Statistical mechanics and the duality of quantum mechanical time evolution

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Abstract

Through the H theorem, Boltzmann attempted to validate the foundations of statistical mechanics. However, it is incompatible with the fundamental laws of mechanics because its deduction requires the introduction of probability. In this paper we attempt a justification of statistical mechanics without deviating from the existing framework of quantum mechanics. We point out that the principle of equal \textit{a priori} probabilities is easily proven in the dual space. The dual of the space of the quantum states is the space of the observations. We then prove that time evolution of the operators of observations obeys Boltzmann equation. This result implies that the difference of the states from equal probability becomes unobservable as time elapses.

Introduction

Boltzmann’s $H$ theorem justifies the existence of irreversible phenomena, if only the introduction of probability can be justified. Since classical mechanics, however, does not allow the existence of probability, the $H$ theorem raised more questions about the foundations of statistical mechanics.

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One can easily imagine that introducing probability into quantum mechanics solves this puzzle, however this is not true. Only the probability of pure states is allowed in quantum mechanics, which does not leave any room for statistical mechanics. The introduction of mixed states becomes necessary for statistical mechanics, however that would constitute a deviation from the law of mechanics. Because mixed states are quantum analogs of classical probability distributions, introduction of mixed states does not change Boltzmann’s classical picture.

Thus, since we don’t have any good theory to explain the foundations of irreversible phenomena, and we can’t describe or predict many irreversible phenomena common in daily life.

This paper considers the time evolution of observations, which is dual to quantum states, making it possible to prove Boltzmann equation without the introduction of mixed states.

We are going to consider a system with a Hamiltonian $H = H_0 + V$, which is divided into a free part and an interaction part. We assume $V$ to be sufficiently small. $|k\rangle$ denotes an eigenstate of $H_0$ having eigenvalue of $E_k$. Perturbatively constructed eigenstate of $H$ is denoted by $|\tilde{k}\rangle$ and its energy is denoted by $\tilde{E}_k$. We consider systems which have a large number of states even in a small interval of energy $I : |\tilde{E}_k - E| < \Delta E$. This is typical for systems which consist of a large number of particles. A linear combination of the states within this interval is written as

$$|\psi\rangle = \sum_k \psi_k |\tilde{k}\rangle.$$ (1)

It is the fundamental assumption of statistical mechanics that $|\psi_k|^2$ goes to constant irrespective of $k$ for any state $|\psi\rangle$. All attempts to deduce this theorem from the equation of motion in quantum mechanics were unsuccessful.

Now, let us view this problem from the opposite side. Equations $a_i = 1$ for all $i$ may be proven if $\sum_i a_i b_i = 1$ holds for all vector $\vec{b}$ such that $\sum_i b_i = 1$. Let us apply this method of duality to our problem by considering that the space of the observation operators is dual to the space of pure states $|\psi\rangle\langle\psi|$. The statement that $|\psi_k|^2$ is constant irrespective of $k$ is dual to the following statement:

$$\text{tr} \, \hat{\rho} |\psi\rangle\langle\psi| = \text{tr} \, \hat{\rho} e^{-iHt} |\psi_{t=0}\rangle\langle\psi_{t=0}| e^{+iHt} \rightarrow \int dk \, \hat{\rho}_k$$ (2)
as time $t$ gets larger for any operator $\tilde{\rho}$ of observation that is diagonal when it is represented in the space of energy eigenstates $|\bar{k}\rangle$:

$$\tilde{\rho} = \sum_k |\bar{k}\rangle \rho_k \langle \bar{k}|.$$  \hfill (3)

Where $\langle \bar{k} | \psi \rangle = \psi_k$ has been used. This statement is the same even if perturbation theory is not applicable. Note that, in this paper, $\tilde{\rho}$ does not represent a density operator of any state but was introduced here for the purpose of calculation, and will come to mean observation later. To prove eq.(2), $e^{iHt} \tilde{\rho} e^{-iHt} \to \sum_{k \in I} |\bar{k}\rangle 1 \langle \bar{k}|$ should hold for any $\tilde{\rho}$, which will be proven in this paper.

