Intrinsic mechanism for entropy change in classical and quantum evolution

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It is shown that the existence of a time operator in the Liouville space representation of both classical and quantum evolution provides a mechanism for effective entropy change of physical states. In particular, an initially effectively pure state can evolve under the usual unitary evolution to an effectively mixed state.

I. INTRODUCTION

The Hamiltonian evolution of states in classical mechanics is known by the Liouville theorem to be non-mixing, i.e., to preserve the entropy of the system [1]. The same property holds for the quantum evolution as well, and follows from the unitarity of the evolution operator. Thus, in both classical and quantum mechanics, the entropy of a (closed) system is rigorously a constant of motion. This has been an obstacle to the consistent description of irreversible processes from first principles [2]. The usual use of techniques of coarse graining or truncation to achieve a realization of the second law does not follow from basic dynamical laws, and is fundamentally not consistent with the underlying Hamiltonian dynamical structure [3].

It is often argued that large systems appear to exhibit irreversible behavior simply because it is impossible to observe the precise state of the system [4–7]. Thus a partial trace over the unobserved degrees of freedom is performed, which leads to an effective coarse graining. However, the exponential decay of a small unstable system, such as an atom in an excited state, or an unstable particle (e.g., a neutron), is also not consistent with the prediction of the (reversible) Wigner-Weisskopf description of decay systems, which is nonexponential at short (and long) times [8–10]. This short-time behavior can be shown to be due to the so-called regeneration terms, which would not appear if the description were truly irreversible [11–13]. It thus appears that the intrinsic reversibility implemented by the unitarity of the evolution operator is fundamentally not consistent with the irreversibility which is the basis not only for statistical mechanics, but also for the description of microscopic unstable systems, and measurement theory. Many attempts have been made in recent years to solve this fundamental problem [3,14–18].

In this work we study one of the aspects of this problem; we show that the existence of a "time" operator T in the framework of Liouville space theory [17] provides a natural and consistent mechanism for which pure states become mixed during the evolution (this operator is not the actual time, but is a function on the Liouville measure space which translates linearly with time). The Liouville space is essential for this construction, since a time operator does not exist in the usual Hilbert space (for a semibounded Hamiltonian).

The notion of a pure state is defined by means of expectation values of observables, i.e., a state is called "pure" if the expectation value of each observable in this state is equal to the corresponding expectation value computed with respect to some well-defined wave function (defined up to a phase), that is, a density matrix which is a projection operator to a one-dimensional subspace. In the following, we consider the subset of a complete set of observables defined on the Liouville space which are not explicitly dependent on the T variable. It is argued that this subset corresponds to the experimentally accessible observables. One obtains all the physical information concerning this subset of observables from an effective state resulting from the reduction of the full state by integration over the degree of freedom which is not relevant for this subset, i.e., the spectrum of the *time operator*. We call this reduced state the *effective* physical state. It is, of course, an old technique of statistical mechanics to trace over unmeasured variables to obtain a reduced density matrix. We show that the selection of the time variable in the Liouville space is natural and appropriate, and provides a natural mechanism for which an initially pure effective state can evolve to a mixed one, under the time evolution of the system. We show that there exist mixed states for which the effective physical state is pure and denote them as effectively pure. These states may become effectively mixed during the evolution of the system. We formulate these ideas in the framework of the quantum Liouville space, and consider later their application to classical mechanics. We also consider a simple explicit example to illustrate this mechanism.

II. REPRESENTATION IN TERMS OF LIOUVILLE TIME

It is well known that one cannot define a time operator T in the usual quantum Hilbert space with semibounded Hamiltonian [19]; however, it is possible to define such an

operator in the framework of Liouville space in which the generator of the evolution is the "Liouvillian" (whose prototype is the commutator with the Hamiltonian) which generally has an absolutely continuous spectrum on the whole real axis [17]. It is defined by [20]

$$e^{-i\mathcal{L}t}\rho = e^{-iHt}\rho e^{iHt} , \tag{1}$$

and $\mathcal{L}_0$ by

$$e^{-i\mathcal{L}_0 t}\rho = e^{-iH_0 t}\rho e^{iH_0 t} . \tag{2}$$

Then, $\mathcal{L}_I \equiv \mathcal{L} - \mathcal{L}_0$.

