalization. It thus seems likely that a significantly weaker but still completely general condition of this type may not exist.
Note that a system of strictly non-interacting particles (or other kinds of sub-systems) that is coupled to a bath (canonical setup) generically gives rise to a total system-plus-bath compound that cannot be decomposed into isolated sub-systems any more and therefore generically fulfils condition (52).

Beyond the realm of 'weak coupling', a partitioning of the total compound into physically meaningful sub-systems becomes questionable. In particular, it does not make much sense to speak about properties of one 'sub-system alone'. Rather, the total compound amounts to an isolated system without any special properties, to which the general discussion of section 8 applies.

11. Thermalization for the canonical setup

The objective of the present section is to establish thermalization without making use of the unproven property (69) in the most important special case, namely the canonical setup from section 9.

As detailed in section 8, it is taken for granted that the system energy

\[ E^* := \langle H \rangle \]  

is known with high accuracy. In other words, the energy density \( \rho(E) \) from (46) exhibits a very narrow peak within the close vicinity of \( E^* \). By combining (46) and (98) one recovers the expected relation

\[ E^* = \int dE E \rho(E). \]  

The 'star' in \( E^* \) emphasizes the fact that the ensemble averaged energy of the 'real' system is fixed. Identifying \( E \) in section 9.3.3 with \( E^* \) establishes the connection between the so far unrelated considerations in section 9.3.3 and our present issue of thermalization.

Formally, the task is to show that in (66) the unknown details of \( p_n \) are (practically) irrelevant. In particular, this then implies that (66) indeed agrees with the prediction of equilibrium statistical mechanics.

As detailed in section 9, the canonical setup consists of a 'small' system (S) that is weakly coupled to a much 'bigger' bath (B). Equilibration of the isolated system-plus-bath compound is taken for granted, i.e. expectation values (32) become practically indistinguishable from (66). Focusing on system observables of the form (74) and observing (76) and (89), those equilibrium expectation values thus take the form

\[ \langle A \rangle = \text{Tr}_S \{ \rho_{eq}^S A^S \}, \]  

\[ \rho_{eq}^S = \sum_n p_n^S |n\rangle_S \langle n|, \]  

where \( \text{Tr}_S \) indicates the trace in \( \mathcal{H}_S \). In other words, as far as system properties are concerned, knowledge of the reduced equilibrium density operator \( \rho_{eq}^S : \mathcal{H}_S \to \mathcal{H}_S \) is sufficient.

11.1. Boltzmann form of \( p_n^S \) and canonical density

Exploiting (93) we can conclude that

\[ p_n^S = \int dE \frac{\rho(E)}{\omega(E)} \sum_m \delta(E - E_{nm}), \]  

where \( \omega(E) \) is the partition function.
where the delta-function is, as usual, considered as washed out. The first term under the integral can be rewritten by means of (14) as

$$\frac{\rho(E)}{\omega(E)} = \frac{\rho(E)}{k_B T(E)} \Omega(E)$$  \hspace{1cm} (103)

Turning to the second term under the integral, we exploit (87), the definition of \(\omega_B(E)\) analogous to (12), and the corresponding relation (14), yielding

$$\sum_m \delta(E - E_{nm}) = \sum_m \delta(E - E_n^S - E^B_m)$$

$$= \omega_B(E - E_n^S) = \frac{\Omega_B(E - E_n^S)}{k_B T_B(E - E_n^S)}.$$  \hspace{1cm} (104)

Making use of (10), (103) and (104), we can rewrite (102) as

$$\tilde{p}_n^S = \int dE \frac{T(E)}{T_B(E - E_n^S)} e^{Q(E)},$$  \hspace{1cm} (105)

$$Q(E) := \frac{S_B(E - E_n^S) - S(E)}{k_B},$$  \hspace{1cm} (106)

where the dependence of \(Q\) on \(n\) has been dropped. Exploiting (95) and (96) we see that

$$k_B Q(E) = S_B(E_B(E) + E_S(E) - E_n^S) - S_B(E_B(E)) - S_S(E_S(E)).$$  \hspace{1cm} (107)