**Selection of the boundary condition and eigenstates**

The explicit formula for the eigenstate $|\bar{k}\rangle$ which appeared in eq.(1) is

$$|\bar{k}^-\rangle \equiv |k\rangle - \frac{1}{H_0 - E_k - i\epsilon} V|k\rangle + \frac{1}{H_0 - E_k - i\epsilon} V \frac{1}{H_0 - E_k - i\epsilon} V|k\rangle - \cdots.$$ \hfill (4)

Let us check that $|\bar{k}^-\rangle$ is an eigenstate of $H$ in the limit of $\epsilon \to 0$. For example, the second-order term of $(H_0 + V)|\bar{k}^-\rangle$ is

$$- \sum_{i,j} |j\rangle \frac{-i\epsilon}{E_j - E_k - i\epsilon} V_{ji} \frac{1}{E_i - E_k - i\epsilon} V_{ik}.$$ \hfill (5)

Since the term in the sum is zero except for the points where $E_j = E_k$ and $E_i = E_k$, the formula above equals

$$- \sum_{i,j} |j\rangle \left( \delta_{jk} V_{ji} \frac{1}{E_i - E_k - i\epsilon} V_{ik} + \frac{1}{E_j - E_k - i\epsilon} V_{ji} \delta_{jk} V_{ik} \right).$$ \hfill (6)

Applying the same relationship to all the order, we obtain

$$(H - E_k)|\bar{k}\rangle = |\bar{k}\rangle \left( V_{kk} - \sum_i V_{ki} \frac{1}{E_i - E_k - i\epsilon} V_{ik} + \cdots \right).$$ \hfill (7)
Here, we see that $|\tilde{k}^-\rangle$ is actually an eigenstate. We also define
\[
\langle \tilde{k}^- | = \langle k | V \frac{1}{H_0 - E_k - i\epsilon} + \cdots. (8)
\]
Furthermore, $|\tilde{k}^+\rangle$ and $\langle \tilde{k}^+ |$ are defined to be those in which the sign of $-i\epsilon$ is changed from that in $|\tilde{k}^-\rangle$ and $\langle \tilde{k}^- |$ respectively.

Which of $|\tilde{k}^-\rangle$ or $|\tilde{k}^+\rangle$ should we take for $|\tilde{k}\rangle$ in the definition of $\tilde{\rho}$, i.e. eq.(3)? We take
\[
\tilde{\rho} = \sum_k |\tilde{k}^+\rangle \rho_k \langle \tilde{k}^- |, (9)
\]
for the following reason.

We assume that every physical state should be a superposition of outgoing waves. Therefore, we should choose $|\tilde{k}^-\rangle$ for a quantum state. This physical state remains physical by positive time evolution $e^{-iHt}$.

On the other hand, which sign should we take for dual bra vector in the operator of observation $\tilde{\rho}$? Let us consider making an observation at a certain time. The extent of the space from where the observation will be affected expands as we go back into the past. Then the region where $\langle b | e^{-iHt}$ has non-zero value will expand as $t$ gets larger. Therefore, the outgoing wave in the direction of the past: $\langle \tilde{k}^- |$ should be taken.\footnote{This choice agrees with our ordinarily taking the Feynman propagator: $\Delta_F(t; \vec{x}' - \vec{x}) = \langle 0 | T \phi(\vec{x}') e^{-iHt} \phi(\vec{x}) | 0 \rangle$ as Green’s function in calculating path integral.} Note that, contrary to this, a bra vector on the right of a physical pure state $|\psi\rangle\langle \psi |$ should be $\langle \tilde{k}^+ |$, since it is complex conjugate of $|k^-\rangle$.

### Time evolution of $\tilde{\rho}$

In the following, we are going to solve a differential equation:
\[
\frac{d\rho(t)}{dt} = -i[H, \rho] 
\]
(10)

to obtain the value of $\tilde{\rho}(t) = e^{+iHt} \tilde{\rho} e^{-iHt}$. For ease of the calculation, we define “Liouvillian formalism”\cite{1} here. A density operator $\rho_{k'k}$ having two indices can be regarded as a vector $\rho(k',k)$ by considering the indices to be
a single index \((k', k)\). Because \(\rho \rightarrow [\rho, V]\) is a linear transformation, it can be regarded as multiplication of a matrix \(L_V\) on the right of this vector \(\rho\), and be denoted by \(\rho L_V\). Similarly, \([\rho, H_0]\) will be denoted by \(\rho L_0\), and \([\rho, H]\) by \(\rho L_H\). Finally, the inverse (for example \((L_0 - \alpha)^{-1}\)), is defined as such an operator \(X\) that satisfies \([\rho X, H_0] - \alpha(\rho X) = \rho\). With these notations, eq.(10) may be written as

\[
\frac{d\rho(t)}{dt} = -i\rho(L_0 + L_V).
\]

(11)

Since this formula is formally parallel to the equation of motion of quantum mechanics, perturbation technique is applicable to it to obtain the solution.