The existence of the time operator has been extensively used in the context of quantum statistical mechanics [18]. The kernel representing a Hilbert-Schmidt operator A on the original Hilbert space of n degrees of freedom, $\langle \mathbf{k}|A|\mathbf{k}'\rangle$, where $\mathbf{k}$ consists of n parameters, corresponds to the function $A(\mathbf{k},\mathbf{k}') \equiv \langle \mathbf{k},\mathbf{k}'|A\rangle$ representing the vector A of the Liouville space. We then change variables from $\mathbf{k},\mathbf{k}'$ to ξ, the spectrum of T, and $(2n-1)$ other independent parameters β. This transformation is defined by a kernel $K(\xi,\beta|\mathbf{k},\mathbf{k}')$ such that

$$A(\xi,\beta) \equiv \langle \xi,\beta|A\rangle = \int K(\xi,\beta|\mathbf{k},\mathbf{k}')\langle \mathbf{k},\mathbf{k}'|A\rangle d\mathbf{k}\,d\mathbf{k}' . \tag{3}$$

In what follows, we shall use the time operator T conjugate to the unperturbed Liouville operator $\mathcal{L}_0$, which is defined according to the decomposition

$$\mathcal{L} = \mathcal{L}_0 + \mathcal{L}_I , \tag{4}$$

i.e., on a suitable domain

$$[T,\mathcal{L}_0] = i . \tag{5}$$

It follows from (5) that

$$(e^{-i\mathcal{L}_0 t}A)(\xi,\beta) = A(\xi+t,\beta) . \tag{6}$$

From (1) and (6), we see that if the free Hamiltonian is diagonal in the (generalized) states $\{|\mathbf{k}\rangle\}$,

$$K(\xi+t,\beta|\mathbf{k},\mathbf{k}') = K(\xi,\beta|\mathbf{k},\mathbf{k}')e^{-i(E_{\mathbf{k}}-E_{\mathbf{k}'})t} , \tag{7}$$

where $E_{\mathbf{k}}$ is the unperturbed energy associated with the variables $\mathbf{k}$, and hence that

$$K(\xi,\beta|\mathbf{k},\mathbf{k}') = K(0,\beta|\mathbf{k},\mathbf{k}')e^{-i(E_{\mathbf{k}}-E_{\mathbf{k}'})\xi} . \tag{8}$$

Under the free evolution, the representation of A on the Liouville space undergoes translation $\xi \to \xi + t$, so that translation in the spectrum of the T operator of the Liouville space reflects the interval of the free evolution. We emphasize that ξ is not the *time*, but a function on the manifold of the Liouville space (which does not exist on the manifold of the Hilbert space), and shifts translationally with the time t under free evolution.

Using this new basis, the expectation value of an observable is written as

$$\langle A \rangle_\rho = \mathrm{Tr}(A\rho) = \int \rho_\xi(\beta)A(\xi,\beta)d\xi\,d\beta , \tag{9}$$

where

$$A(\xi,\beta) = \int K(\xi,\beta|\mathbf{k},\mathbf{k}')\langle \mathbf{k},\mathbf{k}'|A\rangle d\mathbf{k}\,d\mathbf{k}' . \tag{10}$$

It follows from Eq. (6) that ξ-independent observables commute with the free Hamiltonian H_0. In this case, clearly the asymptotic form of the observable A (in the Heisenberg picture) exists if the wave operator for the scattering theory exists, i.e.,

$$\begin{aligned}
\lim_{t\to\pm\infty} e^{-i\mathcal{L}t}A &= \lim_{t\to\pm\infty} U(t)^{-1}AU(t) \\
&= \lim_{t\to\pm\infty} U(t)^{-1}U_0(t)AU_0(t)^{-1}U(t) \\
&= \Omega_\pm A\Omega_\pm^{-1} = A_\pm ,
\end{aligned} \tag{11}$$