According to the mean value theorem there exists for any given \(x\)- and \(y\)-value a \(\vartheta \in [0, 1]\) with the property that

$$S_B(x+y) = S_B(x) + y S_B'(x + \vartheta y).$$  \hspace{1cm} (108)

Choosing \(x = E_B(E)\) and \(y = E_S(E) - E_n^S\) and exploiting (13), we can rewrite (107) as

$$Q(E) = \frac{E_S(E) - E_n^S}{k_B T_B(E_B(E) + \Delta)} - \frac{S_S(E_S(E))}{k_B},$$  \hspace{1cm} (109)

$$\Delta := \vartheta [E_S(E) - E_n^S],$$  \hspace{1cm} (110)

where the dependence of \(\vartheta\) and \(\Delta\) on \(E\) and \(n\) has been dropped.

We first consider the simplest case of a delta-distributed energy density

$$\rho(E) = \delta(E - E^*).$$  \hspace{1cm} (111)

Thus, (105) takes the form

$$\tilde{p}_n^S = \frac{T(E^*)}{T_B(E^* - E_n^S)} e^{Q(E^*)}.$$  \hspace{1cm} (112)

Observing (95), the denominator \(T_B(E^* - E_n^S)\) can first be rewritten as \(T_B(E_B(E^*) + E_S(E^*) - E_n^S)\) and then with (16) as

$$T_B(E^* - E_n^S) = T_B(E_B(E^*)) \left[1 + \mathcal{O} \left(\frac{E_S(E^*) - E_n^S}{E_B(E^*) - E_0^B}\right)\right].$$  \hspace{1cm} (113)

Finally, with (97) and relations like in (15) but with indices \(S\) and \(B\), we can conclude that

$$T_B(E^* - E_n^S) = T(E^*) \left[1 + \mathcal{O} \left(\frac{f_k E_S(E^*) - E_n^S}{f_B E_S(E^*) - E_0^B}\right)\right].$$  \hspace{1cm} (114)
In view of (70), the last summand is negligible and (112) takes the form

\[ p_n^S = e^{Q(E^*)}. \]  

(115)

Similarly to (114), one sees that \( T_B(E_B(E) + \Delta) \) appearing in (109) can be approximated by \( T_B(E_B(E)) = T(E) \), yielding

\[ Q(E^*) = \frac{E_S(E^*) - E_n^S}{k_B T(E^*)} - \frac{S_S(E^*_n(E))}{k_B}. \]  

(116)

With the usual definitions of the free energy \( F_S(E) \) and the partition sum \( Z_S(E) \) of the system \( S \), namely

\[ F_S(E) := E_S(E) - T_S(E) S_S(E), \]

\[ Z_S(E) := e^{-F_S(E)/k_B T_S(E)}, \]

(117)\hspace{1cm}(118)

in combination with (116), we can rewrite (115) as

\[ p_n^S = \frac{1}{Z_S(E^*)} e^{-E_n^S/k_B T(E^*)}. \]  

(119)

Taking into account the normalization condition \( \sum_n p_n^S = 1 \), we recover

\[ Z_S(E^*) = \sum_n e^{-E_n^S/k_B T(E^*)}. \]  

(120)

We finally turn to general energy densities \( \rho(E) \). Since \( \rho(E) \) enters linearly in (105), we simply can superimpose the results (119) for sufficiently many delta-functions approximating the true \( \rho(E) \). The fact that each delta-function brings along a somewhat different value of \( E^* \) in (119) has a negligible effect according to (16) as long as \( \rho(E) \) is still sharply peaked about its mean value. Denoting this mean value, in accordance with (98) and (99), again by the symbol \( E^* \), one thus recovers exactly the same relations as in (117)–(120).