Using this formalism, \(\tilde{\rho} = \sum_k |k^+\rangle \rho_k \langle k^-|\) may be rewritten as

\[
\tilde{\rho} = \rho - \rho L_V \frac{1}{L_0 - i\epsilon} + \rho L_V \frac{1}{L_0 - i\epsilon} L_V \frac{1}{L_0 - i\epsilon} - \cdots
\]

(12)

\[
\rho \equiv \sum_k |k\rangle \rho_k \langle k|.
\]

(13)

Let us check that eq.(12) holds, for example, in the second order, as the first order is too easy. A notation \(1/(E_i - E_k - i\epsilon) \equiv L_{ik}\) is introduced here. The second order term out of \(\tilde{\rho}\) is

\[
\sum_k \sum_j \{ |j\rangle L_{kj} V_{ji} L_{ki} V_{ik} \rho_k \langle k| - |j\rangle L_{kj} V_{jk} \rho_k V_{ki} L_{ik} \langle i| + |k\rangle \rho_k V_{kj} L_{jk} V_{ji} L_{ik} \langle i|\}.
\]

(14)

To this formula,

\[
L_{kj} L_{ik} = (L_{kj} + L_{ik}) \frac{1}{E_i - E_j - 2i\epsilon} = (L_{kj} + L_{ik}) L_{ij}
\]

(15)

will be applied. In the derivation of this equation \(1/(E_i - E_j - 2i\epsilon) = 1/(E_i - E_j - i\epsilon)\) is used. This change is allowed because the value of eq.(2) does not change if the wave function \(|\psi\rangle\) is continuous, which will be proposed later. Therefore it is shown that formula (14) equals

\[
\sum_k \sum_i \{ |j\rangle V_{ji} L_{ki} V_{ik} \rho_k \langle k| - |j\rangle V_{jk} \rho_k V_{ki} (L_{kj} + L_{ik}) \langle i| + |k\rangle \rho_k V_{kj} L_{jk} V_{ji} \langle i|\} \frac{1}{L_0 - i\epsilon}
\]

\[
= \sum_{k,i} \{-|i\rangle L_{ki} V_{ik} \rho_k \langle k| + |k\rangle \rho_k V_{ki} L_{ik} \langle i|\} L_V \frac{1}{L_0 - i\epsilon}
\]

(16)
\[ \rho L V = \frac{1}{L_0 - i\epsilon} L V \frac{1}{L_0 - i\epsilon}. \]

Now let us find how \( \tilde{\rho} \) evolves in time. By multiplying \( L_H \) on eq.(12), we obtain

\[ i \frac{d}{dt} \tilde{\rho} = \tilde{\rho} (L_0 + L_V) = \sum_{k'} \tilde{\rho}_{kk'} \mathcal{L}_{kk'}. \]  \hspace{1cm} (17)

Where,

\[ \mathcal{L}_{kk'} = -(L_V \frac{1}{L_0 - i\epsilon})_{(kk'),(k'k')} + (L_V \frac{1}{L_0 - i\epsilon} L V \frac{1}{L_0 - i\epsilon} L V)_{(kk'),(k'k')} \]

\[ = -(L_V \frac{1}{L_0 - i\epsilon} L V \frac{1}{L_0 - i\epsilon} L V)_{(kk'),(k'k')} \]

\[ = -(L_V \frac{1}{L_0 + L_V - i\epsilon} L V)_{(kk'),(k'k')} \]  \hspace{1cm} (18)

In its derivation, \( (\rho L V)_{(kk)} = 0 \) and equations parallel to eq.(6) are used.