where $U(t)$ is the full evolution operator, and $U_0(t)$ is that of the unperturbed evolution [21]. The ξ-independent observables theretofore have a correspondence with the asymptotic variables in a scattering theory [22]. Ludwig [23] has emphasized that measurements on a quantum system are made by means of the detection of signals corresponding to observables which are operationally on a semiclassical or classical level. These measurable signals which characterize the state are the properties propagating to the detectors, and are therefore asymptotic variables, i.e., ξ independent. We do not argue that observables which are time dependent in the Heisenberg picture (such as the electromagnetic field) play no role. These operators may even be useful for calculations of measurable quantities, and their expectation values can be evaluated using, for example, the Schwinger-Keldysh technique [24]. However, from a physical point of view, based on the above-mentioned theoretical arguments on the nature of measurement, only functions of these observables which have asymptotic limits (in the case of electromagnetic field, the free number density and the momentum, for example) provide for experimental measurement. Measurements carried out upon an evolving system involve, in fact, interactions with apparatus which are essentially asymptotic (e.g., magnetic fields far from an electron beam, or the e-ν or photon signal from the pions in the final state of K-meson decay). These asymptotic observables determine the structure of the state, and hence (with a sufficient number of such measurements) can be used to define the nature of the evolution, i.e., whether a pure state tends to a mixed state. We thus conclude that the subset of ξ-independent observables corresponds to all the experimentally accessible measurements, and is therefore the subset of observables which can be used to characterize experimentally the structure of a physical state.

III. EFFECTIVE STATES

In view of the ideas presented in the preceding section, one sees that since the ξ-dependent observables are experimentally unmeasurable, they form natural candidates for

the reduction of the density matrix through integrating over the unmeasurable variables. Note, however, that in this version of the reduction scheme the set of unmeasured variables is not chosen arbitrarily by specifying the macroscopic measured quantities, but it is rather obtained through a fundamental theoretical argument concerning the nature of the measurement process. Thus this reduction does not depend on the choice of the set of variables used for the characterization of the physical state in some specific experiment, but is rather determined by the set of all measurable variables. Moreover, this reduction applies to unstable microscopic systems as well.

One thus looks for a partial trace over ρ, such that the information concerning expectation values of all the ξ-independent observables can be extracted from the reduced density matrix $\hat{\rho}$. We now show that this desired reduction is obtained by integrating ρ over ξ. If A belongs to the subset of ξ-independent operators, i.e., $A(\xi,\beta) \equiv A(\beta)$, then from Eq. (9) it follows that

$$\langle A \rangle = \mathrm{Tr}(A\rho) = \int \hat{\rho}(\beta) A(\beta) d\beta , \tag{12}$$

where $\hat{\rho}$ is defined as

$$\hat{\rho}(\beta) \equiv \int d\xi \rho_\xi(\beta) . \tag{13}$$

It is therefore clear that with respect to the set of ξ-independent observables, all of the information available in the state is contained in $\hat{\rho}$.

We call a state $\hat{\rho}$ *effectively pure* if there exists a wave function ψ such that for every ξ-independent observable A

$$\langle \psi | A | \psi \rangle = \langle A \rangle_{\hat{\rho}} = \int \hat{\rho}(\beta) A(\beta) d\beta . \tag{14}$$

According to the preceding discussion, the expectation value of experimentally measurable observables can be predicted in this case by means of a wave function. Consequently, an effectively pure state cannot be experimentally distinguished from a state which is described by a wave function in the usual quantum-mechanical Hilbert space (a pure state). However, as we shall see, this effective purity may not be maintained in time.

If ρ is pure in the usual sense, i.e., $\mathrm{Tr}\rho^2 = 1$, then the condition (14) holds for any observable, and therefore the resulting $\hat{\rho}$ is effectively pure. On the other hand, it is clear that the reduction of Eq. (13) is not one to one and therefore each $\hat{\rho}$ corresponds to an *equivalence class* of states in Liouville space. Even if only one of these states is pure, $\hat{\rho}$ would be effectively pure, since it does not distinguish between elements of the equivalence class. A more precise characterization of the effectively pure states can be found in Appendix A. It is easy to demonstrate that $\hat{\rho}(\beta)$ is uniquely determined by the measurement of all the T-independent observables. We thus see that strict purity implies effective purity but not the opposite, i.e., *even mixed states may appear as effectively pure.*