In summary, the canonical formalism (117)–(120) is valid in full generality. Apart from the average energy \( E^* \), all the remaining details of the (unknown) energy density \( \rho(E) \) do not matter. The Boltzmann distribution (119) together with (101) yields the canonical density operator

\[ \rho_{eq}^S = \frac{1}{Z(E^*)} e^{-H_S/k_B T(E^*)} \]  

(121)

where \( T(E^*) \) is the temperature corresponding to the given total energy \( E^* \) of the isolated system-plus-bath compound. In practice, this energy \( E^* \) is usually not known, and one thus rather considers the temperature \( T \) as ‘given’. Accordingly, in (119)–(121) the state function \( T(E^*) \) is replaced by the ‘new’ independent state variable \( T \) and similarly \( Z(E^*) \) by \( Z(T) := Z_S(E^*(T)) \).

12. Summary and conclusions

In the first part of this paper, we considered general, isolated quantum systems with many degrees of freedom \( f \) and being extensive in the sense of equations (11) and (15). As a further ‘generic’ property of the Hamiltonian \( H \), the (generalized) non-resonance condition (52) was taken for granted. Our key assumptions concerning the ‘realistic modeling’ of actual experimental systems were: (i) observables have a ‘reasonably bound’ range-to-resolution ratio
and (ii) initial conditions may be arbitrarily out of equilibrium but, on average over the entire statistical ensemble (many repetitions of the ‘same’ experiment), they give rise to a well-defined population density (average occupation probability of many neighboring energy levels). The latter assumption seems quite plausible per se, but can also be justified via the experimental preparation procedure at the origin of the initial condition.

All further ‘details’ of the initial condition and the Hamiltonian were left unspecified, reflecting the unavoidable actual lack of knowledge in this respect.

Given the initial condition, the exact standard quantum mechanical time evolution was adopted without any approximation or modification.

Our first main result (64) implies that after initial transients have died out, the system looks for all practical purposes as if it were in a steady state described by the so-called generalized Gibbs ensemble ρ_{eq}, in spite of the fact that the ‘true’ density operator ρ(t) never becomes stationary, but rather exhibits the well-known quantum mechanical recurrence and time inversion invariance properties. Our key conclusion was that the mathematically undeniable differences between the ‘apparent equilibrium’ ρ_{eq} and the ‘true’ density operator ρ(t) are either unobservably small or unobservably rare in time.

While the issue of equilibration can thus be considered as settled, that of thermalization still remains an open problem as far as completely general isolated systems are concerned, as detailed in section 8.

In the second part of the paper we focused on a special case of foremost practical relevance, namely the canonical setup, consisting of a system of actual interest (that may be macroscopic or not) that is weakly coupled to a much ‘bigger’ environment. Provided the total system-plus-bath compound satisfies the above conditions for equilibration, the corresponding ‘apparent equilibrium’ ρ_{eq} reduces, after eliminating (tracing out) the bath, to the canonical density operator (121), independently of all the unknown ‘microscopic details’ of the possibly far from equilibrium initial condition. In other words, the ‘small’ system is proven to exhibit ‘thermalization’. The result even goes beyond the claim of statistical mechanics in so far as not only the system but also the bath may be initially out of equilibrium.

It seems not unlikely that our main prerequisites in deriving these results cannot be substantially weakened any further: systems that can be decomposed into strictly non-interacting sub-units (e.g. non-interacting particles) are known not to thermalize and indeed violate the non-resonance condition (52). Likewise, when either an unlimited range-to-resolution ratio or an initial condition without a well-defined population density is admitted, one readily finds examples that do not exhibit equilibration, see sections 3 and 5.6.

Next, we briefly address the issue of low temperatures. Firstly, for extremely low temperatures, the rough estimates from (11) and (15) may break down. Since these estimates are at the heart of our present approach, our main results may not be valid any more. Essentially this happens when the entropy becomes experimentally indistinguishable from zero. This may but need not be the case for Bose–Einstein condensates [14].
Further, the common notion that a Bose–Einstein condensate exhibits a macroscopically populated ground state may be easily misunderstood in our present context. Namely, this notion refers to the fact that the total many particle product state contains a large number of single particle ground states. The word ground state thus refers to the individual (non-interacting) particles, not to the total many particle system. Indeed, besides the numerous single particles in their individual ground states, there may still remain many further particles that are in excited single particle states. Hence, we are in fact not dealing with the actual ground state of the many particle product Hilbert space. Rather, it may easily happen that the maximal population of all the many particle product states is still small and hence the conditions regarding the level populations from section 5 may still be satisfied.