Now, let us examine the meaning of eq.(17). Here, \( \mathcal{L}_{kk'} \) is written up to the second order for simplicity:

\[ \mathcal{L}_{kk'} \approx 2\pi i \delta(E_{k'} - E_k) |V_{k'k}|^2 - \delta_{k'k} \sum_{k''} 2\pi i \delta(E_{k''} - E_k) |V_{k''k}|^2. \]  \hspace{1cm} (19)

This \( \mathcal{L}_{kk'} \) may be understood as transfer of probability from state \( k' \) to \( k \), and eq.(17) may be considered to be the counterpart of Boltzmann equation. The imaginary part of \( \mathcal{L} \) has only negative eigenvalues, because conservation of probability: \( \sum_{k'} \mathcal{L}_{kk'} = 0 \) and \( \mathcal{L}_{kk'} > 0 \) for \( k \neq k' \) hold. Therefore from eq.(17), \( \tilde{\rho} \) will converge to \( \sum_{k\in I} |\tilde{k}\rangle 1\langle \tilde{k} | \) in the long run, as long as no symmetry prevents it.

This time asymmetry comes from the choice of sign of \( i\epsilon \) in eq.(9), that is, from requirement of the outgoing wave. This choice is quite common in the quantum theory of scattering. Thus, this choice of boundary condition solves the reversibility paradox, and the resulting exponential decay solves the recurrence paradox.

Further, we are able to confirm that imaginary part of any eigenvalue of \( \mathcal{L}_{k'k} \) is negative or zero in the following way. We generalize the problem into showing positiveness of eigenvalues of \( L_V (L_0 + L_V - \omega - i\epsilon)^{-1} L_V \), of which \( \mathcal{L}_{k'k} \) is a part. At first, \( L_V \) has real eigenvalues, and \( \text{Im}(L_H - \omega - i\epsilon)^{-1} \) has only
positive eigenvalues. Therefore, \( L_V \Im(L_H - \omega - i\epsilon)^{-1}L_V \) has only positive eigenvalues, because \( \{L_V \Im(L_H - \omega - i\epsilon)^{-1}\}^2 \) has only positive eigenvalues.

Using a similar argument, we find in which case \( \rho \) gets a positive imaginary part of eigenvalue. When \( \rho \) is a continuous function of \( k \), \( \rho L_V \Im(L_0 - i\epsilon)^{-1} \) is

\[
\rho L_V \Im \left( \frac{1}{L_0 - i\epsilon} \right) = \sum_{k, k', l} \pi i \delta(E_{k'} - E_k) \{\rho_{l k'} V_{l k} - V_{l k'} \rho_{k l}\} |k'\rangle \langle k|, \tag{20}
\]

with the assumption that \( \epsilon \) is very small. If \( \rho_{k k'} = f(E_k, E_{k'}) \) with \( f(x, y) \) a continuous function, the above formula gives zero. Then \( \rho_{k'k} \) gets a zero eigenvalue, that is, this mode of \( \rho \) does not decay. Further, even when \( \rho_{k k'} = g(E_k) \times \delta(E_k - E_{k'}) \), in which case \( \rho \) is not continuous in \( E_k - E_{k'} \) direction, \( \rho \) will get a zero eigenvalue. Note that it is possible that \( \rho \) is not continuous in \( E_k \) but continuous in \( k \), since \( k \) has high dimensionality while \( E_k \) is only one dimensional.

**Nature of states and observations**

An argument which is parallel to eq.(17) may be applied to a pure state \(|\tilde{k}\rangle \langle \tilde{k}|\). It results in evolution of the pure state into a mixed state, which disagrees with quantum mechanics. To avoid this problem, we assume that any physical wave function \( \psi(k) = \langle k|\psi \rangle \) is continuous in \( k \). Then a pure state \(|\psi\rangle \langle \psi|\) continues to be a pure state, since irreversibility disappears as was discussed below eq.(20). Please note that this assumption of continuity is independent of what representation we use, because representations are related to one another by continuous unitary transformations.

On the other hand, we do not assume continuity for the operators of observations. The reason why irreversible decay has been seen in \( \rho \) was that \( \rho \) had discontinuity. The dual space of continuous functions is that of hyperfunctions— particularly distributions—some of which are inevitably discontinuous. And the dual space of distributions is that of continuous functions.