As an illustration, consider an unstable atomic state, which decays due to coupling with the electromagnetic field. The unstable state itself is a pure state, described by a well-defined wave function in the quantum-

mechanical Hilbert space (which is an eigenfunction of the unperturbed atomic Hamiltonian). As discussed in the Introduction, the unitarity of the quantum evolution implies that the purity of the state is preserved, and its entropy is not changed. However, as we have just shown, there exist many *mixed* states which are *identical* to the unstable state from an experimental point of view, since no accessible measurement (i.e., measurement of an observable which commutes with the atomic free Hamiltonian, such as the unperturbed energy or the angular momentum) can distinguish between these mixed states and the unstable pure state. These states were just defined as effectively pure. As we shall see, the coupling to the external field may, in general, induce mixing, i.e., the effectively pure states may evolve into effectively mixed states. This mechanism is demonstrated for a simple example later, and will be discussed elsewhere in the context of the unstable atomic state.

IV. DYNAMICAL EVOLUTION

We wish to show now that while unitarity excludes the possibility of the mixing of pure states, mixing of effectively pure states (destruction of the effectively pure property) is still possible. Generally, in the presence of an interaction, the full Liouvillian takes the form [from (4) and (5)]

$$\langle \xi | \mathcal{L} | \xi' \rangle = -i\partial_\xi \delta(\xi - \xi') + \langle \xi | \mathcal{L}_I | \xi' \rangle , \tag{15}$$

where the second term is, in general, not diagonal, but rather acts as an integral operator on ξ. Such an evolution generator was discussed recently in connection with the quantum Lax-Phillips theory [25]. The resulting evolution is also of an integral operator structure and takes the form

$$\rho_\xi^t = \int W_{\xi,\xi'}(t)\rho_{\xi'}^0 d\xi' , \tag{16}$$

where the operator $W_{\xi,\xi'}(t)$ acts only on the β dependence.

For simplicity we use the Fourier-transform representation

$$\rho(\alpha,\beta) = \int e^{-i\xi\alpha}\rho_\xi(\beta)d\xi , \tag{17}$$

$$\bar{W}_{\alpha,\alpha'}(t) = \int e^{-i\xi\alpha}e^{i\xi'\alpha'}W_{\xi,\xi'}(t)d\xi d\xi' . \tag{18}$$

Note that $\hat{\rho}(\beta) = \rho(\alpha,\beta)|_{\alpha=0}$, and therefore

$$\hat{\rho}^t(\beta) = \rho^t(\alpha,\beta)|_{\alpha=0}$$
$$= \int \bar{W}_{0,\alpha'}(t;\beta,\beta')\rho(\alpha',\beta')d\alpha'd\beta' . \tag{19}$$

The initial effective purity of ρ provides information only on its $\alpha=0$ component while the other components may be even effectively mixed, but, as we see from Eq. (19), during the evolution the $\alpha=0$ component develops contributions from the other components, and therefore it may become mixed. The states keep their effective purity, in general, only if $\bar{W}_{0,\alpha'} \sim \delta(\alpha')$.

We wish to consider now a simple concrete example to illustrate the above ideas. Consider the evolution of a particle in three dimensions in the presence of a screened

Coulomb (Yukawa) potential. The matrix elements of the free Liouvillian are given by (we take $2m = 1$)

$$\langle \mathbf{k}_1, \mathbf{k}_2 | \mathcal{L}_0 | \mathbf{k}_3, \mathbf{k}_4 \rangle = \delta^3(\mathbf{k}_1 - \mathbf{k}_3) \delta^3(\mathbf{k}_2 - \mathbf{k}_4)(\mathbf{k}_2^2 - \mathbf{k}_1^2) . \quad (20)$$