We close with a few remarks on the issues of (non-)integrability, ergodicity, chaos, decoherence and entanglement. We first remark that (non-)integrability, ergodicity and chaos are relatively well-defined notions for classical systems, but that their role with respect to equilibration and thermalization is not really clear in the classical case. The corresponding notions in the realm of quantum systems are much less well and uniquely defined [2, 33]. But even if this problem were solved, in view of the classical situation, the usefulness of those concepts for equilibration and thermalization is likely to be limited in the quantum case as well.

The closest connection of our present approach to the above notions may be via the non-resonance condition (52). However, such a connection or analogy does not seem to offer any additional physical insight. Concerning our requirement that the initial condition must exhibit a well-defined population density, we remark that during the preparation phase (which represents the physical origin of the initial condition), a distinction between integrable and non-integrable systems does not make much sense anyhow.

The concepts of integrability, ergodicity and the like may well play a crucial role for the following two issues: (i) the transient relaxation process of the initial state towards equilibrium, both qualitatively (exponential decay or not) and quantitatively (estimating the relaxation time): this is suggested by the well-established role of level statistics in quantum chaos and the importance of energy differences throughout the present appendix D; and (ii) the general problem of thermalization addressed in section 8, in particular the unproven key postulate (69) in this context.

As far as the issue of equilibration is concerned, our present approach and results demonstrate that entanglement and decoherence play no role since we are dealing with isolated systems without any external influence of the rest of the world. With respect to thermalization, the question remains open.

12.1. Comparison with related works

We first address several works with a finite but not too small overlap with the present one and then turn to the two most closely related works [12, 13]. The pertinent literature regarding the ‘missing link’ (69) in the context of thermalization has already been addressed at the end of section 8.

Considering and estimating quantities like (59) is very natural and has a long tradition: merits and shortcomings of the early works are reviewed e.g. in [5], most notably Ludwig’s approach [3]. In particular, many of them [4, 5] involve an extra average over initial conditions with the effect that any specific non-equilibrium initial condition (representing a given experiment) must be excluded as ‘potentially untypical’ from the general conclusions.
Turning to the more recent precursors, Peres’ approach [6] is roughly comparable to ours up to equation (D.12) but then proceeds with the conjecture that the $\tilde{A}_{mn}$ are pseudorandom matrix elements, statistically independent of the $\rho_{nm}$, for which there are general arguments [6] and numerical evidence [32] (and counter-evidence [2]) but no proof. For pure states, Srednicki [9] obtained similar results by exploiting a common conjecture about the semiclassical behavior of classically smooth observables $A$ in systems with a fully chaotic classical limit. Again, this conjecture is based on good arguments [30] but no proof. Moreover, typical classical many-body systems are not expected to behave fully chaotically [28, 37]. Somewhat similar conclusions have been reached even earlier by Deutsch [8] via additional handwaving arguments. Finally, rigorous results comparable to (63) are due to [10, 16], but only for rather special Hamiltonians $H$ and initial conditions. Within the same restrictions, the groundbreaking work by Tasaki [10] also addresses the issue of thermalization by arguments that are similar in spirit to those in section 9 of the present paper.

The first part of the present work (until the end of section 8) represents a generalization and more detailed explanation of [12]. The main extensions consist in the enlarged class of observables admitted in section 4 and the fact that degenerate energy eigenvalues are no longer excluded in the present work.