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2The “eigenstate” in eq.(4) is not strictly a physical state if we follow the assumption on the physical states. This is because the eigenstate extends infinitely, which is never possible physically. Any actually possible state is a convolution of \(|\tilde{k}\rangle\) and a continuous function.
The reader may still wonder why operators of observations are not always continuous despite the operators of pure states being continuous. This is quite natural, though. For example, the simplest instance of observation $1_{k'k}$, that of observing nothing at all, is discontinuous. The next simplest instance of observing only one particle out of a large $N$-particle system does also include the unity operator $1_{k'k}$ in it. It is a very common nature of observations that only a very limited aspect of a system is observed at once, and we should think that this nature is the reason why discontinuity appears.

So far, we have only treated the case where $\rho$ has only diagonal elements. However, some of observation operators can have nondiagonal elements. For example, an operator $\rho' = \int_{x \in I} dx \langle x \rangle \langle x \rangle$ to observe the position of a particle is not diagonal but has finite width around the diagonal elements. Does irreversibility take place even for such an observation operator that is not diagonal? As already discussed, $L_V \text{Im}(L_0 - i\epsilon)^{-1}L_V$ is zero if $\rho$ is a continuous function of energy. If this $\epsilon$ is not infinitesimal but has finite value, that condition will be looser and irreversible decay can occur. It is seen from eq.(17) and the argument following it that $L_0 + L_V$ can have imaginary eigenvalues. Therefore $L_0 + L_V$ in the denominator of $L_V(L_0 + L_V - i\epsilon)^{-1}L_V$ can also have imaginary eigenvalues, which has the same effect as $\epsilon$ having finite value.

Furthermore, an operator $L_V(L_0 + L_V - \omega - i\epsilon)^{-1}L_V$ can have imaginary eigenvalue. Therefore, decay can take place even for nondiagonal $\rho$, and this part is related to decorrelation of phases. This fact has important meaning in considering such systems as a system with many particles in a finite box. The condition of the physical states all being outgoing waves is not applicable to a system in a finite box. In that case, $L_{k'k}$ goes to zero, which means that we won’t see irreversible phenomena in a finite box. However, self-consistent induction of $i\lambda$ makes it possible for $L_{k'k}$ to have imaginary eigenvalue even when the system has discrete spectra only.

3In reality, every box radiates and absorbs radiation, so it is actually not a system that is finite in space. Furthermore, any box has much shorter lifetime than the inverse of the spacing of spectra, so it seems that this problem is not worth worrying about.
Discussion

Eq.(17) signifies that the operators of observations lose some of their detail as time elapses. This means that we can obtain a lot of information from an observation for a new state. However, there is something that can never be observed for old states, and it increases with time. That is to say, there exists something that can never be observed owing to the laws of physics.

What has been shown here is not directly that all the eigenstates have equal probability, but that it is unobservable that the states have unequal probability after long time. This statement may be thought of as a proof of inexistence, if we admit a pragmatic proposition that something that is proven to be never observable does not exist. A physical system will appear to have an equal probability for all the eigenstates if inequality of probabilities is unobservable by any means. Moreover, this picture is in agreement with the ordinary understanding of statistical mechanics: uncertainty, i.e. ignorance, increases as time elapses.

Let us compare the present results with two preceding works by the other authors. In [2], a simple quantum model having one discrete state and continuous states was analyzed. There, it was shown that one of the eigenstates decays exponentially as $e^{-iEt-\gamma t}$. In the paper, it was found that the choice of outgoing wave, that is $-i\epsilon$ prescription, is the origin of time-asymmetrical decay. However, this work suggests the opposite view on the point that uncertainty decreases since some quantum states decay to nil.

Before making the next point, let us note that two different probabilistic assumptions are implied in the derivation of the classical $H$ theorem. The first is that a system is described by a probability distribution. The second is that the result of a scattering process of particles which have definite positions and momenta is probabilistic.

In [3], it was shown that a physical system shows irreversibility and the principle of equal probability holds, if the density operator of the system is a mixed state from the beginning, i.e., probability of the first kind, and if the mixed state has discontinuity. This work is evaluated because it showed that the $H$ theorem can be proven without assumption of probability of the second kind by making use of quantum mechanics. Even so, probability of the first kind still remains an assumption and a mystery.

On the other hand, our theory uses only the fact that operators of observations have discontinuity and can not be written as a direct product of
a vector, that is, a counterpart of a pure state. Thus, in the current paper, a theory to justify one of the principles of statistical mechanics has been presented avoiding the introduction of probability of the first kind by the use of generally accepted facts only.

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