We change the variables in Liouville space from $(\mathbf{k}_1, \mathbf{k}_2)$ to $(\alpha, \bar{\beta}, \Omega_1, \Omega_2)$ by the transformation

$$\alpha = \mathbf{k}_2^2 - \mathbf{k}_1^2 , \quad \bar{\beta} = \mathbf{k}_2^2 + \mathbf{k}_1^2 , \quad (21)$$

and Ω_1, Ω_2 are the angle variables of the momenta $\mathbf{k}_1, \mathbf{k}_2$, respectively. We denote the set of variables $\bar{\beta}, \Omega_1, \Omega_2$ by β. In this new basis the matrix elements of the free Liouvillian are given by

$$\langle \alpha, \beta | \mathcal{L}_0 | \alpha', \beta' \rangle = \alpha \delta(\alpha - \alpha') \delta(\beta - \beta') . \quad (22)$$

The variables α, β defined by this change of basis coincide with the α, β of our general discussion above.

As mentioned before, effectively pure sates are mixed during the evolution unless $\bar{W}_{0,\alpha'} \sim \delta(\alpha')$. We therefore look at the evolution operators induced by the perturbation to see whether this is the case. The matrix elements of the interaction Liouvillian are given by

$$\langle \mathbf{k}_1, \mathbf{k}_2 | \mathcal{L}_I | \mathbf{k}_3, \mathbf{k}_4 \rangle = \delta^3(\mathbf{k}_1 - \mathbf{k}_3) \tilde{V}_{\mathbf{k}_2 - \mathbf{k}_4}$$
$$- \delta^3(\mathbf{k}_2 - \mathbf{k}_4) \tilde{V}_{\mathbf{k}_1 - \mathbf{k}_3} , \quad (23)$$

where $\tilde{V}_{\mathbf{k}}$ is the Fourier transform of the potential V, taken at the point $\mathbf{k}$.

For the screened Coulomb potential

$$V(r) = \frac{A e^{-\mu r}}{\mu r} , \quad (24)$$

$\tilde{V}_{\mathbf{k}}$ is given by

$$\tilde{V}_{\mathbf{k}} = \frac{4\pi A}{\mu(\mathbf{k}^2 + \mu^2)} , \quad (25)$$

and the matrix element takes the form

$$\langle \mathbf{k}_1, \mathbf{k}_2 | \mathcal{L}_I | \mathbf{k}_3, \mathbf{k}_4 \rangle = \frac{4\pi A}{\mu} \left[\frac{\delta^3(\mathbf{k}_1 - \mathbf{k}_3)}{(\mathbf{k}_2 - \mathbf{k}_4)^2 + \mu^2} - \frac{\delta^3(\mathbf{k}_2 - \mathbf{k}_4)}{(\mathbf{k}_1 - \mathbf{k}_3)^2 + \mu^2} \right] . \quad (26)$$

Changing the variables to (α, β), one obtains

$$\langle \alpha, \beta | \mathcal{L}_I | \alpha', \beta' \rangle \equiv \mathcal{L}_I(\alpha, \alpha', \beta, \beta')$$

$$= \frac{64\pi A}{\sqrt{2}\mu} \left[\frac{\left[\delta(\bar{\beta} - \alpha - \beta' + \alpha') \dfrac{1}{\sqrt{\bar{\beta} - \alpha}} \right] \delta(\Omega_1, \Omega_3)}{\bar{\beta} + \bar{\beta}' + \alpha + \alpha' - 2\sqrt{(\bar{\beta} + \alpha)(\bar{\beta}' + \alpha')} B(\Omega_2, \Omega_4) + \mu^2} \right.$$

$$\left. - \frac{\left[\delta(\bar{\beta} + \alpha - \beta' - \alpha') \dfrac{1}{\sqrt{\bar{\beta} + \alpha}} \right] \delta(\Omega_2, \Omega_4)}{(\bar{\beta} + \bar{\beta}' - (\alpha + \alpha') - 2\sqrt{(\bar{\beta} - \alpha)(\bar{\beta}' - \alpha')} B(\Omega_1, \Omega_3) + \mu^2} \right] , \quad (27)$$

where $B(\Omega_1, \Omega_2)$ is defined by

$$B(\Omega_1, \Omega_2) = \sin\theta_1 \sin\theta_2 \cos(\phi_1 - \phi_2) + \cos\theta_1 \cos\theta_2 . \quad (28)$$

It is therefore clear that the kernel $\mathcal{L}_I(\alpha, \alpha', \beta, \beta')$ is *not* of the form $\delta(\alpha - \alpha') \hat{A}(\beta, \beta')$ and therefore the evolution operators do not have this form either. In particular, for weak interactions, first-order perturbation theory gives

$$\bar{W}_{0,\alpha}(t; \beta, \beta') = \delta(\alpha) \delta(\beta - \beta') - it \mathcal{L}_I(0, \alpha, \beta, \beta')$$
$$+ O(t^2 A^2) , \quad (29)$$

where the second term induces mixing.