We finally turn to the closely related work [13]. In contrast to the present work, the paper [13] is focused on Hilbert spaces, which are finite dimensional and which exhibit a ‘system-plus-bath’ product structure of the form (72). Apart from a non-resonance condition (excluding degeneracies, see below (52)), the Hamiltonian may still be completely arbitrary. Further, the system is assumed to be in a pure state on the total system-plus-bath Hilbert space, while the obtained results mainly concern the reduced (usually mixed) state of the ‘small’ system after tracing out the ‘large’ bath. Apart from these quite significant overall differences, the main findings with respect to equilibration are rather similar in character to ours. In particular, observables with a finite range are implicitly taken for granted according to the discussion below equation (3) in [13], and the ‘effective dimension’ $d_{\text{eff}}$ from [13] is basically equivalent to $\text{Tr}(\rho_{\text{eq}}^2)$ in our present approach, as discussed below (60). With respect to thermalization, the results from [13] are of quite a different character from ours, mostly concerning ‘typical’ [22, 26, 36] properties of pure states which are randomly sampled according to a uniform probability density from certain sub-Hilbert spaces. In the opinion of the present author (see also sections 1 and 5.2), the main open question of this approach is how far one particular pure state or an ensemble of uniformly distributed pure states are suitable to describe a real experimental setup.

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Appendix A

In this appendix we establish the relations (96) and (97). As detailed above (94), analogous definitions and equations as in (9)–(17), but with indices ‘S’ and ‘B’, hold true and are exploited in the following.
With the help of (12) and (87) we can conclude that
\[
\omega(E) = \sum_{nm} \delta(E - E_n^S - E_m^B) = \sum_n \omega_B(E - E_n^S)
\]
\[
= \int dE' \omega_B(E - E') \sum_n \delta(E' - E_n^S)
\]
\[
= \int dE' \omega_B(E - E') \omega_S(E'),
\]  
(A.1)

where \(\sum_{nm}\) indicates a summation over all \(n, m = 0, 1, 2, \ldots\). It follows from (12) that \(\omega_S(E') = 0\) for \(E' < E_0^S\) and, similarly, that \(\omega_B(E - E') = 0\) for \(E' > E - E_0^B\). Taking for granted that the integrand \(\omega_B(E - E') \omega_S(E')\) is a sufficiently smooth function of \(E'\), it thus will have an absolute maximum in the interior of the interval \([E_0^S, E - E_0^B]\). For any given \(E\)-value exceeding the ground state energy \(E_{00} = E_0^S + E_0^B\) of the compound system, the absolute maximum will furthermore be generically unique.

Next we rewrite (A.1) by means of (11) and (14) as
\[
\frac{e^{S(E)/k_B}}{k_B T(E)} = \int dE' \frac{e^{(S_B(E') + S_S(E - E'))/k_B}}{k_B T_B(E') k_B T_S(E - E')}.
\]  
(A.2)

Similarly to the integrand in (A.1), the exponent in (A.2) generically exhibits a unique absolute maximum at some \(E'\)-value in the interior of \([E_0^S, E - E_0^B]\), henceforth denoted as \(E_B(E)\). The next step is to evaluate (A.2) by means of a saddle point approximation, i.e. by expanding the exponent around its maximum up to the second order. At the maximum, the derivative of the exponent vanishes, yielding with (13) the relation
\[
T_B(E_B(E)) = T_S(E_S(E)),
\]  
(A.3)

where we have introduced
\[
E_S(E) := E - E_B(E).
\]  
(A.4)

We emphasize that, like in sections 2.1 and 9.3.3, we avoid speaking about system states. If we give up this viewpoint for a moment, then (A.3) is nothing else than the so-called equilibrium condition for two systems with negligible (but nonzero) interaction in thermal equilibrium, sharing the total system energy \(E\) according to (A.4).

Expanding the exponent on the right-hand side of (A.2) up to the second order about its maximum at \(E' = E_B(E)\) in combination with (17) yields
\[
\frac{S_B(E') + S_S(E - E')}{k_B} = \frac{S_B(E_B(E)) + S_S(E_S(E))}{k_B} - O\left( f_B \left[ \frac{E' - E_B(E)}{E_B(E) - E_0^B} \right]^2 + f_S \left[ \frac{E' - E_B(E)}{E_S(E) - E_0^S} \right]^2 \right).
\]  
(A.5)