We have shown that no mixing occurs if the unperturbed Liouvillian is nondegenerate (see Appendix A), and the result (29) shows that no mixing occurs for the free motion. We do not yet have a general classification.

V. ENTROPY

We next define the notion of *entropy* for the effective states and show that this entropy is not constant during the motion as in traditional quantum (and classical) mechanics.

We now remark that since, according to Eq. (8), the density operator in (ξ, β) representation can be written as

$$\rho_\xi(\beta) = \int K(0, \beta | \mathbf{k}, \mathbf{k}') e^{-i(E_k - E_{k'})\xi} \rho(\mathbf{k}, \mathbf{k}') , \quad (30)$$

one obtains

$$\hat{\rho}(\beta) = \int d\xi \rho_\xi(\beta)$$
$$= 2\pi \int K(0, \beta | \mathbf{k}, \mathbf{k}') \delta(E_k - E_{k'}) \rho(\mathbf{k}, \mathbf{k}') . \quad (31)$$

The necessary and sufficient condition for a state to be effectively pure, as pointed out in Appendix A, is that the function $\rho(\mathbf{k}, \mathbf{k}')$ be factorizable in the equal energy subspaces.

The entropy of a quantum system, defined as

$$S = -\text{Tr}\rho \ln\rho \quad (32)$$

to satisfy the requirements of convexity and additivity, vanishes for a pure state, i.e., a density operator of the form $\rho = |\psi\rangle\langle\psi|$, where the norm squared $\langle\psi|\psi\rangle$ is unity. We therefore define the entropy of the effective state as the sum of entropies associated with $\rho(\mathbf{k}, \mathbf{k}')$ in each energy subspace, i.e., with the reduced operator

$$\hat{\rho} = \int d\mathbf{k}\, d\mathbf{k}' \delta(E_k - E_{k'}) \rho(\mathbf{k},\mathbf{k}') |\mathbf{k}\rangle\langle\mathbf{k}'| \ . \qquad (33)$$

For simplicity, we defer to Appendix B all the precise mathematical details required for the above reduction, and state here only the result

$$S = \int dE\, S_E = -\int dE\, \mathrm{Tr}\hat{\rho}_E \ln\hat{\rho}_E \ , \qquad (34)$$

where $\hat{\rho}_E$ is the (normalized, see Appendix B) density matrix restricted to the E-energy subspace. In case $\rho(E,\Omega_k; E,\Omega_{k'})$ is factorizable, S_E vanishes. Hence, for effectively pure ρ, where this factorizability condition holds for each equal-energy subspace, the entropy is zero. However, in case ρ is not effectively pure, since S is convex, the admixture of nonfactorizable elements inside the equal-energy subspaces [as induced by the evolution (29)] induces an increase of entropy. One therefore sees that the entropy is *increased* in the course of the evolution for a general effectively pure initial state unless it is a strictly pure state, i.e., described by a wave function, whose entropy is constant. We do not study here the conditions under which the entropy increases given some nonzero entropy initial state.

VI. CONCLUDING REMARKS

We have shown that the class of observables which are constants of the free motion determine a reduced density matrix which, even when the original density matrix of the system corresponds to a mixed state, may be effectively pure. Such states correspond to an equivalence class which includes, therefore, both pure and mixed states. An equivalence class of effectively pure states contains only pure states if and only if it is nonzero in only one energy subspace; due to the trace condition, such an equivalence class can be realized on a discrete spectrum.

Under the evolution of the system, an effectively pure state may become effectively mixed, i.e, the elements in equal-energy subspaces may become nonfactorizable. We have defined the entropy of such a system which vanishes for an effectively pure state. We have shown that the system may evolve from any initial effective state to an effective state for which the entropy has changed. In particular, if the initial state is effectively pure, evolution can lead to an effectively mixed state with nonvanishing entropy. The example of the screened Coulomb potential which we worked out here illustrates this effect, and furthermore shows explicitly that the free evolution does not change the entropy.

The method that we have described above applies as well to the formulation of classical mechanics on a Hilbert space defined on the manifold of phase space which was introduced by Koopman [26] and used extensively in statistical mechanics [3]. Misra [17] has shown that dynamical systems which admit a Lyapunov operator necessarily have an absolutely continuous spectrum; therefore one can construct a time operator on the classical Liouville space for such systems. We identify the variables $\mathbf{k}, \mathbf{k}'$ with the variables of the classical phase space, and consider the trace as an integral over this space. The expectation value of a ξ-independent operator

defines a reduced density function in the form (13). Since a pure state is defined by a density function concentrated at a point of the phase space, a state which is effectively pure must have the form $\hat{\rho}(\beta) = \delta(\beta - \beta_0)$. The equivalence class associated with this reduced density contains mixed states as well, such as $\rho(\xi,\beta) = \delta(\beta - \beta_0) f(\xi)$ corresponding to a nonlocalized function on the phase space $(\mathbf{k}, \mathbf{k}')$. The structure of the theory, and the conclusions we have reached, are therefore identical to those of the quantum case.

APPENDIX A

In this appendix we intend to characterize an effectively pure state more explicitly. Since α is the Fourier dual of the variable ξ, which is the spectrum of the T operator, it follows from (5) that α is the spectrum of the unperturbed Liouvillian $\mathcal{L}_0$, the canonical conjugate of T. Hence the $\alpha = 0$ component of a state $\int d\mathbf{k}\, d\mathbf{k}' c(\mathbf{k},\mathbf{k}') |\mathbf{k}\rangle\langle\mathbf{k}'|$, for a basis $\{|\mathbf{k}\rangle\}$ which are (generalized) eigenfunctions of H_0 with (generalized) eigenvalues $E_\mathbf{k}$, is the partial integral over the terms for which the unperturbed Liouvillian vanishes, i.e., $E_\mathbf{k} = E_{\mathbf{k}'}$.

For a pure state corresponding to $\psi = \int a(\mathbf{k}) |\mathbf{k}\rangle$, $c(\mathbf{k},\mathbf{k}') = a(\mathbf{k}) a(\mathbf{k}')^*$ is factorizable. An effectively pure state is a state which has the same reduced density matrix $\hat{\rho}$ as some pure state. Since this reduction is given by taking the $\alpha = 0$ component of $\rho(\alpha,\beta)$, it follows that the $\alpha = 0$ component of an effectively pure state coincides with the $\alpha = 0$ component of a pure state, and therefore satisfies this factorizability condition in the equal-energy subspaces. On the other hand, this condition in the equal-energy subspaces does not imply its general validity (for $\alpha \neq 0$). Hence an effectively pure state is associated with an equivalence class which includes mixed states as well.

As an example, note that the mixed state

$$\rho = \int dE\, dE' \mu(E,E') |\phi_E\rangle\langle\phi_{E'}| \ , \qquad (A1)$$

where $\mu(E,E')$ is a positive kernel, $\int dE\, \mu(E,E) = 1$, and the generalized states $|\phi_E\rangle$ correspond to normalized elements of $\mathcal{H}_E$ (and for which H_0 is a multiplication operator), is effectively pure.

If H_0 is nondegenerate, the effective purity condition holds trivially for every state (diagonal elements of the density matrix in H_0 representation are positive definite), and, with the mechanism we propose, the evolution *cannot induce mixing*. Note that for classical systems, this condition implies that the system is integrable.