Since \(f_B\) is at least of the order of \(10^{23}\) (see below (70)), it follows that only an extremely small neighborhood of the maximum notably contributes to the integral in (A.2), and within this neighborhood the variations of the non-exponential factors on the right-hand side of (A.2) are negligibly small according to (16). Performing the remaining Gaussian integral in (A.2) yields
\[
\frac{S(E)}{k_B} = \frac{S_B(E_B(E)) + S_S(E_S(E))}{k_B} + \ln(O(R)),
\]  
(A.6)
From (15) and (71) one can infer that \( R \) is of the order of \( f \). Considering that the quantity in (A.6) scales like \( f \) according to (15) and that \( f \) is at least of the order of \( 10^{23} \), the contribution of \( \ln(O(R)) \) in (A.6) is negligible. We thus obtain in extremely good approximation the relation

\[
S(E) = S_B(E_B(E)) + S_S(E_S(E)).
\]  
(A.9)

Differentiating this relation with respect to \( E \) and taking into account (13), (A.3), and (A.4), we obtain

\[
T(E) = T_B(E_B(E)) = T_S(E_S(E)).
\]  
(A.10)

The latter two relations are identical to (96) and (97) in the main text.

**Appendix B**

In this appendix we derive the relation

\[
\sum_n \rho_{nn}^2(0) \leq \max_n p_{E_n}.
\]  
(B.1)

To do so, we first exploit (25) to conclude that

\[
P_{E_n}^2 = \sum_{E_m=E_n} \sum_{E_{m'}=E_n} \rho_{mm}(0) \rho_{m'{m'}(0)}
\geq \sum_{E_m=E_n} \rho_{mm}^2(0)
\]  
(B.2)

and hence

\[
\sum_n \rho_{nn}^2(0) = \sum_{E_n} \sum_{E_m=E_n} \rho_{mm}^2(0)
\leq \sum_{E_n} P_{E_n}^2 \leq \sum_{E_n} p_{E_n} \max_m p_{E_m}.
\]  
(B.3)

With (26) we obtain (B.1).

**Appendix C**

In this appendix, the derivation of (48) is provided. To start with, we recall that the delta-functions in (46) and (47) are understood to be ‘washed out’ over many energy levels. Hence, smoothing \( \rho(E) \) with the help of yet another washed out delta-function actually does not change \( \rho(E) \) any more:

\[
\rho(E) = \int dE' \delta(E - E') \rho(E).
\]  
(C.1)
Introducing (45) and (47) on the right-hand side yields
\[ \rho(E) = \int dE' \delta(E - E') \sum_n h(E_n) \delta(E' - E_n) + \sum_n \delta p_n \delta(E - E_n). \] (C.2)

Since the delta-functions are washed out, the last summand essentially amounts to a local average over many \( \delta p_n \) and is thus negligible (see below (45)). In turn, the function \( h(E) \) hardly changes within the peak region of the delta-functions. Hence, \( h(E_n) \) can be replaced by \( h(E') \) and then by \( h(E) \). Altogether, we thus obtain
\[ \rho(E) = h(E) \int dE' \delta(E - E') \sum_n \delta(E' - E_n). \] (C.3)

The sum can be identified with \( \omega(E') \) from (12). Since the latter is once again already a locally averaged quantity, the integral over the last remaining delta-function is trivial, yielding (48).

### Appendix D

According to (54) it follows that
\[ \bar{e} \Omega = \begin{cases} 1 & \text{for } a = 0, \\ 0 & \text{for } a \neq 0. \end{cases} \] (D.1)

Next we exploit (54) and (22) to conclude that
\[ \bar{\rho}(t) = \sum_{mn} \rho_{mn}(0) e^{-i[E_m - E_n]/\hbar} |m\rangle \langle n|. \] (D.2)

In combination with (27) and (D.1), we thus recover (55).