APPENDIX B

In this appendix we describe the formal mathematical reduction of the density matrix into the equal-energy subspaces. To extract the density operator associated with each equal-energy subspace, we define the projection density

$$P_E = \int d\mathbf{k}\, \delta(E - E_k) |\mathbf{k}\rangle\langle\mathbf{k}| \ , \qquad (B1)$$

and carry out the operation

$$P_E\hat{\rho} = \int d\mathbf{k}\, d\mathbf{k}' \delta(E - E_k)\delta(E_k - E_{k'})\rho(\mathbf{k},\mathbf{k}')|\mathbf{k}\rangle\langle\mathbf{k}'| \ .$$

$$(B2)$$

This operator is well defined; writing $d\mathbf{k} = dE_k\, d\Omega_k$, where Ω_k is the degeneracy manifold associated with E_k, one obtains

$$P_E\hat{\rho} = \int d\Omega_k\, d\Omega_{k'}\rho(\mathbf{k},\mathbf{k}')|_{E=E_k=E_{k'}}|E\Omega_k\rangle\langle E\Omega_{k'}| \ .$$

$$(B3)$$

The trace of this operator on the full Hilbert space does not exist (a well-known problem associated with a continuous spectrum, and related to the Van Hove singularity arising from the fact that the equilibrium state for the unperturbed evolution is not an element of the Hilbert-Schmidt space). We therefore consider the foliation

$$\mathscr{H} = L^2(\mathbb{R}, \mathscr{H}_E) \ ,$$

$$(B4)$$

with Lebesgue measure on $\mathbb{R}$, and for which $\mathscr{H}_E$ corresponds to the degeneracy subspace at each E (pointwise). For $f \in \mathscr{H}$, the norm in this foliation is defined as

$$\|f\|^2 = \int \|f_E\|^2_{\mathscr{H}_E} dE \ ,$$

$$(B5)$$

or in terms of the original manifold $\{\mathbf{k}\}$,

$$\int \|f_E\|^2_{\mathscr{H}_E} dE = \int |f(E,\Omega_E)|^2 dE\, d\Omega_E = \int |f(\mathbf{k})|^2 d\mathbf{k} \ .$$

$$(B6)$$

The trace Tr_E restricted to $\mathscr{H}_E$ then corresponds to a trace over the degeneracy subspace alone. For the operator (B3),

$$\mathrm{Tr}_E P_E\hat{\rho} = \int \rho(\mathbf{k},\mathbf{k})|_{E=E_k} d\Omega_k \ .$$

$$(B7)$$

Note that

$$\int dE\, \mathrm{Tr}_E P_E\hat{\rho} = \int \rho(\mathbf{k},\mathbf{k})|_{E=E_k} dE\, d\Omega_k = 1 \ .$$

$$(B8)$$

We define, however,

$$\lambda_E = \mathrm{Tr}_E P_E\hat{\rho} \ ,$$

$$(B9)$$

so that

$$\hat{\rho}_E = \frac{1}{\lambda_E} P_E\hat{\rho}$$

$$(B10)$$

is a (dimensionless, normalized) operator in the Hilbert space $\mathscr{H}_E$ with representation

$$\hat{\rho}_E = \int d\Omega_k d\Omega_{k'}\rho(E,\Omega_k;E,\Omega_{k'})|E\Omega_k\rangle\langle E\Omega_{k'}| \ .$$

$$(B11)$$

The entropy is then defined as

$$S = \int dE\, S_E = -\int dE\, \mathrm{Tr}\hat{\rho}_E\ln\hat{\rho}_E \ .$$

$$(B12)$$

[1] See, for example, J. Yvon, *Correlations and Entropy in Classical Statistical Mechanics* (Pergamon, Oxford, 1969).

[2] See, for example, I. E. Antoniou and I. Prigogine, Physica A **192**, 443 (1993).

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[19] See, for example, K. Gottfried, *Quantum Mechanics* (Benjamin, New York, 1966), Vol. 1, p. 248.

[20] We thank I. Antoniou for a discussion on this point, as well as for his comments on the interpretation of Eq. (4).

[21] In fact, it is shown in Ref. [22] that asymptotic observables may exist even if the usual wave operators do not.

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[24] See, e.g., E. Lifshitz and L. P. Pitaevskii, *Physical Kinetics* (Pergamon, Oxford, 1981), Chap. 10.

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