With (32) and (58) we can rewrite the variance from (59) as
\[ \sigma_A^2 = \frac{[\text{Tr}[\rho(t)A] - \text{Tr}[\rho_{eq}A]]^2}{[\text{Tr}[\bar{\rho}(t)A]]^2}, \] (D.3)
\[ \bar{\rho}(t) := \rho(t) - \rho_{eq}. \] (D.4)

Exploiting (22), (27) and (55) we obtain
\[ \bar{\rho}(t) = \sum_{mn}' \rho_{mn} e^{-i[E_m - E_n]/\hbar} |m\rangle \langle n| \] (D.5)
where \( \sum_{mn}' \) indicates a summation over all \( m, n = 0, 1, 2, \ldots \) with \( E_m \neq E_n \), and where we adopted the abbreviation
\[ \rho_{mn} := \rho_{mn}(0). \] (D.6)

It follows that \( \text{Tr}[\bar{\rho}(t)] = 0 \) and hence
\[ \text{Tr}[\bar{\rho}(t)(A + 1_H c)] = \text{Tr}[\bar{\rho}(t)A] \] (D.7)
for any \( c \in \mathbb{R} \), where \( 1_H \) is the identity on \( \mathcal{H} \).
As mentioned below (33), we can and will replace $\mathcal{H}$ and $A$ by $\mathcal{H}_+$ and $A_+$ in the rest of this appendix. Introducing

$$\tilde{A} := A_+ - 1_{\mathcal{H}_+} \min_{\mathcal{H}_+} \langle \psi | A | \psi \rangle,$$

we can infer from (38) that

$$0 \leq \langle \psi | \tilde{A} | \psi \rangle \leq \Delta'_{\tilde{A}} \quad \text{for all normalized } | \psi \rangle \in \mathcal{H}_+.$$  \hspace{1cm} (D.9)

Taking into account (D.7) and (D.8), the variance (D.3) can be rewritten as

$$\sigma^2_{\tilde{A}} = \langle \text{Tr}[\tilde{\rho}(t) \tilde{A}] \rangle^2.$$  \hspace{1cm} (D.10)

Introducing (D.5) into (D.10), we obtain

$$\sigma^2_{\tilde{A}} = \sum_{jkn} \tilde{A}_{jk} \rho_{kj} \tilde{A}_{mn} \rho_{nm} \frac{e^{i(E_k - E_k + E_m - E_m)/\hbar}}{E_k - E_k + E_m - E_m}$$

where $\sum jkmn$ indicates a summation over all $j, k, m, n = 0, 1, 2, \ldots$ with $E_j \neq E_k$ and $E_m \neq E_n$.

Since, according to (D.1), the time-averaged exponentials in (D.11) vanish if $E_j - E_k + E_m - E_n \neq 0$, we can conclude from the non-resonance condition (52) that

$$\sigma^2_{\tilde{A}} = \sum_{mn} |\tilde{A}_{mn}|^2 |\rho_{mn}|^2 \leq \sum_{mn} |\tilde{A}_{mn}|^2 |\rho_{mn}|^2$$

where the first sum runs over all $m, n$ with $E_m \neq E_n$ and the second over all $m, n$. With (24) and (55) we thus obtain

$$\sigma^2_{\tilde{A}} \leq \sum_{mn} \tilde{A}_{mn} \rho_{mn} \tilde{A}_{mn} \rho_{mn}$$

$$= \sum_{mn} \langle m | \tilde{A} \rho_{eq} | n \rangle \langle n | \tilde{A} \rho_{eq} | m \rangle.$$  \hspace{1cm} (D.13)

The sum over $n$ amounts to an identity operator and that over $m$ yields

$$\sigma^2_{\tilde{A}} = \text{Tr}[\tilde{A} \rho_{eq}]^2.$$  \hspace{1cm} (D.14)

Next, we evaluate this trace with the help of the eigenvectors $|\chi_n\rangle$ of $\tilde{A}$, yielding

$$\sigma^2_{\tilde{A}} \leq \sum_{mn} \langle \chi_m | \rho_{eq} \tilde{A} | \chi_n \rangle \langle \chi_n | \rho_{eq} \tilde{A} | \chi_m \rangle.$$  \hspace{1cm} (D.15)

Observing that $\tilde{A} |\chi_n\rangle = |\chi_n\rangle \langle \chi_n | \tilde{A} |\chi_n\rangle$ (since $|\chi_n\rangle$ is an eigenvector of $\tilde{A}$), we can exploit (D.9) to obtain

$$\sigma^2_{\tilde{A}} \leq (\Delta'_{\tilde{A}})^2 \sum_{mn} \langle \chi_m | \rho_{eq} | \chi_n \rangle \langle \chi_n | \rho_{eq} | \chi_m \rangle.$$  \hspace{1cm} (D.16)

The sum over $n$ yields the identity operator and that over $m$ amounts to $\text{Tr}[\rho_{eq}^2]$, yielding

$$\sigma^2_{\tilde{A}} \leq (\Delta'_{\tilde{A}})^2 \text{Tr}[\rho_{eq}^2].$$  \hspace{1cm} (D.17)

Finally, we note that according to (56) and (D.4) we can subtract from $A$ in (D.3) an arbitrary function $B(b)$ of the form (39) with the only consequence in the final result (D.17) that $\Delta'_{\tilde{A}}$ goes over into $\Delta'_{\tilde{A} - B(b)}$. Since this conclusion holds for arbitrary $B(b)$, the inequality even remains true after minimization over all $B(b)$, i.e. we can replace $\Delta'_{\tilde{A}}$ in (D.17) by $\Delta'_{\tilde{A}}$ from (41). In other words, we recover (60).

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Appendix E

The purpose of this appendix is a more detailed justification of the non-degeneracy assumption adopted in equation (79). More precisely, we will argue that the energy levels \( E_n(\lambda) \), considered as functions of \( \lambda \), do not cross each other for generic Hamiltonians \( H(\lambda) \).

Intuitively, one expects that the \( E_n(\lambda) \) will be highly nontrivial functions of \( \lambda \) and that for different \( n \) these functions will behave notably ‘different’ from each other. Since the energy levels are unimaginably dense (cf section 2.1), crossings of neighboring levels \( E_n(\lambda) \) upon variation of \( \lambda \) thus might seem to be almost unavoidable.

But closer inspection shows that, on the contrary, such level crossings are actually avoided for generic Hamiltonians \( H(\lambda) \) due to the so-called level-repulsion mechanism: the levels \( E_n(\lambda) \), considered as functions of \( \lambda \), are governed by the following exact evolution equation, originally due to Pechukas and Yukawa [38]:

\[
\frac{d^2}{d\lambda^2} E_n(\lambda) = 2 \sum_{m \neq n} \frac{|V_{nm}(\lambda)|^2}{E_n(\lambda) - E_m(\lambda)},
\]

(E.1)

\[
V_{nm}(\lambda) := \langle n(\lambda) | \frac{d}{d\lambda} H(\lambda) | m(\lambda) \rangle,
\]

(E.2)

where \( E_n(\lambda) \) and \( |n(\lambda)\rangle \) are the ‘accompanying’ eigenvalues and eigenvectors of \( H(\lambda) \). The closing evolution equations for \( V_{nm}(\lambda) \) are also known, but are not explicitly needed for our purpose. The main point is that looking upon \( \lambda \) as ‘time’ and \( E_n(\lambda) \) as ‘particle positions’, equation (E.1) is nothing else than the Newtonian equation of motion for a one-dimensional ‘gas’ of point particles, the so-called Pechukas–Yukawa gas [38]. The particles are repelling each other with ‘coupling strengths’ \( |V_{nm}(\lambda)|^2 \), which depend on ‘time’ \( \lambda \). In the generic case (no special symmetries or ‘selection rules’), the coupling of two neighboring particles, say \( |V_{nn+1}(\lambda)|^2 \), will be positive with the exception of at most a discrete set of time points \( \lambda \), and as a consequence, any ‘attempt’ of the two neighboring levels \( E_n(\lambda) \) and \( E_{n+1}(\lambda) \) to cross each other is inhibited by a repulsive ‘force’ term in (E.1) of the form \( |V_{nn+1}(\lambda)|^2 [E_n(\lambda) - E_{n+1}(\lambda)]^{-1} \), which diverges as \( E_n(\lambda) \to E_{n+1}(\lambda) \).

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